

## Lecture 1: Review and Introduction

### Course structure

Thermodynamics and Statistical Mechanics comprise a very broad area of study that encompasses fundamental topics from physics, chemistry, engineering, biology, statistics and even finance.

Thermodynamics is the study of the macroscopic behavior of physical systems comprised of very large numbers of microscopic constituents. Thermodynamics can be cleanly separated from statistical mechanics in the sense that thermodynamic theory does not mention the properties or the behaviors of the microscopic constituents (particles) themselves – one can treat a system as a material continuum. For any system, thermodynamics assumes the existence of a fundamental relation (FR) that governs its properties. Given this relation, we can answer virtually any question about its macroscopic behavior. But thermodynamics, as a theory, can't actually give us the fundamental relation – it must either be obtained empirically via extensive experimentation and modeling, or from a more fundamental theory.

Statistical mechanics is such a fundamental theory. By applying probability methods to the microscopic degrees of freedom, one can compute the fundamental relation and thereby determine a system's macroscopic properties.

In thermodynamics, we will pursue two main lines of inquiry. The first pertains to general principles and practices that are independent of the details of the FR. The second is the application of these principles to specific systems (e.g. an ideal gas) and processes (e.g. adiabatic compression). We will frequently stop and ask the question, “Are we doing something general here, or is this specific to a particular system or process?”

In statistical mechanics, we will learn how to count states, how to compute a partition function, and how to elegantly redefine entropy. We will also learn how to treat a wide variety of physical systems that are more interesting than the ideal gas.

We will spend roughly the first 1/2 of the course on thermodynamics, and the last 1/2 on statistical mechanics. We will use separate textbooks for thermodynamics and statistical mechanics (see the syllabus). The notations used in these books are mostly, but not entirely, consistent. The biggest difference is that  $N$  will refer to mole number in thermodynamics and will refer to particle number in statistical mechanics, so that  $NR$  and  $Nk_B$  become easily confused, where  $R = N_A k_B$  = (Avogadro's number)(Boltzmann's constant). Our weekly lecture notes will further extend the course content and notation beyond what you'll find in the textbooks.

In addition to your textbooks and these lecture notes, we also provide a glossary of thermodynamic concepts to supplement your reading during the first half of the semester.

## Review of introductory thermal physics

Basic definitions:

- Thermodynamic system
- Equilibrium and non-equilibrium states
- Thermodynamic properties/variables
- Intensive state variables (e.g. temperature, pressure, chemical potential)
- Extensive state variables (e.g. volume, mole or particle number, internal energy)
- Process variables (e.g. heat and work)
- System vs global changes

Laws of Thermodynamics:

Temperature, pressure, heat, work, internal energy, entropy

0<sup>th</sup> If  $T_a = T_b$  and  $T_b = T_c$  then  $T_a = T_c$

1<sup>st</sup>  $dU = dQ_{in} + dW_{on}$

2<sup>nd</sup> Total entropy never decreases

3<sup>rd</sup>  $S \rightarrow \text{const}$  (often zero) as  $T \rightarrow 0$ .

Monatomic ideal gas

Ideal gas law (a nice test system for much of thermal physics):  $PV = NRT$  or  $\tilde{N}kT$

Historically derived from the combination of empirical laws by Boyle ( $P \propto 1/V$ ), Charles ( $V \propto T$ ),

Gay-Lussac ( $P \propto T$ ), and Avogadro ( $N$  depends on  $P$ ,  $V$ , and  $T$ ).

“Ideal” assumes molecules have zero intrinsic volume and don’t collide – an approximation.

Equipartition theorem: every microscopic variable stores the same amount of energy

Calculate  $v_{rms}$  in terms of  $T$ :  $\frac{1}{2}mv_{rms}^2 = \frac{3}{2}kT$

Second ideal-gas state equation:  $U = \frac{3}{2}NRT$

Third ideal-gas state equation: not taught in intro classes

Specific heat of an ideal gas:  $c_V = \frac{3}{2}R$ ,  $c_P - c_V = R$ ,  $\frac{c_P}{c_V} = \frac{5}{3}$

Maxwell-Boltzman velocity distribution:  $p(v) \propto (m/kT)^{3/2} v^2 e^{-mv^2/2kT}$

Reversible adiabatic expansion:  $dQ = 0$  and  $PV^{5/3} = \text{const}$

Isothermal expansion or free expansion (not the same thing):  $PV = \text{const}$

Heat capacity and specific heat (at constant  $P$  or  $V$ ):  $C = cM = \frac{\Delta Q}{\Delta T}$

Heat transfer:  $\Delta Q = c_1 M_1 \Delta T_1 = -c_2 M_2 \Delta T_2$ .

Phase diagrams, phase transitions, latent heat

Coefficient of thermal expansion (constant  $P$ ):  $\alpha_P = \frac{1}{V} \frac{dV}{dT} = \frac{3}{L} \frac{dL}{dT}$

Isothermal compressibility:  $\kappa_T = -\frac{1}{V} \left( \frac{dV}{dP} \right)_T$

Heat conduction: heat-energy flux:  $H = -kA \frac{dT}{dx} = -kA \frac{(T_h - T_c)}{L} = -A \frac{(T_h - T_c)}{R}$

## Heat engines

Iso-variable process (adiabatic, isothermal, isobaric, etc).

Work done by the system:  $W = |Q_h| - |Q_c|$

Thermal engine efficiency:  $\epsilon = \frac{W}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$

Carnot heat engines have maximal efficiency:  $\epsilon = 1 - \frac{T_c}{T_h}$ .

## Blackbody radiation

Stefan's power law:  $P = \sigma e A T^4$

Planck's radiation law:  $I = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$

Wien's displacement law:  $\frac{dI}{d\lambda} = 0 \rightarrow \lambda T = 0.002898 \text{ mK}$

## Thermodynamic entropy:

$\Delta S = \int \frac{dQ}{T}$  which is  $\frac{\Delta Q}{T}$  when  $T$  is constant.

Ideal gas:  $\Delta S = NR \ln \left[ \left( \frac{T_f}{T_i} \right)^{3/2} \left( \frac{V_f}{V_i} \right) \right]$

Thermodynamic cycle of a system:  $\Delta S = 0$

Global entropy change:  $\Delta S \geq 0$

Quasi-static, reversible, and irreversible processes

## Statistical entropy ( $S = k_B \ln(\Omega)$ )

Macrostates and microstates.

Macrostate multiplicity

Counting problems

Combinations and permutations, ordered vs unordered selection, coin tosses, and dice rolls

Macrostate probability:  $P_i = \Omega_i / \Omega_{\text{total}}$

Entropy of mixing of two equal volumes of distinct ideal gasses:  $\Delta S = k_B \ln(2)$

## Kinetic theory derivation of the second ideal-gas state equation

Consider a monatomic ideal gas (single-atom molecules with no collisions) in a cubic box of width  $L$ , each of which bounces around in the box independently. Review and understand each step of the following pressure derivation. Let  $v_{zi}$  be the  $z^{\text{th}}$  vector component of the velocity vector of the  $i^{\text{th}}$  particle.  $\Delta t$  is the time between collisions of a specific particle with a specific wall. An overbar indicates an mean value.  $\Delta p$  is momentum transfer.

$$P = \frac{F}{A} = \frac{1}{A} \frac{\Delta p}{\Delta t} = \frac{1}{A} \sum \frac{\Delta p_i}{\Delta t} = \frac{1}{L^2} \sum \frac{(2\tilde{m}v_{zi})}{\left(\frac{2L}{v_{zi}}\right)} = \frac{1}{L^3} \sum \tilde{m} v_{zi}^2 = \frac{1}{L^3} \tilde{N} \tilde{m} \overline{v_z^2} = \frac{\tilde{N}}{V} \tilde{m} \frac{\overline{v^2}}{3} = \frac{1}{3} \frac{\tilde{N}}{V} \tilde{m} v_{rms}^2$$

Define internal energy:  $U = \sum \frac{1}{2} \tilde{m} v_i^2 = \frac{1}{2} \tilde{N} \tilde{m} \overline{v^2} = \frac{1}{2} \tilde{N} \tilde{m} v_{rms}^2$

Combine these two results to obtain  $U = \frac{3}{2} PV$ . This is the second ideal-gas state equation.

Invoke the ideal gas law to reexpress the second state equation as  $U = \frac{3}{2} NRT$ .

## Lecture 2: Entropy, the fundamental relation, and the laws of thermodynamics

### 1) Important preliminary concepts

- a. Equilibrium states defined by a set of macroscopic state variables.
- b. Heat and work. When referring to a system, it is most convenient to refer to heat and work so that a positive change increases the internal energy of the system. We'll use this convention.
- c. First law of thermodynamics (special case of energy conservation law).
- d. System boundaries can facilitate some combination of thermal, mechanical, and chemical contact between systems or subsystems of a system.
- e. An extensive thermodynamic property scales with system size, whereas an intensive thermodynamic property is independent of system size. If all intensive properties are fixed, and one extensive property is doubled, then all other extensive properties also double.
- f. Contact with thermal, mechanical, and chemical reservoirs fix intensive system properties. Internal boundaries or other constraints can partition a system into subsystems with different values of the intensive parameters. Simple constraints might include diathermal, immovable, or impermeable boundaries.
- g. An extensive property is also *additive* in the sense that if the system is divided up into subsystems, the value of that property for the whole system is the sum of its values in each of the subsystems.
- h. A homogeneous function to first order has the property that  $f(\lambda x, \lambda y, \lambda z) = \lambda f(x, y, z)$ . If  $x$ ,  $y$ , and  $z$  are extensive variables, then  $\lambda$  merely scales the system size. Setting  $\lambda = 2$  doubles the system size and every extensive state variable including  $f$ . As an example,  $x^3/yz$  is homogeneous. An additive property must also be homogeneous to first order in the extensive state variables.
- i. Mutual thermodynamic equilibrium.

### 2) Thermodynamic entropy

- a. Sadi Carnot, who was mystified by the fact that he could not create an engine that wasted no heat, postulated the existence of a new extensive state variable  $S$  called *entropy*. He proposed that entropy conservation requires that heat be wasted into the low-temperature reservoir.
- b. There are a number of loose and inaccurate definitions of entropy, such as messiness, disorder, or complexity.
- c. Volume is the extensive quantity that changes when work is done on a system according to ( $dW = -PdV$ ). We also need an extensive quantity that goes up when heat flows into the system. So textbooks often declare that  $dQ = TdS$  and define entropy change as heat over temperature. This concept has merit, but not as a definition. Entropy is more fundamental than temperature. We will soon define temperature in terms of entropy, so that defining entropy in terms of temperature would be circular.
- d. Rigorous definition: the thermodynamic entropy  $S$  is a function of the extensive state variables of the system (specifically a complete and independent set of them) with the following properties.
  - i.  $S$  is a differentiable (and hence continuous) and monotonically-increasing function of the internal energy  $U$ .
  - ii.  $S$  is additive over subsystems, and therefore homogeneous to 1<sup>st</sup> order.
  - iii. The values assumed by the extensive variables in the absence of an internal constraint maximize  $S$  over the manifold of internally-constrained equilibrium states. In other words, releasing any internal constraint will cause entropy to increase.
  - iv.  $S$  approaches zero (or some other constant value) as  $T = \frac{\partial U}{\partial S}$  approaches zero.

This is quite a mouthful. No wonder they didn't teach this in high school.

- e. We have merely defined the desired properties of thermodynamic entropy here without proving it exists. Entropy is hard to really understand from a purely macroscopic perspective. In statistical mechanics, for a given set of internal constraints, entropy is a measure of how many equivalent microscopic configurations the system has access to. This determines how microscopically spread out the internal energy is. More on this later in the semester.

### 3) The laws of thermodynamics

- a. The **fundamental problem of thermodynamics**: If we have an internally-constrained system, and we remove or relax an internal constraint, what will be the final equilibrium state of the system? The laws of thermodynamics answer this question.
- b. One must first assume that **there exist system states (called *equilibrium* states) which are defined entirely by a set of macroscopic extensive state variables**. This is not usually presented as one of the laws. But it is a critical assumption. Callen's axiomatic treatment of thermodynamics invoked this assumption as a first postulate.
- c. You are already familiar with the **1<sup>st</sup> law (energy conservation)**.
- d. The most rigorous form of the **2<sup>nd</sup> law (and 3<sup>rd</sup> law) is the simple declaration of the existence of an entropy function with the properties presented in the definition above**. All other common formulations are corollaries of this rigorous definition.
  - i. The total entropy of an isolated system can't decrease.
  - ii. The total entropy of a system and its environment can't decrease.
  - iii. A system in a non-equilibrium state will evolve towards equilibrium because the equilibrium state consistent with the constraints of the system will maximize entropy.
  - iv. Heat can't spontaneously flow from low-temperature to high-temperature region.
  - v. No heat engine can have the sole effect of converting heat energy into work – some heat energy must be wasted by transferring it to a lower-temperature entity.
- e. One cannot prove the second law within the context of thermodynamics. But it can be proven in the context of statistical mechanics. Other fundamental laws of physics are empirical statements of what we observe when we probe the universe, and are inherently unprovable. The 2<sup>nd</sup> law of thermodynamics is different. It is ultimately a simple statistical statement, which is why great minds like Einstein were so confident in its veracity.

4) Fundamental relation

- a. A fundamental relation (FR) is a functional relationship between the system entropy and some complete and independent set of extensive state variables, including the internal energy, which governs the behavior of all equilibrium states of the system; it contains everything there is to know about a thermodynamic system in equilibrium, which means that one can use it to compute expressions for all other system properties. In contrast, state equations do not generally contain everything there is to know about a system.
- b. The 2<sup>nd</sup> law of thermodynamics declares that the entropy function  $S(U, V, N)$  exists and that it is the fundamental relation.
- c. It doesn't matter how we algebraically rearrange the FR, or which variable (if any) we isolate on the left-hand side. Thus, the FR can have many forms. For example, if  $S = NU/V$  is an FR of a given system, then so is  $V = NU/S$ .
- d. For a simple system,  $S(U, V, N)$  is an FR, but  $S(T, V, N)$  and  $S(U, P, N)$  are not. It is NOT sufficient to merely express the entropy as a function of state variables. An FR must be expressed purely in terms of the extensive state variables of the system. Otherwise, it is merely a state equation. Remember this!
- e. Sackur-Tetrode equation: FR of an ideal gas:  $S = NR \left\{ \ln \left( \frac{VU^c}{N^{c+1}} \right) + \text{constant} \right\}$ . The state equations  $U/c = PV = NRT$  are derived from this expression. Recall that  $c = 3/2$  for a monatomic gas.
- f. Few textbooks adequately emphasize the FR, which leaves readers with a bag full of seemingly disconnected tricks. Entropy as the FR is the big idea that draws everything else together. The FR of a system can be assembled empirically, to within an integration constant, from a complete set of state equations. The FR of a system can be obtained from first principles from statistical mechanics.

5) Entropy maximization (see page 43 of K&T)

- a. Back to the fundamental problem of thermodynamics. Consider a box which has been separated into two subvolumes by a rigid, adiabatic and impermeable wall. The gas on one side is hot and dense, while the gas on the other side is cold and sparse. The two gasses consist of different molecular species. What will be the final state of the system if we suddenly make the wall diathermal, or diathermal and moveable, or diathermal and permeable?
- b. Problems like this are solved by obtaining entropy as the FR, computing the total entropy of the composite system as a function of the constraint variable, maximizing the entropy with respect to the constraint variable, and using the value of the constraint variable to find the values of the state variables affected by the constraint. This is the final state after removing the constraint. See the last homework problem.

## Lecture 3: Equations of state as derivatives of the FR, process variables (heat and work), equilibrium processes, reversible processes, and simple processes

- 1) Thermodynamic concept glossary
  - a. State equations as derivatives of the FR
  - b. Process variables (heat and work)
  - c. Equilibrium (quasi-static) processes, reversible processes (subset of equilibrium processes)
  - d. Simple fixed-variable process
- 2) The differential form of the FR gives us the intensive state variables.
  - a.  $dU(S, V, N) = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial N} dN = TdS - PdV + \mu dN$
  - b. Rigorous definitions of  $(T, P, \mu)$ :  $T \equiv \left(\frac{\partial U}{\partial S}\right)_{V, N}$ ,  $P \equiv -\left(\frac{\partial U}{\partial V}\right)_{S, N}$ , and  $\mu \equiv \left(\frac{\partial U}{\partial N}\right)_{S, V}$
  - c. Conjugate (intensive, extensive) variable pairs:  $(P, V)$ ,  $(T, S)$  and  $(\mu, N)$
  - d. Intuitive definitions of these intensive variables
    - i. Pressure measures the tendency to transmit mechanical energy.
    - ii. Temperature measures the tendency to transmit heat energy.
    - iii. Chemical potential measures the tendency to transmit chemical energy.
  - e. Each first derivative of the FR yields a distinct state equation. We'll soon derive all three state equations of an ideal gas this way, and will also explore a variety of other systems.
- 3) Process variables
  - a. Process variables depend on the trajectory of a process between two states rather than on the states themselves. Heat  $Q$  and work  $W$  are classic examples that apply to simple systems.
- 4) Equilibrium (quasi-static) processes
  - a. An equilibrium process is a process whose trajectory consists entirely of equilibrium states. The system never leaves equilibrium along the way. This is difficult to achieve in practice, but even small disturbances can knock the system out of equilibrium, causing the system to disappear from one point in equilibrium state space and eventually reappear in at another point in equilibrium state space without following an equilibrium trajectory between them.
  - b. To follow a trajectory in equilibrium state space, the system must evolve slowly and carefully. In this spirit, we refer to an equilibrium process as a "quasi-static" process.
- 5) Reversible processes
  - a. The entropy of a system decreases when entropy leaves the system. But the 2<sup>nd</sup> law declares that the global (system + environment) entropy can never decrease.
  - b. In a reversible process, global entropy must be constant. If global entropy increased, reversing the process would require a decrease in global entropy, which is impossible.
  - c. All reversible processes must be quasi-static. But not all quasi-static processes are reversible.
  - d. For reversible processes:  $dQ = TdS$  (heat transfer) and  $dW = -PdV$  (work transfer). It is important to understand that these relations **may not apply for an irreversible process**.
  - e. For a reversible process, there's a well defined strategy for calculating  $\Delta U$  (internal energy change),  $\Delta Q$  (heat transfer), and  $\Delta W$  (work) when working in the  $P - V$  plane.
    - i. From the initial and final states  $(P_i, V_i)$  and  $(P_f, V_f)$ , calculate their internal energies,  $U_f$  and  $U_i$ , and find their difference  $\Delta U = U_f - U_i$ .
    - ii. Determine  $P(V)$ , and calculate  $\Delta W = -\int PdV$  along the trajectory.
    - iii. Calculate  $\Delta Q = \Delta U - \Delta W$  from the first law.

- 6) The state of a simple system is completely defined by specifying three independent state variables, at least one of which must be extensive. A simple system has four extensive state variables ( $N, V, U, S$ ) and three intensive state variables ( $T, P, \mu$ ), so that we have 7 in all to choose from. Because we haven't talked much about open systems yet, we'll fix  $N$ . Many practically-achievable processes involve fixing a second variable as well, and then varying the third independent variable to achieve a one-dimensional trajectory or process through state space. Depending on the FR, some combinations of independent variables may be unavailable; in an ideal gas, for example, one can't independently assign values to each of  $N, T$ , and  $U$  (each one depends on the other two).
- If  $P$  is held constant, the state-space trajectory is called an "isobar".
  - If  $T$  is held constant, the state-space trajectory is called an "isotherm".
  - If  $V$  is held constant, the state-space trajectory is called an "isochore", and  $\Delta W = 0$ .
  - If  $S$  is held constant, the state-space trajectory is called an "isentropes".
  - If  $dQ = 0$ , the state-space trajectory is called an "adiabat". Note that  $Q$  is not a state variable. However, any reversible adiabat is also an isentropes, in which case  $S$  is constant.
- 7) Consider some simple processes in a closed ideal-gas system (fixed  $N$ ) that also fix one other variable. Recall that  $U/c = PV = NRT$ . Ways can be devised for conducting any of these processes in a reversible (or irreversible) manner.
- Isothermal (constant  $T$ ) expansion from  $V_i$  to  $V$ 
    - $PV = NRT = \text{const} \rightarrow P \propto V^{-1}$
    - $\Delta U = \Delta(cNRT) = cNR\Delta T = 0$
    - $dW = -PdV = -P_i \left(\frac{V_i}{V}\right) dV$
    - $\Delta W = -\int PdV = -\int P_i \left(\frac{V_i}{V}\right) dV = -P_i V_i \ln\left(\frac{V}{V_i}\right)$
    - $\Delta Q = \Delta U - \Delta W = -\Delta W = P_i V_i \ln\left(\frac{V}{V_i}\right)$
  - Isobaric (constant  $P$ ) expansion from  $V_i$  to  $V$ 
    - $\frac{V}{T} = \frac{NR}{P} = \text{const} \rightarrow V \propto T$
    - $\Delta W = -P\Delta V$
    - $\Delta U = cP\Delta V$
    - $\Delta Q = \Delta U - \Delta W = cP\Delta V - (-P\Delta V) = (c + 1)P\Delta V$
  - Isovolumetric heating (constant  $V$ ) from  $P_i$  to  $P$  or  $T_i$  to  $T$ 
    - $P = \left(\frac{NR}{V}\right)T \rightarrow P \propto T$
    - $\Delta U = cV\Delta P = cNR\Delta T$
    - $dW = -PdV = 0$  so that  $\Delta W = 0$
    - $\Delta Q = \Delta U$
  - Adiabatic compression/expansion from  $(P_i, V_i)$  to  $(P, V)$ 
    - Adiabatic and reversible = isentropic:  $dQ = TdS = 0$
    - $dU = dQ + dW = dW = -PdV$
    - $dU = d(cPV) = c(PdV + VdP)$
    - Set these two expressions for  $dU$  equal to one another to obtain
 
$$(c + 1)PdV + cVdP = 0 \rightarrow \frac{c+1}{c} \frac{dV}{V} + \frac{dP}{P} = \gamma \frac{dV}{V} + \frac{dP}{P} = 0$$



- v. Integrate to obtain  $\ln \left[ \left( \frac{P}{P_i} \right) \left( \frac{V}{V_i} \right)^\gamma \right] = 0$ .
- vi. Thus,  $PV^\gamma = P_i V_i^\gamma \rightarrow P \propto V^{-\gamma}$ .
- vii.  $P = P_i (V_i/V)^\gamma$
- viii.  $\Delta U = U - U_i = c(PV - P_i V_i)$
- ix. 
$$\begin{aligned} \Delta W &= - \int P dV = - \int P_i \left( \frac{V_i}{V} \right)^\gamma dV = \frac{1}{\gamma-1} P_i V_i^\gamma (V^{-\gamma+1} - V_i^{-\gamma+1}) \\ &= c(P_i (V_i^\gamma / V^\gamma) V - P_i V_i) = c(PV - P_i V_i) = U - U_i = \Delta U \end{aligned}$$
- x. This last step, the calculation of  $\Delta W$ , was unnecessary. Because  $\Delta Q = 0$ , we already knew from the 1<sup>st</sup> law that  $\Delta W = \Delta U - \Delta Q = \Delta U$ .

## Lecture 4: Non-equilibrium and irreversible processes

### 1) Review thermodynamic glossary definitions:

- a. Quasi-static and equilibrium are interchangeable terms; a quasi-static process traverses and equilibrium state-space trajectory ( $\Delta Q$  and  $\Delta W$  are well defined).
- b. Non-equilibrium process (involves non-equilibrium states,  $\Delta Q$  and  $\Delta W$  are not well defined)
- c. Reversible process ( $\Delta S_{global} = 0$ ,  $dQ = TdS$  and  $dW = -PdV$ ): In a reversible process, any change in the system entropy is associated with a transfer of entropy to or from the environment; entropy moves from one place to another with the heat flow rather than being created or destroyed. Because no entropy is created, the process can be reversed. A reversible process must be quasi-static, but a quasi-static process need not be reversible.
- d. Irreversible process: Some of the entropy increase of the system is not balanced by entropy transfer into the system, so that the global entropy increases ( $\Delta S_{global} > 0$ ). Energy conservation still requires that  $dU = TdS - PdV = dQ + dW$ . The entropy imbalance, which we state as  $dQ < TdS$ , further implies that  $-dW < PdV$ , which means that part of the volume increase did no work on the environment.
- e. Spontaneous process (no external control, global entropy increases, irreversible)
- f. Joule's theorem

### 2) Discuss schemes for executing a variety of reversible quasi-static processes.

- a. A vertical piston full of gas is initially in thermal contact with a temperature reservoir (a large variable-temperature hot plate) and in mechanical contact with a pressure reservoir (the top is weighed down by a sand pile of known mass so that  $P = mg/A$ ).
- b. Reduce external pressure by removing sand in small increments, waiting at each step for heat to enter from the thermal reservoir and for volume to expand (isothermal,  $P \propto V^{-1}$ ).
- c. Break contact with thermal reservoir. Continue to slowly remove sand slowly, and see the volume expand more quickly until it reaches its initial value (adiabatic,  $P \propto V^{-5/3}$ ).
- d. Restore thermal contact with the hot plate, and slowly raise its temperature, while adding sand at just the right rate, so these two effects balance each other and thereby maintain a constant volume (isochoric,  $P \propto T$ ).
- e. Now decrease the external temperature without changing the amount of sand on the piston until the pressure returns to its initial value (isobaric,  $V \propto T$ ).
- f. By returning to the initial pressure and volume (and temperature), we have completed a cycle in state space.
- g. None of these processes were spontaneous. In each step, we had to DO something to make the process go. We actively moved the system from one state to another. And each process could be run in the opposite direction by reversing our original action.

### 3) Spontaneous processes occur without external control. They have an inherent driving force, which is entropy maximization. A spontaneous always increases global entropy, and is therefore irreversible. Any irreversible process will occur spontaneously unless prevented from doing so by constraints.

### 4) Cyclic process: starts and ends on same state so that $\Delta U = 0$ and $\Delta Q = -\Delta W$ . Can an irreversible process be cyclic? Yes, if it is an equilibrium process and if external reservoirs take away the entropy created during each cycle; but this would not work for an isolated system.

- 5) Quasi-static adiabatic **free expansion of ideal case ( $dU = TdS - PdV = dQ = dW = 0$ )**.
- Let the gas initially be compressed inside a piston and floating in outer space. Program the piston to slide out very slowly (quasi-statically), so that the gas is always in equilibrium as it expands. No heat enters the system. No work is done by the system because the system encounters no opposition. The internal energy of the system therefore remains constant.
  - $U = cPV = cNRT$
  - $T = \text{const}$
  - $PV = \text{const}$
  - $\Delta S = NR \ln\left(\frac{V_2}{V_1}\right) > 0$
  - $\int PdV = \int \left(\frac{P_1 V_1}{V}\right) dV = NRT \ln\left(\frac{V_2}{V_1}\right) = T\Delta S > 0$
  - Look carefully to verify that  $0 = \Delta Q < \int TdS$  and  $0 = -\Delta W < \int PdV$ .
  - The global entropy increases, which can never be undone. The process is irreversible, even though it wasn't allowed to occur spontaneously. The spontaneous version of this process would simply release the piston and let it expand freely to max volume. The resulting final state, and the net impact on the universe, are identical either way.
- 6) Compare this to reversible isothermal expansion. The initial and final states are the same. Only the process is different. First, bring the system into contact with temperature (hot plate) and pressure (sand on lid) reservoirs. Then slowly remove mass from the lid (storing at it removal height) to allow the gas to expand quasi-statically.
- The system endpoint states and trajectory ( $U, S, T, V, P, N, \mu$ ) are identical to those of free expansion. As far as the system itself is concerned, the reversible and free expansion processes are identical! The world outside the system, however, has a very different experience this time.
  - An amount of entropy  $\Delta S = NR \ln\left(\frac{V_2}{V_1}\right)$  is transferred from the heat reservoir into the gas with the incoming heat  $\Delta Q = T\Delta S$ . The entropy of the environment (the hot plate) decreases, which allows the global entropy remains constant.
  - The positive heat transfer into the system is matched by work transfer out of the system ( $\Delta Q = -\Delta W$ ) so that  $\Delta U = \Delta Q + \Delta W = 0$ .
  - The work done by the system is stored in the increased gravitational potential energy of the sand that was on the lid.
  - The entire process can be reversed by slowly placing the mass back on the lid, which does work on the system in compressing the gas, and also pushes heat (and entropy) back into the temperature reservoir.
  - After reversible expansion and compression, the universe (system plus temperature and pressure reservoirs) is returned to its origin states without a change in the global entropy.

- 7) Adiabatic isovolumetric stirring of an ideal gas (closed system). Internal energy increases due to mechanical stirring rather than heat input from a temperature reservoir.
- Since  $V$  is constant, pressure and temperatures rise proportionally.
  - $\Delta U = \Delta W_{stir} = c \Delta P V = c NR \Delta T$ .
  - Entropy increases. Therefore, not reversible. Stirring cannot be “undone”.
  - Joule’s theorem. For any two points in state-space, there is an equilibrium trajectory (possibly one-way) between them that involves no heat transfer. First follow an adiabat from the first state to a point directly below the second point in the  $P - V$  plane, and then raise the pressure (and temperature) to the desired state through stirring or some other non-heat energy transfer. Such methods are conceptually important because heat transfer can’t be measured directly.
- 8) The word “adiabatic” typically implies “fast” in a system that is not well insulated against heat transfer; in other words, it happens quickly enough that there is no time for heat to enter or leave the system. However, a quasi-static adiabatic process must still be slow enough not to substantially knock the system out of equilibrium. In some contexts (like classical mechanics), the word adiabatic is paradoxically used to mean a “slow” change – slow enough to not to disturb the essential characteristics of the observed motion.
- 9) For an irreversible process, degradation occurs when macroscopic mechanical energy is redistributed over the internal microscopic degrees of freedom (think of free expansion), and thereby increases the system entropy without extracting the maximum possible heat ( $dQ < dQ_{max} = TdS$ ) from the environment or doing the maximum possible work ( $-dW < -dW_{max} = PdV$ ) on the environment. Degradation quantifies the amount of energy that could have employed doing useful work but was wasted instead (analogous to the number of hours spent playing Warcraft or browsing Facebook rather than solving thermal-physics problems).
- General expansion (differential degradation indicated by  $dD > 0$ )
    - $-dW = -dW_{max} - dD = PdV - dD < PdV$
    - $dQ = dQ_{max} - dD = TdS - dD < TdS$
    - $dU = dQ + dW = (dQ_{max} - dD) + (dW_{max} + dD)$   
 $= dQ_{max} + dW_{max} = TdS - PdV$ . Still true as expected!
  - Reversible isothermal expansion:  $dD = 0$ 
    - $-dW = -dW_{max} = PdV$
    - $dQ = dQ_{max} = TdS$
    - $dU = dQ + dW = TdS - PdV$
  - Free expansion:
    - No work done ( $-dW = 0 < PdV$ )
    - No heat extracted ( $dQ = 0 < TdS$ ).
    - No internal energy change:  $dU = 0$ .
    - Total degradation:  $dD = dQ_{max} = -dW_{max} = TdS = PdV$

## Lecture 5: State equations and the fundamental relation, the Euler equation, and the Gibbs-Duhem relation

### 1) Euler equation

- Single-component ( $U = TS - PV + \mu N$ ) and multi-component ( $U = TS - PV + \sum \mu_i N_i$ ) versions of the Euler equation.
- The Euler equation is related to the differential FR,  $dU = TdS - PdV + \mu dN$ , though it cannot be obtained from the differential FR for just any set of functions  $T$ ,  $P$ , and  $\mu$ . The Euler equation holds simply because the internal energy is homogeneous to first order in the extensive system variables:  $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$ .
- Integrate the total energy of the system by integrating the differential fundamental relation over a state space trajectory for which the intensive parameters are constant, and only the overall scale  $\lambda$  changes from 0 to 1. Thus the extensive variables each rise in sync from zero to  $\lambda S$ ,  $\lambda V$ , and  $\lambda N$ , where  $S$ ,  $V$ , and  $N$  are also treated as constants.

#### d. Integral version of the derivation:

$$\begin{aligned} U &= \int dU = \int \left( \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} d(\lambda S) + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} d(\lambda V) + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} d(\lambda N) \right) \\ &= \int \left( \frac{\partial U(S, V, N)}{\partial S} S d\lambda + \frac{\partial U(S, V, N)}{\partial V} V d\lambda + \frac{\partial U(S, V, N)}{\partial N} N d\lambda \right) \\ &= \int (TS d\lambda - PV d\lambda + \mu N d\lambda) = (TS - PV + \mu N) \int_0^1 d\lambda = TS - PV + \mu N \end{aligned}$$

#### e. Usual version of the derivation:

$$\begin{aligned} U(S, V, N) &= \frac{\partial(\lambda U(S, V, N))}{\partial \lambda} = \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial \lambda} \\ &= \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} \\ &= \frac{\partial U(S, V, N)}{\partial S} S + \frac{\partial U(S, V, N)}{\partial V} V + \frac{\partial U(S, V, N)}{\partial N} N \\ &= T(S, V, N)S - P(S, V, N)V + \mu(S, V, N)N \end{aligned}$$

- It's critical to appreciate that if we have a complete set of state equations in terms of the extensive system variables,  $T(S, V, N)$ ,  $P(S, V, N)$ , and  $\mu(S, V, N)$ , we can use the Euler equation to construct the FR:  $U(S, V, N)$ .

- For example, let  $S(U, V, N) = \alpha(UVN)^{1/3}$ , so that  $U(S, V, N) = \frac{S^3}{\alpha^3 V N}$ .

- $U(\lambda S, \lambda V, \lambda N) = \frac{(\lambda S)^3}{\alpha^3 \lambda V \lambda N}$
- $T(S, V, N) = \frac{\partial U(S, V, N)}{\partial S} = \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} = \frac{3(\lambda S)^2}{\alpha^3 \lambda V \lambda N} = \frac{3 S^2}{\alpha^3 V N}$
- $P(S, V, N) = -\frac{\partial U(S, V, N)}{\partial V} = -\frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} = -\frac{(\lambda S)^3}{\alpha^3 (\lambda V)^2 \lambda N} = -\frac{S^3}{\alpha^3 V^2 N}$
- $\mu(S, V, N) = \frac{\partial U(S, V, N)}{\partial N} = \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} = -\frac{(\lambda S)^3}{\alpha^3 \lambda V (\lambda N)^2} = -\frac{S^3}{\alpha^3 V N^2}$

#### h. Now go back the other way using the Euler equation.

- $U = TS - PV + \mu N = 3 \frac{S^2}{\alpha^3 V N} S - \frac{S^3}{\alpha^3 V^2 N} V - \frac{S^3}{\alpha^3 V N^2} N = (3 - 1 - 1) \frac{S^3}{\alpha^3 V N} = \frac{S^3}{\alpha^3 V N}$
- $S(U, V, N) = \alpha(UVN)^{1/3}$

## 2) Gibbs-Duhem relation

- a.  $dU = d(TS - PV + \mu N) = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$   
 $= (TdS - PdV + \mu dN) + (SdT - VdP + Nd\mu)$   
 $= TdS - PdV + \mu dN$  Must be true. Recall that this is the differential FR.
- b. Thus,  $SdT - VdP + Nd\mu = 0$  or  $d\mu = -sdT + vdP$ , where  $s = S/N$  and  $v = V/N$ .
- c. Chemical potential can be expressed as a function of only  $T$  and  $P$ . We can express any one of  $T$ ,  $P$ , and  $\mu$  in terms of the other two!
- d. Consider this rather complicated and general recipe for obtaining the function  $\mu(T, P)$ :
  - i. Start with the fundamental relation  $U(S, V, N)$ .
  - ii. Calculate  $T(S, V, N) = \partial U(S, V, N)/\partial S$ , and rearrange it to obtain  $S(T, V, N)$ .
  - iii. Calculate  $P(S, V, N) = -\partial U(S, V, N)/\partial V$ , and rearrange it to obtain  $S(P, V, N)$ .
  - iv. Calculate  $\mu(S, V, N) = \partial U(S, V, N)/\partial N$ .
  - v. Set  $S(T, V, N) = S(P, V, N)$  and eliminate  $S$  to obtain  $V(T, P, N)$ .
  - vi. Substitute  $V(T, P, N)$  into  $S(T, V, N)$  to obtain  $S(T, V(T, P, N), N) = S(T, P, N)$ .
  - vii. Because  $S(T, P, N)$  and  $V(T, P, N)$  are extensive and only depend on one extensive variable ( $N$ ), the molar entropy  $s = S/N$  and molar volume  $v = V/N$  can't depend on  $N$ , but only on  $T$  and  $P$ . So  $S(T, P, N) = N s(T, P)$  and  $V(T, P, N) = N v(T, P)$ .
  - viii. Substitute  $S(T, P, N)$  and  $V(T, P, N)$  into  $\mu(S, V, N)$  to obtain  $\mu(N s(T, P), N v(T, P), N)$ .
  - ix. Because Gibbs-Duhem relation shows that  $\mu$  can depend only  $T$  and  $P$ , and because the extensive variable  $N$  cannot be expressed solely in terms of  $T$  and  $P$ , the factors of  $N$  must cancel out to leave  $\mu(s(T, P), v(T, P), 1) = \mu(T, P)$ .
  - x. Don't worry about reproducing this. You only need to know that it can be done!
- e. The Gibbs-Duhem relation leads directly to the well-known Gibbs phase rule and to a relationship between the slope of the coexistence line of a phase transition in the  $P - T$  plane and the volume change that occurs there (e.g. freezing of ice). More on this later.

 3) Use the ideal gas FR to obtain state equations for  $T$ ,  $P$ , and  $\mu$ , and rearrange them into familiar forms:

- a. Sackur-Tetrode equation:  $S = NR \left\{ \ln \left[ \left( \frac{V}{V_0} \right) \left( \frac{U}{U_0} \right)^c \left( \frac{N_0}{N} \right)^{c+1} \right] + (c+1) \right\}$
- b.  $S = NR \{ \ln(I/I_0) + (c+1) \}$  where  $\frac{I}{I_0} = \frac{(VU^c/N^{c+1})}{(V_0U_0^c/N_0^{c+1})} = \left( \frac{V}{V_0} \right) \left( \frac{U}{U_0} \right)^c \left( \frac{N_0}{N} \right)^{c+1}$
- c.  $U_0, V_0, N_0$  indicate a reference state with an entropy of  $NR(c+1)$ .
- d. Entropic differential FR:  $dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$
- e. Consider the partial derivatives of  $I(U, V, N)$ .
  - i.  $\frac{1}{I} \frac{\partial I}{\partial U} = \frac{1}{I} \frac{c(VU^{c-1}/N^{c+1})}{1} = \frac{1}{I} \frac{c(VU^c/N^{c+1})}{U} = \frac{1}{I} \frac{cI}{U} = \frac{c}{U}$ .
  - ii.  $\frac{1}{I} \frac{\partial I}{\partial V} = \frac{1}{I} \frac{(U^c/N^{c+1})}{1} = \frac{1}{I} \frac{(VU^c/N^{c+1})}{V} = \frac{1}{I} \frac{I}{V} = \frac{1}{V}$
  - iii.  $\frac{1}{I} \frac{\partial I}{\partial N} = \frac{1}{I} \frac{1-(c+1)(VU^c/N^{c+2})}{1} = -\frac{1}{I} \frac{(c+1)(VU^c/N^{c+1})}{N} = -\frac{1}{I} \frac{(c+1)I}{N} = -\frac{(c+1)}{N}$
- f.  $\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N} = NR \frac{1}{I} \frac{\partial I}{\partial U} = \frac{cNR}{U} \rightarrow U = cNRT$
- g.  $\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{U,N} = NR \frac{1}{I} \frac{\partial I}{\partial V} = \frac{NR}{V} \rightarrow PV = NRT$
- h.  $\frac{\mu}{T} = -\left( \frac{\partial S}{\partial N} \right)_{U,V} = -\frac{S}{N} - NR \frac{1}{I} \frac{\partial I}{\partial N} = -\frac{S}{N} + (c+1)R = -R \ln \left( \frac{I}{I_0} \right) \rightarrow \frac{\mu}{T} + s = (c+1)R$

4) Substitute the state equations into the Euler equation to recover the ideal gas FR.

a.  $U = TS - PV + \mu N$

b.  $S = \frac{1}{T}U + \frac{P}{T}V - \frac{\mu}{T}N = \frac{cNR}{U}U + \frac{NR}{V}V + R \ln\left(\frac{I}{I_0}\right)N = NR \left\{ \ln\left(\frac{I}{I_0}\right) + (c+1) \right\}$

5) Alternatively, integrate the  $T$  and  $P$  state equations to obtain the ideal gas FR.

a. Molar intensive variables:  $\left\{ u = \frac{U}{N}, s = \frac{S}{N}, v = \frac{V}{N} \right\} \rightarrow Pv = RT$  and  $u = cPv$

b.  $ds = \frac{1}{T}du + \frac{P}{T}dv = \frac{cR}{u}du + \frac{R}{v}dv$

c.  $\frac{ds}{R} = c \frac{du}{u} + \frac{dv}{v}$  integrates as  $\frac{S-S_0}{R} = \ln \left[ \left( \frac{v}{v_0} \right) \left( \frac{u}{u_0} \right)^c \right]$

d.  $S = NR \ln \left[ \left( \frac{V}{V_0} \right) \left( \frac{U}{U_0} \right)^c \left( \frac{N_0}{N} \right)^{c+1} \right] + Ns_0 = N \left\{ R \ln \left( \frac{I}{I_0} \right) + s_0 \right\}$

e. Leaves an unknown integration constant, which turns out to be  $s_0 = (c+1)R$ .

6) Find  $\Delta S$  between any two states:  $\Delta S = NR \left\{ \ln \left( \frac{I_f}{I_i} \right) \right\}$

a. Other useful state equations can be obtained via variable substitutions ( $U/c = PV = NRT$ ).

b.  $\frac{I_f}{I_i} = \left( \frac{V_f}{V_i} \right) \left( \frac{U_f}{U_i} \right)^c \left( \frac{N_i}{N_f} \right)^{c+1} = \left( \frac{V_f}{V_i} \right) \left( \frac{T_f}{T_i} \right)^c \left( \frac{N_i}{N_f} \right) = \left( \frac{P_i}{P_f} \right) \left( \frac{U_f}{U_i} \right)^{c+1} \left( \frac{N_i}{N_f} \right)^{c+1} = \left( \frac{P_f}{P_i} \right)^c \left( \frac{V_f}{V_i} \right)^{c+1} \left( \frac{N_i}{N_f} \right)^{c+1} = \left( \frac{P_i}{P_f} \right) \left( \frac{T_f}{T_i} \right)^{c+1}$

c. Copy this to a convenient place. You'll use it often to calculate  $\Delta S$  for various processes!

7) Find  $\frac{\Delta \mu}{RT}$  between any two states:  $\frac{\Delta \mu}{RT} = \frac{\mu}{RT} - \frac{\mu_0}{RT} = \frac{\Delta S}{NR} = -\ln \left( \frac{I_f}{I_i} \right)$ .

8) Black-body radiation FR and state equations (photon gas inside cavity within a warm object)

a. Two state equations:  $U = bVT^4 = 3PV$ , where  $b = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} = 7.56 \times 10^{-16} \text{ J/m}^3/\text{K}^4$ .

$$\frac{1}{T} = \left( b \frac{V}{U} \right)^{1/4} \quad \text{and} \quad \frac{P}{T} = \frac{1}{3} \left( b \frac{U^3}{V^3} \right)^{1/4}$$

b. Photons in the cavity and within the cavity walls are in equilibrium, which means that  $\mu_{\text{cavity}} = \mu_{\text{wall}}$ . Because there are no photons in the wall,  $\mu_{\text{wall}} = 0$ . So,  $\mu_{\text{cavity}}$  also equals 0. Having a zero chemical potential is related to the fact that boson number is not conserved.

c. Euler equation:  $S = \frac{1}{T}U + \frac{P}{T}V = \left( b \frac{V}{U} \right)^{1/4} U + \frac{1}{3} \left( b \frac{U^3}{V^3} \right)^{1/4} V$

d. This reduces nicely to  $S = \frac{4}{3} (bVU^3)^{1/4}$ .

e. Conversely, we can obtain the state equations from the FR.

i.  $\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N} = \frac{4}{3} \frac{1}{4} \frac{1}{U} (bVU^3)^{1/4} = \left( \frac{bV}{U} \right)^{1/4} \rightarrow U = bVT^4$

ii.  $\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{U,N} = \frac{4}{3} \frac{1}{4} \frac{1}{V} (bVU^3)^{1/4} = \frac{1}{3} \left( \frac{bU^3}{V^3} \right)^{1/4} \rightarrow 3P = \left( \frac{bU^3}{V^3} \right)^{1/4} \left( \frac{U}{bV} \right)^{1/4} = \frac{U}{V}$   
 $\rightarrow U = 3PV$

f. Since  $S \propto N$ , it seems weird that  $\mu = \left( \frac{\partial S}{\partial N} \right)_{U,V} = 0$ . We will derive this FR in statistical mechanics, and use it to show that  $N \propto VT^3 \propto (VU^3)^{1/4}$ , where  $N$  depends on  $U$  and  $V$

rather than being another independent variable. Thus when  $U$  and  $V$  are fixed,  $S$  has no  $N$  dependence. Just use this relationship as a bonus for now (see photon-gas Wikipedia page).

- g. The claim is that the expansion of the universe is a reversible adiabatic process. It's a dynamic expansion, and the cosmic-microwave-background (CMB) equilibrium is simply following it adiabatically. But if that's true, then as  $V$  goes up,  $U$  comes down – the system is doing work against gravitational attraction. In the lab, work is done on external systems. But with the universe, there is no external system. Imagine an internal spring inside an ideal-gas piston that is stretched during expansion. This is analogous to the universe working against gravity. Someday, this stored gravitational potential energy could be used to reverse the expansion (the big crunch).

- h. Derive the form of the photon-gas adiabat in various state-space planes:

$$P \propto V^{-4/3}, U \propto T, P \propto T^4 \propto U^4, V \propto T^{-3} \propto U^{-3}$$

- 9) Van der Waals (non ideal) gas [might use later – no homework on this for now]

a. Van der Waals FR:  $S = Ns_0 + NR \ln \left[ \left( \frac{V}{N} - b \right) \left( \frac{U}{N} + a \frac{N}{V} \right)^c \right] = N \{ R \ln(v' u'^c) + s_0 \}$

b.  $\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N} = NR \frac{c}{u'} \frac{\partial u'}{\partial U} = NR \frac{c}{u'} \frac{1}{N} = \frac{cR}{u'} = \frac{cR}{\left( \frac{U}{N} + a \frac{N}{V} \right)} \rightarrow \left( U + a \frac{N^2}{V} \right) = cNRT$

c.  $\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{U,N} = NR \frac{1}{v'} \frac{\partial v'}{\partial V} + NR \frac{c}{u'} \frac{\partial u'}{\partial V} = NR \frac{1}{v'} \frac{1}{N} + NR \frac{c}{u'} \left( -\frac{aN}{V^2} \right) = \frac{R}{\left( \frac{V}{N} - b \right)} - \frac{\frac{acRN^2}{V^2}}{\left( \frac{U}{N} + a \frac{N}{V} \right)} =$   
 $\frac{NR}{(V-bN)} - \frac{aN^2}{TV^2} \rightarrow \left( P + \frac{aN^2}{V^2} \right) (V - bN) = NRT$



## Lecture 6: Common ideal-gas engine cycles

### 1) Integrated area as a signed quantity.

a. The area under a curve is an integral whose value depends on the direction of the integration.

b.  $\int_0^1 x dx = \left(\frac{x^2}{2}\right)_0^1 = \frac{1}{2} - 0 = \frac{1}{2}$  and  $\int_1^0 x dx = \left(\frac{x^2}{2}\right)_1^0 = 0 - \frac{1}{2} = -\frac{1}{2}$

### 2) Reversible cyclic processes

a. For a reversible cyclic process,  $\Delta Q = \oint T dS$  and  $\Delta W = -\oint P dV$  are computed as the areas inside the respective  $TS$  and  $PV$  state-space loops.

b. State variables like  $S$ ,  $U$  and other thermodynamic potentials experience zero change after a complete cycle. Because heat and work are not state variables, they are not conserved quantities, and can accumulate after a full cycle. The net heat and work-energy transfers for a complete cycle are constrained by the first law:  $\Delta Q + \Delta W = 0$ .

c. If we integrate a **closed loop in the CW direction** we get a large positive quantity going right across the top, and a smaller negative quantity going left across the bottom. The result is positive. So the net work done *by* the system ( $-\Delta W > 0$ ) and the net heat added *to* the system ( $+\Delta Q > 0$ ) around a CW loop in the  $PV$  or  $TS$  planes are positive. Such a cycle is called a *heat engine*. We say that **a heat engine converts heat into work**; but technically, heat and work only exist as transfer quantities.

d. If we integrate a **closed loop in the CCW direction** we get a large negative quantity going left across the top, and a smaller positive quantity going right across the bottom. The result is negative. So the net work done *by* the system ( $-\Delta W < 0$ ) and the net heat added *to* the system ( $+\Delta Q < 0$ ) around a CCW loop in the  $PV$  or  $TS$  planes are negative. Such a cycle is called a *refrigerator*. We say that **a refrigerator converts work into heat**; but technically, heat and work only exist as transfer quantities.

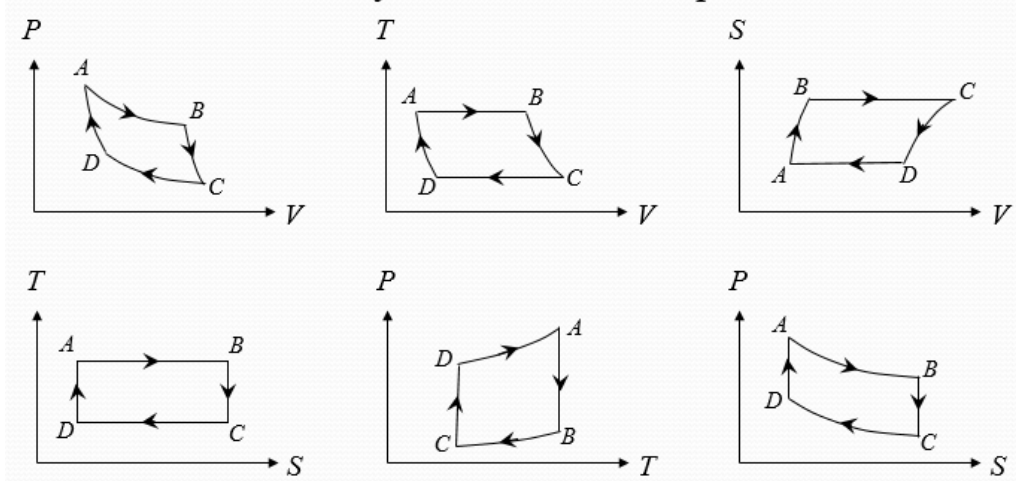
### 3) Six simple thermodynamic cycles (coordinates listed in the order giving a CW engine loop)

- Carnot: rectangular in the  $TS$  plane
- Ideal cycle: rectangular in the  $PV$  plane.
- Brayton: rectangular in the  $PS$  plane.
- Otto: rectangular in the  $SV$  plane
- Stirling: rectangular in the  $TV$  plane.
- Ericsson: rectangular in the  $PT$  plane.

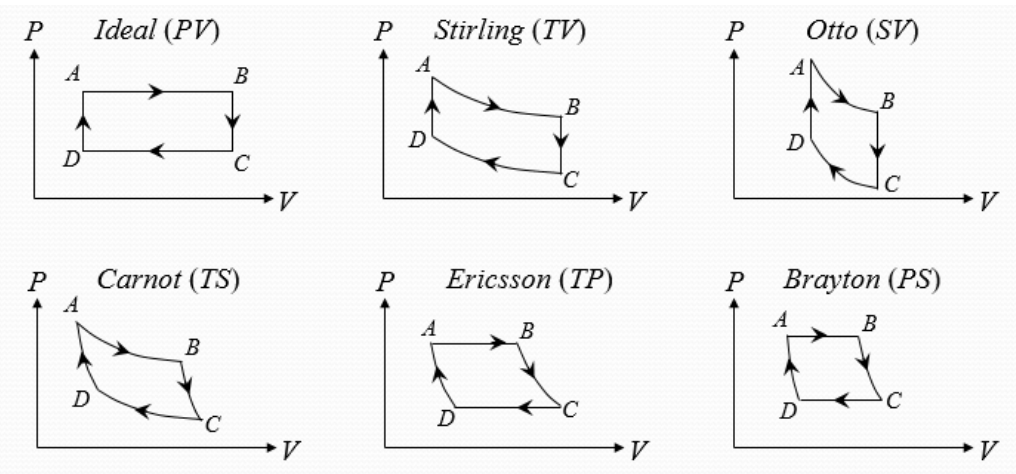
### 4) Ideal-gas FR and state equation reminder: $\frac{S}{NR} = \ln \left[ \frac{I}{I_0} \right] + (c + 1)$ and $\frac{U}{c} = PV = NRT$ .

$$\frac{I}{I_0} = \left(\frac{V}{V_0}\right) \left(\frac{U}{U_0}\right)^c \left(\frac{N_0}{N}\right)^{c+1} = \left(\frac{V}{V_0}\right) \left(\frac{T}{T_0}\right)^c \left(\frac{N_0}{N}\right) = \left(\frac{P_0}{P}\right) \left(\frac{U}{U_0}\right)^{c+1} \left(\frac{N_0}{N}\right)^{c+1} = \left(\frac{P_0}{P}\right) \left(\frac{T}{T_0}\right)^{c+1} = \left(\frac{P}{P_0}\right)^c \left(\frac{V}{V_0}\right)^{c+1} \left(\frac{N_0}{N}\right)^{c+1}$$

## Carnot cycle in six different planes



## The six simple cycles, represented in the PV plane



- 5) One can draw any of the six simple cycles in any of the 6 planes in the “engine” direction.
  - a. There are only isothermal, isovolumetric, isobaric and adiabatic/isentropic segments in any cycle. For a reversible process, “isentropic” and “adiabatic” mean the same thing.
  - b. For a given cycle type, the figure will either be rectangular (both coordinates are natural), have no flat sides (both coordinates are non-natural), or have two flat sides (one natural and one non-natural coordinate).
  - c. If there are two flat sides, always draw them first. Then figure out whether the curvature of the other two sides are positive or negative (not terribly difficult). Note that in the  $P$ - $V$  plane, adiabats and isotherms have the same curvature, but the adiabats fall off much more quickly during expansion (like  $V^{-\gamma}$  rather than  $V^{-1}$ ).
  - d. Pick a segment and figure out which direction is positive in the corresponding CW  $P$ - $V$  loop. Add an arrow in this direction on the segment, and to each of the others.
  - e. Figure out which segment corresponds to the uppermost segment of the corresponding CW  $P$ - $V$  loop, and label the vertices of this segment so that its arrow points from A to B. Then add C and D to complete the loop.

## 6) Efficiency

- a. For reversible processes, they run CW in PV and TS planes. Their efficiency is limited.
- b. The Carnot, Otto and Brayton cycles draw all of their input heat ( $Q_{in}$ ) in a single process (either isothermal or isentropic) and emit all of their waste heat ( $Q_{out}$ ) in a single process, making the calculation of efficiency rather straightforward.
- c. Some cycles have non-zero heat transfer in every segment. To calculate  $Q_{in}$ , sum up only the heat transfers of processes with heat flowing into the system ( $Q > 0$ ). And to calculate  $Q_{out}$ , sum up only the heat transfers of processes with heat flowing out of the system ( $Q < 0$ ). In general, a single segment can have heat flowing in during part of a segment and flowing out again during another part of the segment; when this happens, count heat coming in as part of  $Q_{in}$  and count the heat flow out as part of  $Q_{out}$ . Treat  $Q_{in}$  and  $Q_{out}$  as positive quantities.
- d. Recall that  $\Delta U = W_{tot} + Q_{tot} = 0$  for a cycle since internal energy is a state variable. Thus  $-W_{tot} = Q_{tot} = Q_{in} - Q_{out}$ .
- e. The engine efficiency is the fraction of input heat that gets converted to useful work, or in other words, the ratio of work energy produced ( $-W_{tot}$ ) over heat energy input ( $Q_{in}$ ). Obviously, if less heat is wasted, more work gets done.
- f.  $\epsilon = \frac{(-W_{tot})}{Q_{in}} = \frac{Q_{tot}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$
- g. Refrigerators (and heat pumps) convert work to heat. For reversible processes, they run CCW in the PV and TS planes. The *coefficient of performance* (COP) of a refrigerator is  $COP = \frac{Q_{out}}{-W_{tot}} = \frac{Q_{out}}{Q_{in} - Q_{out}} = \frac{Q_{out}/Q_{in}}{1 - Q_{out}/Q_{in}}$ , which is not exactly the inverse of the reverse engine efficiency, because the  $Q_{in}$  and  $Q_{out}$  get switched when the cycle direction gets reversed.

## 7) Carnot cycle (isothermal – adiabatic) in detail

- a. Define isothermal volume ratio  $r_T = \frac{V_B}{V_A} = \frac{V_C}{V_D}$  and adiabatic volume ratio  $r_Q = \frac{V_C}{V_B} = \frac{V_D}{V_A}$ .
- b. Isothermal ( $\Delta U = 0$ ) expansion at  $T_h$  -- step AB  
 $Q = -W = \int P dV = NRT_h \ln(r_T) > 0$
- c. Adiabatic ( $\Delta Q = 0$ ) expansion – step BC  
 $-\Delta U = -W = \int P dV = cNRT_h \left[ 1 - r_Q^{-1/c} \right] > 0$
- d. Isothermal ( $\Delta U = 0$ ) compression at  $T_c$  – step CD  
 $\Delta Q = -W = \int P dV = -NRT_c \ln(r_T) < 0$
- e. Adiabatic ( $\Delta Q = 0$ ) compression – step DA  
 $\Delta U = W = -cNRT_h \left[ 1 - r_Q^{-1/c} \right] < 0$
- f. Steps BC and DA are isentropic:  $\oint dS = \Delta S_{AB} + \Delta S_{CD} = \frac{Q_{in}}{T_h} - \frac{Q_{out}}{T_c} = 0 \rightarrow \frac{Q_c}{Q_h} = \frac{T_c}{T_h}$ .
- g.  $\epsilon = \frac{-W_{tot}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_c}{T_h}$
- h. Few if any real engines actually follow the Carnot cycle. But the Carnot cycle plays an important conceptual role in the theory of thermodynamic engines. It is the most efficient engine cycle operating between two fixed-temperature reservoirs.
- i. Do we really need to waste heat? Suppose that an engine operating between temperature reservoirs at  $T_h$  and  $T_c$  skips the step of wasting heat at  $T_c$ . Entropy is drawn into the system at high temperature, but not subsequently eliminated at low temperature. The energy saved can be used to do additional work instead, so that  $W_{tot} = -Q_{tot} = -Q_{in}$  and efficiency increases to  $\epsilon = -W_{tot}/Q_{in} = 1$ . Sounds great! But if heat and entropy are only imported

into the system (never exported), and if the system returns to its initial state after every cycle, then entropy is being magically destroyed, which violates the 2<sup>nd</sup> law. One must waste heat in order to prevent the destruction of entropy.

8) Hurricanes as Carnot engines (K&T)

- a. The upper atmosphere is cooler than the earth's surface due to the greenhouse effect. This temperature difference powers a heat engine that transports heat and entropy into the atmosphere.
- b. Cool air is drawn downward from the upper atmosphere, getting compressed and heated adiabatically along the way. This air then expands and draws heat isothermally at the ocean surface as it spirals inward towards the center. In the middle of the hurricane, the air is funneled upward as it expands and cools adiabatically. The air then dumps its waste heat and entropy isothermally in the upper atmosphere.
- c. Two phenomena that generate entropy are the mixing of humid and dry air, and wind friction. Mixing and the subsequent precipitation are relatively gentle processes, whereas wind can get pretty violent. Hurricanes are self-stabilizing in the sense that the spiraling air flow suppresses mixing with outside air, so that wind then becomes the only viable means of generating the required entropy.

9) Otto cycle (isovolumetric – adiabatic)

- a. Uses adiabatic (isentropic) and isovolumetric processes.
- b. Otto was an engine developer in Germany in the 1800's. He invented the first practical four-stroke engine in 1876. Worked with Gottlieb Daimler and Wilhelm Maybach to develop engines for boats and aircraft. Daimler and Maybach left on unhappy terms, and later secretly developed a very compact high-efficiency engine based on the Otto cycle to power the first horseless carriage in 1895. At the same time, Karl Benz independently developed his own horseless carriage based on a different four-stroke engine. The two became competitors, but never interacted with one another. After their deaths, the two companies merged.
- c. View animation of a four-stroke engine: [http://en.wikipedia.org/wiki/Four-stroke\\_engine](http://en.wikipedia.org/wiki/Four-stroke_engine) and possibly the video at <https://www.youtube.com/watch?v=Pu7g3ulG6Zo>.
- d. The two adiabatic processes are apparent from the motion of the piston. The isovolumetric heating occurs very quickly when the fuel is burned. It isn't practical to wait for the gas to cool isovolumetrically. So the waste heat is eliminated by exhausting and replacing the gas (the other two piston strokes).
- e. The story of Bertha Benz: [http://en.wikipedia.org/wiki/Bertha\\_Benz](http://en.wikipedia.org/wiki/Bertha_Benz)

10) Diesel cycle (isovolumetric/isobaric-adiabatic)

- a. Similar to the Otto cycle. The Diesel cycle uses adiabatic (isentropic) compression and expansion. Whereas the Otto cycle combusts at constant volume (ignited with a spark), the Diesel cycle combusts at constant pressure.
- b. The Diesel engine was invented by Rulolph Diesel in 1893 – very rich within a few years.
- c. The amount of compression is limited in an Otto engine because the fuel is added before the compression is complete, and if you squeeze too hard, the high temperature will ignite the fuel early and force the piston backwards (back-fire). A Diesel engine compresses the gas hot enough for self ignition of the fuel, and the fuel is added slowly beginning at the top of the piston up stroke, so that the fuel is burned at constant pressure during the first part of the

down stroke. As a result, Diesel engines run much hotter and see higher pressures and greater compression ratios.

- d. Diesel engines are more efficient, are able to use a much less volatile fuel. But historically, they are noisier, smokier, harder to start (especially when cold), and require fuel injection. These disadvantages have largely been eliminated now. Diesel is very popular in Europe.

11) Brayton cycle (isobaric – adiabatic)

- a. Models the behavior of an air-breathing jet engine.
- b. History: [https://en.wikipedia.org/wiki/Brayton\\_cycle](https://en.wikipedia.org/wiki/Brayton_cycle)
- c. Illustrations: [http://en.wikipedia.org/wiki/Components\\_of\\_jet\\_engines](http://en.wikipedia.org/wiki/Components_of_jet_engines)
- d. The turbines compress the air adiabatically in stages, until it is very dense and hot, at which point injected fuel vapors spontaneously ignite, causing the gas to expand rapidly at constant pressure. Part of this work energy is borrowed by back-end turbines and used to power the front-end turbines; the rest is exhausted at high speed to provide thrust. In by-pass turbofan engines, the front-end turbine is fed a greater fraction of the total generated power, which then pushes air through a large bypass channel to provide greater thrust.
- e. Video content:  
<https://www.youtube.com/watch?v=GF-70yncAVY>  
<https://www.youtube.com/watch?v=7lcKOc9YQbg>  
[https://www.youtube.com/watch?v=0rnaFDOJ\\_Xc](https://www.youtube.com/watch?v=0rnaFDOJ_Xc)
- f. RAM/SCRAM jet engines are also based on the Brayton cycle:  
<http://en.wikipedia.org/wiki/Scramjet>.  
<https://www.youtube.com/watch?v=Mbat7sASj7A>  
<https://www.youtube.com/watch?v=xpOa3B03gYg>  
<https://www.youtube.com/watch?v=8F4uSI3CXVc>

12) Waste-heat regeneration (recycling) in the Stirling cycle (isothermal – isovolumetric)

- a. Like the Carnot cycle, the Stirling cycle has isothermal heat import and export processes, which tend to be slow, making them less practical than other engine cycles.
- b.  $Q_{in} = Q_{highT} + Q_{lowV}$  and  $Q_{out} = Q_{lowT} + Q_{highV}$ , where  $Q_{highT}$  from the high-temperature isothermal expansion and  $Q_{lowV}$  from the low-volume pressurization are positive, and where  $Q_{lowT}$  from the low-temperature isothermal compression and  $Q_{highV}$  from the low-volume depressurization are negative.
- c. Stirling engines are often designed to reuse waste heat  $Q_{highV}$  from the high-volume leg as input heat  $Q_{lowV}$  for the low-volume leg. These are called “regenerative” engines. This very useful trick confuses the definition of  $Q_{in}$  in the efficiency.
- d. Suppose that your juicer yields 4 g of orange juice for every 10 g of raw orange that you process (40% efficient). If you later reveal that you have been processing the waste material a second time in order to obtain such a high yield, that doesn’t mean that your efficiency is actually  $4/(10 + 6) = 25\%$ ? You still get 4 g of output for every 10 g of input. If reprocessing makes a difference, that improvement is already built into your stated efficiency. Moral of the story: don’t double-count recycled input.
- e. To prevent the double counting of recycled energy, use  $\epsilon = -W_{tot}/(Q_{in} - Q_{recovered})$ .
- f. For simplicity, we’ll assume 100% waste-heat recycling, so that  $Q_{recovered}$  is equal to  $-Q_{highV} = Q_{lowV}$ . Thus,  $Q_{in} - Q_{recovered} = (Q_{highT} + Q_{lowV}) - Q_{lowV} = Q_{highT}$ .

- g. Now the efficiency of the regenerative Stirling cycle is expressed as  $\epsilon = -W_{tot}/Q_{highT}$ . This nicely depends only on a single heat-input process.
- h. Stirling-cycle history: [https://en.wikipedia.org/wiki/Stirling\\_engine](https://en.wikipedia.org/wiki/Stirling_engine) (animations)
- i. Stirling-cycle examples and illustrations:  
<https://www.youtube.com/watch?v=PamhI7ZJiFs>  
[https://www.youtube.com/watch?v=wGRmcvxB\\_dk](https://www.youtube.com/watch?v=wGRmcvxB_dk)  
<https://www.youtube.com/watch?v=BmhMAaRCou0>

13) Ericsson (isothermal-isobaric) cycles

- a. Also involves isothermal processes, which tend to be slow and therefore less practical.
- b. Also employs waste heat regeneration between the isobaric processes.
- c. Ericsson-cycle history: [https://en.wikipedia.org/wiki/Ericsson\\_cycle](https://en.wikipedia.org/wiki/Ericsson_cycle)
- d. Ericsson-cycle examples and illustrations  
<https://www.youtube.com/watch?v=jW4pFAACOhE>  
<https://www.youtube.com/watch?v=C-JFQFfmm7k>

14) The Deutsches Museum of science and technology in Munich has incredible exhibits on the history of engines and power production (among many other topics). This is really a museum for grown-ups! It helps to either read German or take along a German friend. See for example, the exhibits on steam engines or jet-turbine engines. If you ever get the chance to visit, plan to spend at least a day at the museum. I also recommend the Mercedes-Benz museum in Stuttgart if you like engines.

<https://www.deutsches-museum.de/en/collections/machines/power-engines>  
<https://www.youtube.com/watch?v=g8LrAsL4oH0>

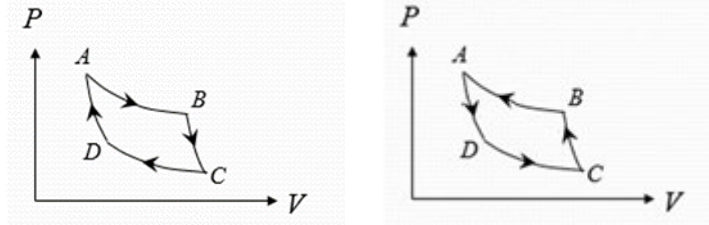
## Lecture 7: Irreversible cycles and perpetual-motion machines of the 2<sup>nd</sup> kind

### 1) Irreversible cycles

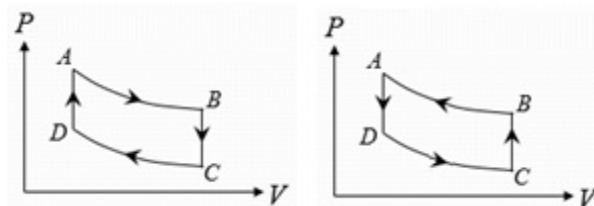
- a. For an irreversible process,  $\Delta Q < \oint TdS$  and  $(-\Delta W) < \oint PdV$ . In this case, the accumulated heat transferred to the system, or the accumulated work-energy done by the system, is smaller than the area inside the respective state-space loop. Equality is achieved in these relationships only for a reversible process.
- b. Imagine now that you run an irreversible process backwards. Every quantity in these inequalities changes, yielding  $\Delta Q > \oint TdS$  and  $(-\Delta W) > \oint PdV$ , which violates the 2<sup>nd</sup> law. The moral of the story: you can't run an irreversible process backwards.
- c. Recall that an reversible isothermal expansion and a free expansion of an ideal gas can traverse the same trajectory, though one is used to do work while the other is not. The final system state is the same for both cases, and has more entropy than the initial state. In the case of free expansion, the entropy increase occurs within the system itself, so that the global entropy goes up. In the reversible case, entropy is imported from the environment during isothermal heating, so that the global entropy is constant.
- d. Reversible cycles import and export the same amount of entropy, so that the local and global entropies return to their original values after one cycle. Irreversible cycles export more entropy than they import – local entropy returns to initial value and outside entropy increases.
- e. The fact that two processes traverse the same state-space trajectory doesn't mean that two processes are identical (unless they are reversible). Many different irreversible processes can traverse the same trajectory of equilibrium states.
- f. A real engine is at least somewhat irreversible. Run backwards, it also acts as a real refrigerator, which is also somewhat irreversible. Thus, we can safely conclude that even if the real engine and refrigerator traverse the same state-space trajectory in opposite directions, their processes are not the reverse of one another.
- g. Perpetual motion machines of the 1<sup>st</sup> kind violate energy conservation (the 1<sup>st</sup> law of thermodynamics) by producing more energy than they consume. Perpetual motion machines of the 2<sup>nd</sup> kind respect energy conservation but consume (decrease) entropy in violation of the 2<sup>nd</sup> law. Claims of the 2<sup>nd</sup> kind typically either report the conversion of thermal energy into work without waste heat (e.g. 100% efficiency), or require the spontaneous flow of heat from low to high temperature.

## 2) A “psycho” Carnot cycle (isothermal and adiabatic)

- a. We illustrate the PV-plane cycle diagrams for engine and refrigerator.



- b. Consider a CW Carnot engine cycle (ideal gas) in the  $PV$  plane, comprised of both isothermal and adiabatic expansion and compression segments. Because the two adiabatic processes  $BC$  and  $DA$  involve no heat, the areas under their  $P(V)$  curves equal the corresponding internal energy changes:  $W_{BC} + W_{DA} = \Delta U_{BC} + \Delta U_{DA} = cNR(\Delta T_{BC} + \Delta T_{DA})$ . Because these adiabats operate between the same two isotherms ( $\Delta T_{BC} = -\Delta T_{DA}$ ), the two areas add to zero; they are equal and opposite. Ditto for the CCW refrigerator cycle.
- c. Thus, the area inside the CW engine loop is obtained from the two isothermal processes alone  $\text{Area} = -W_{tot} = NRT_h \ln\left(\frac{V_B}{V_A}\right) - NRT_c \ln\left(\frac{V_C}{V_D}\right) > 0$ . As expected, the work done on the system is negative ( $W_{tot} < 0$ ). Net energy enters the system as heat and leaves as work.
- d. Now, imagine modifying the cycle so that the reversible isothermal expansion process ( $AB$ ) is replaced by a free-expansion process, so that no work or heat energy is exchanged with the environment. Dream up an apparatus for accomplishing this. We'll call this a *psycho* cycle.
- e. The total work done on the system during the cycle is determined solely by isothermal process  $CD$ , so that  $-W_{tot} = -NRT_c \ln\left(\frac{V_C}{V_D}\right) < 0$ , which means that  $W_{tot} > 0$  and  $Q_{tot} < 0$ . Net energy enters the system as work and leaves as heat! This is a very strange engine indeed. It behaves like a refrigerator despite running CW in the  $PV$  plane.
- f. Can such a psycho engine cycle really behave as a refrigerator (convert work to heat)? Does that break some fundamental rule of thermodynamics? Energy is clearly conserved. Show that the 2<sup>nd</sup>-law inequalities ( $-W \leq \oint PdV$ ,  $Q \leq \oint TdS$ ) are also obeyed. Looks OK.
- g. Suppose we want to run a psycho cycle in reverse (CCW) so as to recover engine-like behavior. Is this possible? Describe the meaning and viability of spontaneous free compression. Distinct but similar homework problem.
- h. We can do the same thing for a Stirling cycle (isothermal and isovolumetric). We'll even include waste-heat regeneration (as done above) so that the efficiency is the same as that of a Carnot cycle. Because the two isovolumetric processes  $BC$  and  $DA$  involve no work, the areas under their  $P(V)$  curves are zero, and the area inside the CW engine loop is obtained from the two isothermal processes alone. When the reversible isothermal expansion process ( $AB$ ) is replaced by a free-expansion process, the details are just as for a Carnot cycle.





## Lecture 8: Exam Review

## Lecture 9: Entropy maximization and the equalization of the intensive parameters of two systems in contact

### 1) Entropy maximization:

- a. Consider an isolated composite system containing two-subsystems separated by a wall.
- b.  $U = U_1 + U_2$ ,  $V = V_1 + V_2$ ,  $N = N_1 + N_2$  are all three constant
- c.  $dS = dS_1 + dS_2 = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2 + \frac{P_1}{T_1} dV_1 + \frac{P_2}{T_2} dV_2 - \frac{\mu_1}{T_1} dN_1 - \frac{\mu_2}{T_2} dN_2$
- d. The composite system is isolated from the global environment, which implies the following equalities:  $dU_1 = -dU_2$ ,  $dV_1 = -dV_2$ ,  $dN_1 = -dN_2$ .
- e. Simplify  $dS = \left(\frac{1}{T_2} - \frac{1}{T_1}\right) dU_2 + \left(\frac{P_2}{T_2} - \frac{P_1}{T_1}\right) dV_2 - \left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1}\right) dN_2$ .
- f. In equilibrium, entropy is maximized with respect to the internal constraints so that  $dS = 0$ . This can only occur when the intensive parameters are balanced between the two sides.
- g. Suppose, for example, that the wall remains impermeable and rigid, but becomes diathermal so as to allow a redistribution of  $U_1$  and  $U_2$  at constant  $V_2$  and  $N_2$  ( $dV_2 = 0$  and  $dN_2 = 0$ ). When  $dU_2 \neq 0$ , maximum entropy ( $dS = 0$ ) implies that  $T_1 = T_2$ .
- h. Suppose we start in mutual equilibrium ( $T_1 = T_2$ ), and then transfer a finite amount of energy from side 1 to side 2, so that  $\Delta U_2 = -\Delta U_1 = \Delta U > 0$ , which also makes  $T'_2 > T'_1$ . In that case,  $\frac{1}{T'_2} - \frac{1}{T'_1} < 0$  so that  $\Delta S = cNR \left(\frac{1}{U_2 + \Delta U} - \frac{1}{U_1 - \Delta U}\right) \Delta U < 0$ . The deviation from equilibrium caused the isolated-system entropy to decrease. Thus, the second law forbids spontaneous departures from equilibrium, (except for appropriately small fluctuations that average to zero over time and space). This same sort of thing happens for volume and particle exchanges -- the intensive prefactor imbalance has the opposite sign as the constraint-variable shift, implying an entropy decrease.
- i. We normally don't have to solve internal-constraint problems by formally calculating and maximizing the entropy as a function of the constraint variables. Instead, we just equalize the contacted intensive variables, which accomplished the same thing.
  - i. If the wall is diathermal ( $dV = 0$  and  $dN = 0$ ), the temperatures equalize.
  - ii. If the wall is diathermal and moveable, both  $P$  and  $T$  equalize.
  - iii. If the wall is diathermal and permeable, both  $T$  and  $\mu$  equalize.
  - iv. If two intensive variables (e.g.  $T$  and  $P$ ) equalize, the third (e.g.  $\mu$ ) must also equalize due to the Gibbs-Duhem relation.
  - v. Weird stuff happens if you make the wall movable or permeable without also making it diathermal. See the "subtlety alert" below (near the end of these notes).

### 2) The ideal-gas case

- a. Two ideal-gas systems in initial states  $(U_1, V_1, N_1)$  and  $(U_2, V_2, N_2)$  are brought into some kind of contact leading to final states  $(U'_1, V'_1, N'_1)$  and  $(U'_2, V'_2, N'_2)$ . Entropy maximization requires the equalization of the contacted intensive variables.
- b. The wall becomes diathermal
  - i.  $T'$  is equalized, total  $U$  is conserved, and  $U'_i = cN_i RT'$  on each side. It's easy to find the equalized  $T'$ , which turns out to be a mole-weighted average of the initial  $T_i$ .
  - ii. With  $T'$  in hand, it's easy to find the  $U'_i$  on each side.
  - iii. The  $V_i$  and  $N_i$  didn't change, making it easy to determine the  $P'_i$  on each side.
  - iv. Then the  $\mu'_i$  can be determined from the state equation that describes  $\mu'(P', T')$ .
- c. The wall becomes diathermal and moveable
  - i.  $T'$  is equalized to the same value as the diathermal-only case.
  - ii. The  $N_i$  are unchanged, so that the  $U'_i$  on each side are also like diathermal-only case.

- iii.  $P'$  is also equalized, and  $P'V_i' = N_iRT'$  on each side. It's easy to determine the equalized  $P'$ , which then also gives the  $V_i'$  on each side.
- iv. The Gibbs-Duhem relation says that  $\mu'$  is also equalized. It's value can be determined from the state equation that describes  $\mu'(P', T')$ .
- d. The wall becomes diathermal and permeable
  - i.  $T'$  is equalized to the same value as the diathermal-only case.
  - ii. Because temperature and chemical potential are both equalized, the Gibbs-Duhem relation says that pressure is also equalized, which must go to the same value obtained above with the diathermal movable wall.
  - iii. The  $U_i'$  and  $V_i'$  are also as before.
  - iv. Use the chemical potential state function to obtain  $\mu'(P', T')$ .

### 3) Subtlety Alert

- a. In the constrained two-subsystem problem above, suppose that we make the wall moveable but not diathermal or impermeable. Assume that  $P_2 > P_1$  initially so that  $V_1$  shrinks when the constraint is removed:  $dV_2 = -dV_1 > 0$ . Mathematically, the maximum entropy condition ( $dS = 0$ ) seems to require only that  $\frac{P_2}{T_2} = \frac{P_1}{T_1}$ . But a simple application of Newtonian mechanics demonstrates that the pressures on either side must be balanced. Why doesn't the maximum entropy condition give us this obvious requirement? Actually, it does. The troublesome issue here is that  $U_1$  and  $V_1$  are not independent of one another.
- b. The work done on the first subsystem is  $dW_1 = -P_1dV_1$ . One might naively think the work done on the second subsystem is  $-P_2dV_2$ , but this is *not* correct. Though not as bad as the free-expansion case, where no work is done during expansion due to the absence of an opposing force, the opposing force in this case is weaker than the applied force, so that the work done by the second system is smaller than anticipated:  $-dW_2 = dW_1 = -P_1dV_1 = P_1dV_2 < P_2dV_2$ . This spontaneous motion results in degradation (entropy increase).
- c. Total energy is conserved and no heat is transferred on either side, so that  $dQ_1 = dQ_2 = 0$  and  $dU_2 = -dU_1 = dW_2 = -dW_1 = -P_1dV_2$ .
- d. 
$$dS = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)dU_2 + \left(\frac{P_2}{T_2} - \frac{P_1}{T_1}\right)dV_2 = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)(-P_1dV_2) + \left(\frac{P_2}{T_2} - \frac{P_1}{T_1}\right)dV_2$$

$$= \left(\frac{-P_1}{T_2} - \frac{-P_1}{T_1} + \frac{P_2}{T_2} - \frac{P_1}{T_1}\right)dV_2 = \left(\frac{P_2}{T_2} - \frac{P_1}{T_2}\right)dV_2 = \frac{1}{T_2}(P_2 - P_1)dV_2$$
- e. When  $dS = 0$ , the prefactor has  $T_2$  in both terms, so that we clearly obtain  $P_1 = P_2$ . However, there is no guarantee that temperatures  $T_1$  and  $T_2$  will also equalize.
- f. Even though the pressures equalize, the final position of the wall is indeterminate in general. Weird but true! The wall's position depends on how the internal energy is distributed at the end of the process. A careful process wherein the wall is released in tiny increments, will lead to a predictable final state. But if the wall is released abruptly, it can mechanically oscillate around the equal-pressure point, causing the temperature of both sides to adiabatically oscillate over time. Furthermore, the motion of the wall stirs the gasses on both sides, so that viscous forces within each subsystem slowly transform mechanical energy into internal energy. When the motion finally decays away, and both sides reach an equilibrium that balances the pressure, the internal energy (and temperature) on each side will depend on how strong the viscous forces on that side were (Callen, problem 2.7-3).
- g. Suppose the system consists of two ideal gasses ( $PV = NRT = U/c$ ).
  - i. Let  $U_A = xU$ ,  $U_B = (1 - x)U$ , and let  $V_A = yV$ ,  $V_B = (1 - y)V$ .
  - ii. Easy to show that final pressure is  $P = \frac{U}{cV}$ , and  $x = y = \left(1 + \frac{N_B T_B}{N_A T_A}\right)^{-1} = \frac{N_A R T_A}{P V}$ .
  - iii. So  $P$  is fully determined, and the energy partition  $x$  turns out to be equal to the volume partition  $y$ . But temperatures  $T_A$  and  $T_B$  can adapt to any wall position  $x$ .
- h. There's another way to *think* about the pressure equalization problem – in terms of energy minimization rather than entropy maximization. Instead of assuming constant total energy

and variable total entropy, we'll assume constant total entropy and variable total energy. Start in equilibrium and carefully do work on the system to slide the wall to a new position, which increases the system energy. Because we act reversibly and adiabatically, the entropy remains constant as the energy increases. Use the energetic FR, which is  $U(S, V, N)$ .

- i.  $dU = T_1 dS_1 + T_2 dS_2 - P_2 dV_2 - P_1 dV_1 + \mu_1 dN_1 + \mu_2 dN_2$
- ii. Assume  $dS_1 = dS_2 = 0$  and  $dN_1 = dN_2 = 0$ , and  $dV_2 = -dV_1$ .
- iii.  $dU = -(P_2 - P_1)dV_2$
- iv. If we start in equilibrium and instigate a pressure difference, where gas 2 is compressed and pressurized ( $dV_2 < 0$  and  $P_2 > P_1$ ), or gas 1 is compressed and pressurized ( $dV_1 < 0$  and  $P_1 > P_2$ ), the energy must increase ( $dU > 0$ ).
- v. In equilibrium, where  $P_1 = P_2$ , a small volume change does not affect the energy ( $dU = 0$ ), which has been minimized over the constraint manifold. Perhaps we should have started with this approach.
- vi. The moral of the story is that energy minimization plays a role very similar to entropy maximization in thermodynamics. They provide two different ways to think about the same problem. Depending on the situation, one will be easier to implement than the other.
- vii. With either approach, the wall-position weirdness is still an issue.

## Lecture 10: Manipulating partial derivatives; second derivatives of the FR and common material properties (e.g. heat capacity and thermal expansion); the heat capacities of polyatomic gasses

- 1) Important rules for partial derivatives (see K&T Appendix A). Assume that  $\varphi(x, y, z)$  is a state equation involving specific intensive or extensive state variables.

a.  $\left(\frac{\partial x}{\partial y}\right)_{\varphi, z} \left(\frac{\partial y}{\partial x}\right)_{\varphi, z} = 1$  (inversion)

b.  $\left(\frac{\partial y}{\partial t}\right)_{\varphi, z} = \left(\frac{\partial y}{\partial x}\right)_{\varphi, z} \left(\frac{\partial x}{\partial t}\right)_{\varphi, z}$  (chain rule)

c.  $\left(\frac{\partial x}{\partial y}\right)_{\varphi, z} \left(\frac{\partial y}{\partial z}\right)_{\varphi, x} \left(\frac{\partial z}{\partial x}\right)_{\varphi, y} = -1$  (permutation)

- d. To compute any partial derivative such as  $\left(\frac{\partial x}{\partial y}\right)_{\varphi, z}$ , one first needs to obtain the differentiated function in terms of all of the variables to be explicitly varied or held constant, e.g.  $x(y, z, \varphi)$ . This concept is central to thermodynamics!

- 2) Apply these rules to  $S(U, V, N)$  to show that  $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$ .

a. Recall that  $T = \left(\frac{\partial U}{\partial S}\right)_{V, N}$  and  $P = -\left(\frac{\partial U}{\partial V}\right)_{S, N}$  and  $\mu = \left(\frac{\partial U}{\partial N}\right)_{S, V}$ .

- b. In the homework, use these three derivatives together with the rules above to demonstrate that  $\left(\frac{\partial S}{\partial U}\right)_{V, N} = \frac{1}{T}$  and  $\left(\frac{\partial S}{\partial V}\right)_{U, N} = \frac{P}{T}$  and  $\left(\frac{\partial S}{\partial N}\right)_{U, V} = -\frac{\mu}{T}$ .

- 3) Common material properties (2<sup>nd</sup> derivatives of the FR)

a.  $\alpha_P \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P, N}$  -- coefficient of thermal expansion (relative volume increase per  $dT$ )

b.  $\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T, N}$  -- isothermal compressibility (relative volume increase per  $dP$ )

c.  $c_V \equiv \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_{V, N}$  -- molar heat capacity at constant  $V$  (molar heat intake per  $dT$ )

d.  $c_P \equiv \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_{P, N}$  -- molar heat capacity at constant  $P$  (molar heat intake per  $dT$ )

- e. Each of the four system properties can be described in terms of 2<sup>nd</sup> derivatives of the FR.

For example,  $\frac{1}{c_V} = \frac{N}{T} \left(\frac{\partial T}{\partial S}\right)_{V, N} = \frac{N}{T} \left(\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial S}\right)_{V, N}\right)_{V, N} = \frac{N}{T} \left(\frac{\partial^2 U}{\partial S^2}\right)_{V, N}$ .

- f. At constant volume, the first law requires  $dQ = dU - dW = dU + PdV = dU$ , so that the molar heat capacity is  $\frac{1}{N} \frac{dQ}{dT} = \frac{1}{N} \left(\frac{dU}{dT}\right)_{V, N} = \frac{1}{N} \left(\frac{dU}{dS}\right)_{V, N} \left(\frac{dS}{dT}\right)_{V, N} = \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_{V, N} = c_V$ , as expected.

- g. In contrast, at constant pressure, the molar heat capacity is  $\frac{1}{N} \frac{dQ}{dT} = \frac{1}{N} \left(\frac{\partial U}{\partial T} + P \frac{\partial V}{\partial T}\right)_{P, N} =$

$\frac{T}{N} \left(\frac{1}{T} \frac{\partial U}{\partial T} + \frac{P}{T} \frac{\partial V}{\partial T} - \frac{\mu}{T} \frac{\partial N}{\partial T}\right)_{P, N} = \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_{P, N} = c_P$ , as expected.

- h. Regarding  $c_P$ , it is true that  $\left(\frac{dS}{dT}\right)_{P, N} = \left(\frac{dS}{dU}\right)_{P, N} \left(\frac{dU}{dT}\right)_{P, N}$ , though it is incorrect to assume that

$\left(\frac{dU}{dS}\right)_{P, N}$  is equal to  $T$  because the wrong variables are held constant ( $P$  rather than  $V$ ). To

determine  $c_P$ , we need either  $S(T, P, N)$  or else both  $S(U, P, N)$  and  $U(T, P, N)$ .

4) The case of an ideal gas ( $U/c = PV = NRT$ )

- a.  $\alpha_P = \frac{1}{V} \left( \frac{\partial(NRT/P)}{\partial T} \right)_{P,N} = \frac{NR}{PV} = \frac{1}{T}$  (decreases at high temperature)
- b.  $\kappa_T = -\frac{1}{V} \left( \frac{\partial \left( \frac{NRT}{P} \right)}{\partial P} \right)_{T,N} = \frac{NRT}{P^2 V} = \frac{1}{P}$  (decreases at high pressure)
- c.  $c_V = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_{V,N} = \frac{1}{N} \left( \frac{\partial U}{\partial T} \right)_{V,N} = \frac{1}{N} \left( \frac{\partial(cNRT)}{\partial T} \right)_{V,N} = cR$
- d.  $c_P = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_{P,N} = \frac{T}{N} \left( \frac{\partial}{\partial T} \left\{ Ns_0 + NR \log \left[ \frac{I}{I_0} \right] \right\} \right)_{P,N} = \frac{T}{N} \frac{NR}{I} \frac{\partial I}{\partial T} = \frac{TR}{I} \frac{(c+1)I}{T} = (c+1)R$

5) The case of a black-body cavity ( $U = bVT^4 = 3PV, N = aVT^3$ )

- a.  $\alpha_P = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  is not defined because  $P = \frac{b}{3} T^4$ . But  $\alpha_U = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_U = -\frac{4}{T}$
- b.  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$  is not defined. But  $\kappa_U = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_U = \frac{1}{P}$
- c.  $c_V = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_V = \frac{1}{N} \left( \frac{\partial U}{\partial T} \right)_V = \frac{1}{N} 4bVT^3 = \frac{4b}{a}$  (constant).
- d.  $c_P$  is not defined for such a system

6) Heat capacity

- a. The heat capacity of a polyatomic gas effectively counts the number of accessible molecular modes ( $n_{modes}$ ) available to store energy, which depends on the number of atoms per molecule ( $n_{poly}$ ). Because some modes have higher quantized energies than others, not all of these modes are accessible at a given temperature. To be accessible, the energy of the mode must be less than or comparable to  $kT$ . Translation modes are always accessible. Molecular rotation modes tend to activate well below room temperature. Molecular vibration modes tend to activate above room temperature. Translations are always accessible. Rotations become accessible well below room temperature ( $\sim 100$  K). Vibrations tend to become accessible only above room temperature.
- b. An important gas constant:  $c = \frac{n_{modes}}{2}$
- c. Molar heat capacity of an ideal gas:  $c_V = cR, c_P = c_V + R = (c+1)R$ .
- d. The adiabatic gas constant:  $\gamma \equiv \frac{c_P}{c_V} = \frac{c+1}{c}$
- e. Non-linear molecules with at least three atoms (the general case)
  - i. 3 translational kinetic-energy modes and 3 rotational kinetic-energy modes
  - ii.  $2(3n_{poly} - 6)$  vibrational modes -- counts kinetic and potential energy terms
  - iii.  $n_{modes} = 3 + 3 + 2 * (3n_{poly} - 6) = 6n_{poly} - 6$
- f. Monatomic-molecule special case:
  - i. 3 translational kinetic energy modes, but no rotational or vibrational modes
  - ii.  $n_{modes} = 3$
- g. Linear-molecule special case:
  - i. 3 translational modes, but only 2 rotational modes (can spin around linear axis)
  - ii.  $n_{modes} = 3 + 2 + 2 * (3n_{poly} - 5) = 6n_{poly} - 5$

- 7) Worm-like chain (WLC) model of a polymer chain (stretchability of a rubber band).
- The chain natural tends to twist up in a ball. Grab the two ends of the chain and apply tension force  $f$  to stretch it out.
  - Let  $L_c$  be the maximum length of the chain when fully stretched, and let  $L(T)$  be the current length, which depends on temperature. Define  $x = L/L_c$  to be the currently realized fraction of the maximum length.
  - The persistence length  $L_p$  of the molecule is its average orientational-correlation distance along the chain, or the average separation distance between adjacent sharp bends in the chain. It is roughly inversely proportional to temperature so that it can be written as  $L_p(T) = \lambda/T$ , where  $\lambda$  is a constant.
  - A state equation for this one-dimensional system can be presented in terms of the end-to-end tension force  $f$  required to achieve a given length  $L$  or fractional length  $x$ . This equation is 
$$f = \frac{kT}{L_p(T)} \left[ \frac{1}{4(1-L/L_c)^2} + L/L_c - 1/4 \right] = \frac{kT^2}{\lambda} \left[ \frac{1}{4(1-x)^2} + x - 1/4 \right].$$
  - The isothermal compressibility (or stretchability) can be defined as the relative length change per change in tension, or  $\kappa_T = +\frac{1}{L} \left( \frac{\partial L}{\partial f} \right)_T$ . The inverse stretchability is then  $1/\kappa_T$ .
  - $$\frac{1}{\kappa_T} = +L \left( \frac{\partial f}{\partial L} \right)_T = \frac{L}{L_c} \left( \frac{\partial f}{\partial x} \right)_T = \frac{kT^2}{\lambda} x \left[ 1 + \frac{1}{2(1-x)^3} \right].$$
  - At small length fractions, the stretchability trend is  $\kappa_T \approx \frac{2\lambda}{3kT^2} \frac{1}{x} = \frac{2\lambda}{3kT^2} \frac{L_c}{L}$ , which decreases at a moderate rate with increasing length. At large length fractions, the stretchability trend is  $\kappa_T \approx \frac{2\lambda}{kT^2} (1-x)^3 = \frac{2\lambda}{kT^2} \left( 1 - \frac{L}{L_c} \right)^3$ , which decreases rapidly to zero as  $x \rightarrow 1$ .
  - In either case, the chain becomes less stretchable (more twisty and tight) with increasing temperature.
  - This example was hard to follow in the textbook. For example, Eq 5.44 is incomprehensible and the  $1/T$  state equation is flawed. But the  $f/T$  state equation is quite interesting. Don't waste too much time on this section.

## Lecture 11: Multi-component systems, chemical potential, quantum concentration, law of mass action

- 1) Entropy of mixing: Start with a collection of ideal gasses which have different mole numbers ( $N_i$ ) and volumes ( $V_i$ ), but all have identical intensive parameters ( $T, P, \mu$ ). Then let the barriers become permeable so that each gas expands to fill the whole volume.
  - a. Gas mixing is the only interesting thing happening here. The total energy doesn't change; neither can the temperature. The total mole number and total volume, and hence the moles/volume density don't change; neither can the pressure.
  - b. New extensive parameter totals:  $N = \sum N_i$ ,  $V = \sum V_i$ , and  $U = \sum U_i$ .
  - c. Define mole fractions of each species:  $x_i = N_i/N$ , which sum to 1.
  - d. Though the mole number  $N_i$  and energy  $U_i$  of each species don't change during mixing, the volume available to each species expands from  $V_i$  to  $V$ .
  - e. Before mixing:  $S = \sum N_i \left\{ s_{0i} + R \ln \left[ \left( \frac{V_i}{V_{0i}} \right) \left( \frac{U_i}{U_{0i}} \right)^c \left( \frac{N_{0i}}{N_i} \right)^{c+1} \right] \right\}$
  - f. After mixing:  $S' = \sum N_i \left\{ s_{0i} + R \ln \left[ \left( \frac{V}{V_{0i}} \right) \left( \frac{U_i}{U_{0i}} \right)^c \left( \frac{N_{0i}}{N_i} \right)^{c+1} \right] \right\}$  (only volumes changed)
  - g.  $\Delta S = S' - S = \sum N_i R \ln \left( \frac{V}{V_i} \right)$
  - h. Because the intensive parameters ( $T, P, \mu$ ) are equal for each species before mixing, it is easy to show that the initial molar concentration of each species is equal to the overall molar concentration, i.e.  $n_i = \frac{N_i}{V_i} = \frac{N}{V}$ , and that  $\frac{U_i}{U} = \frac{V_i}{V} = \frac{N_i}{N} = x_i$ . Thus,  $\Delta S = NR \sum x_i \ln \left( \frac{1}{x_i} \right)$ .
  - i. For two species with equal volumes,  $x_1 = x_2 = \frac{1}{2}$  and  $\Delta S = NR \ln(2)$ .
  - j. The assumption of initially equal intensive parameters restricts the validity of this analysis to the case where the entropy change is entirely due to mixing. One can imagine a more complicated scenario in which energy or volume transfer between the two sides also contributed to the entropy change.
  
- 2) The text surrounding Fig. 2 of K&T 5.2 describes a clever reversible process for mixing equal volumes of two different gas species at the same temperature and pressure.
  - a. The key is to maintain the same volume for each species throughout the mixing, which is accomplished with two synchronized pistons at opposite ends of a cylinder, the left piston being permeable to both species A and B and the right piston being impermeable to both, as well as a middle wall that is permeable only to species B. Because total entropy remains constant, one could just as easily reverse the piston motion to separate the gasses again.
  - b. The pressure exerted by gas A is the same on both sides of the left piston, thus exerting zero net force. The pressure exerted by gas B has the same magnitude but opposite directions on the two pistons; because they are mechanically attached, the net force of gas B on the piston pair is zero. With no net force on the pistons, no work is required to move them. And the walls are adiabatic. Thus, they can be slid freely without increasing  $U$  or  $T$ .
  - c. If the two pistons were not tied together, the left piston could slide spontaneously to the left and thereby increase the entropy of the system by mixing A and B on the left-hand side.
    - i.  $\Delta U = \Delta Q = \Delta W = 0$
    - ii.  $\Delta S = \Delta S_A + \Delta S_B = 0 + \Delta S_B = \frac{1}{2} NR \log(2V/V) = \frac{1}{2} NR \log(2)$



## 3) Partial pressures in a gas mixture

- Suppose that we mix several distinct species of gas in the same volume  $V$ .
- Each gas species independently exerts partial pressure  $P_i$  on the walls of its container through collisions. Partial pressures add linearly so that total pressure is  $P = \sum P_i$ .
- Dalton's law:  $P_i = x_i P = \frac{N_i}{N} \frac{NRT}{V} = \frac{N_i RT}{V}$ . Partial pressure is proportional to mole fraction.
- $n_i = \frac{N_i}{V} = \frac{P_i}{RT} = x_i \left( \frac{P}{RT} \right) \rightarrow$  concentration (molarity) is also proportional to mole fraction.
- During a chemical synthesis involving a gaseous reactant (e.g. oxygen), the partial pressure of the reactant often determines which one among many possible products will be stable. The stabilities of many copper-oxide superconductors, for example, are quite sensitive to  $P_{O_2}$  during formation.

## 4) Vapor pressure

- Suppose that we evacuate the top half of a can that has liquid water in the bottom half and then seal the can airtight. The pressure will initially be near zero; but steam would evaporate into the otherwise empty top half until the chemical potentials of the liquid and gas states of  $H_2O$  became equal. In other words, the pressure of the water vapor will rise at constant temperature until the chemical potentials of the gas and liquid phases are equal, at which point the liquid and gas phases will be in mutual equilibrium. The gas pressure under these conditions is referred to as the liquid-gas equilibrium *vapor pressure*.
- The function  $\mu_i(T, P)$  is different for each species. Imagine a 3D graph of this function where  $T$  and  $P$  are orthogonal axes in the horizontal plane, and the value is  $\mu$  is plotted along the vertical axis. If we set two functions equal,  $\mu_{liquid}(T, P) = \mu_{gas}(T, P)$ , we can then solve to obtain the function  $P(T)$ , which traces what we call the liquid-gas *coexistence line* in the  $P - T$  plane. This is line along which the two chemical potential landscapes coincide.
- The liquid-gas coexistence line  $P(T)$  generally has a positive slope. You know that at  $P = 1$  atmosphere,  $H_2O$  liquid and vapor coexist at  $T = 100^\circ \text{C}$ . But at a lower temperature, they will coexist at a lower pressure.
- Fluid vapor pressure depends on temperature approximately according to the Clausius-Clapeyron equation,  $\log(P) = \log(P_\infty) - \frac{q/R}{T}$ , where  $q$  is molar latent heat. Antoine's law,  $\log(P) = A - \frac{B}{C+T}$ , where  $A$ ,  $B$  and  $C$  are purely empirical constants (i.e. not derived from a theory), is more accurate and works for both liquid-gas and solid-gas coexistence curves.

## 5) Gas-phase chemical reactions in equilibrium

- A chemical reaction proceeds in both directions simultaneously, but at different rates, until equilibrium is reached, at which point the forward and reverse rates become equal. In equilibrium, what are the mole fractions of each of the reactant and product species?
- In general, this is written as  $0 \rightleftharpoons \sum v_i A_i 0$  where the  $A_i$  are the species involved and  $v_i$  are their stoichiometric coefficients.
- Consider the dissociation of water into hydrogen and oxygen, which can be written as  $H_2O \rightleftharpoons H_2 + \frac{1}{2} O_2$ , or alternatively as  $0 \rightleftharpoons H_2 + \frac{1}{2} O_2 - H_2O$ . Here, the coefficients  $v_i$  are  $+1$  for  $H_2$ ,  $+1/2$  for  $O_2$ , and  $-1$  for  $H_2O$ .
- Chemical potential state equation for an ideal gas:  $\frac{\mu}{T} + \frac{s}{N} - (c + 1)R = 0$ . Relative to an arbitrary reference state with  $\mu_0(P_0, T_0)$ , it can be written as  $\frac{\mu}{RT} - \frac{\mu_0}{RT} = -\ln \left[ \left( \frac{P_0}{P} \right) \left( \frac{T}{T_0} \right)^c \right]$ .
- Recalling that  $P_i = x_i P$ , the chemical potential of a single species can be separated into contributions due to mole fraction, total pressure and temperature.

$$\frac{\mu_i}{RT} - \frac{\mu_{0i}}{RT} = -\ln \left[ \left( \frac{P_0}{P_i} \right) \left( \frac{T}{T_0} \right)^{c_i+1} \right] = \ln(x_i) + \ln(P) - (c_i + 1) \ln(T)$$

It would have been better for KT Eq. 5.28 to include the reference term containing  $\mu_{0i}$ , which is the chemical potential of the  $i^{th}$  species in the reference state ( $P_0, T_0$ ).

- f. As the reaction proceeds, the reactants/products are consumed/produced in stoichiometric ratios, so that the  $dN_i$  are not independent. So  $dN_i = \nu_i dN$ , where  $dN$  tracks the progress of the reaction rather than corresponding to any one species.
- g. In equilibrium, the entropy is maximized ( $dS = 0$ ), and  $U$  and  $V$  are constant.  
 $TdS = dU + PdV - \sum \mu_i dN_i = -\sum \mu_i (\nu_i dN) = -(\sum \mu_i \nu_i) dN = 0$
- h. This gives us an important balance equation:  $\sum \mu_i \nu_i = 0$ .
- i.  $\frac{1}{RT} \sum \mu_i \nu_i = \sum \nu_i \left[ \ln(x_i) + \ln(P) - (c_i + 1) \ln(T) + \frac{\mu_{i0}}{RT} \right]$   
 $= \ln(\prod x_i^{\nu_i}) + \ln(P^{\sum \nu_i}) - \ln(T^{\sum (c_i+1)\nu_i}) + \frac{\epsilon_{diss}}{RT}$   
 $= \ln(\prod x_i^{\nu_i}) + \ln(P^{\sum \nu_i}) - \ln(K(T)) = 0$   
 where  $\epsilon_{diss} = \sum \nu_i \mu_{i0}$  is the molar disassociation energy of the reaction, and where the temperature dependence is all swept into  $K(T) = T^{\sum (c_i+1)\nu_i} e^{-\epsilon_{diss}/RT}$ . The function  $K(T)$  is often referred to as an *equilibrium constant*.
- j. Rearrange to get the *law of mass action*:  $\prod x_i^{\nu_i} = P^{-\sum \nu_i} K(T)$ . It has  $T$  and  $P$  dependence.
- k. It is important that the reactant species on the left were moved to the right hand side of the reaction equation above, so that the signs of the coefficients ( $\nu_i$ ) follow convention. In other words, the definition of the equilibrium constant  $K$  of a reaction depends on how the chemical equation is written.
- l. For systems other than ideal gasses, the details of the pressure and temperature dependence on the right-hand side of the law of mass action will be different. The ideal gas is a particularly simple system for which the functional form vs  $T$  and  $P$  can be determined.
- m. Chemists often use concentration (molarity) rather than mole fraction in the mass action law. This simply redefines the equilibrium constant ( $K$ ), into which they also absorb the pressure dependence.  $\prod n_i^{\nu_i} = K(T, P)$ . We could use either approach depending on the problem. When looking up the equilibrium constant of a reaction in a database or table, take care to check which definition/convention is being used and which temperature and pressure it corresponds to.
- n. For the example above,  $x_{H_2} x_{O_2}^{1/2} x_{H_2O}^{-1} = P^{-1/2} K(T)$ . Starting with with  $N$  moles of pure  $H_2O$ ,  $\alpha$  moles of  $H_2O$  will dissociate to produce  $\alpha$  moles of  $H_2$  and  $\alpha/2$  moles of  $O_2$ , so that the total gas mole number will be  $N - \alpha + \alpha + \alpha/2 = N + \alpha/2$ . By inserting symbolic expressions for the final mole fractions of each species into the law of mass action at a given temperature and pressure, one can solve for the unknown value of  $\alpha$ , and hence obtain numerical values for each mole fraction.

## Lecture 12: Thermodynamic potentials as fundamental relations, Legendre transforms, free energies

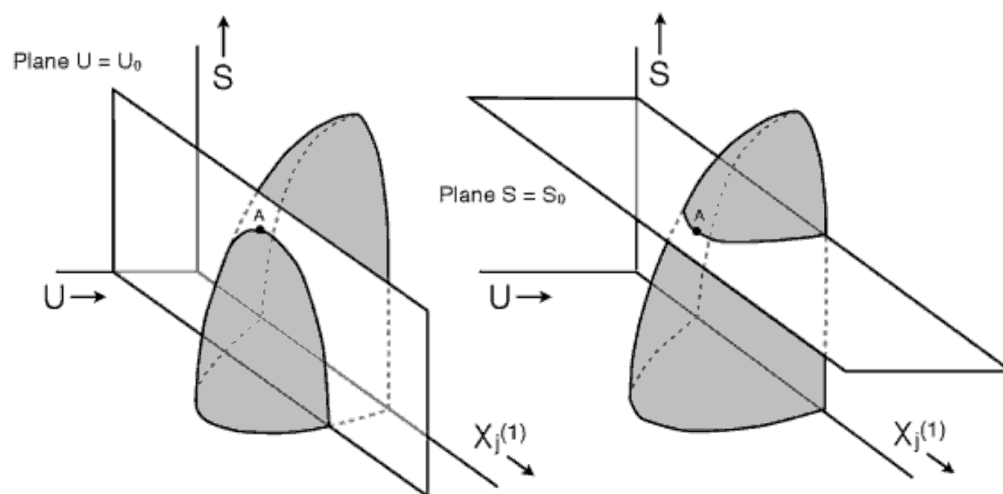
### 1) Glossary

- Natural variables: The fundamental relations we have defined so far were functions of only extensive variables. There should be a way to define the FR of a system in terms an intensive variable fixed by contact with a reservoir.
- Extremum principles, curvature, and generalized extremum principles
- Thermodynamic potentials, free energy

### 2) Extremum principle (for an isolated system):

- If  $U$  is held constant while a constraint is varied,  $S$  will be maximized at the equilibrium constraint value, and if  $S$  is held constant while a constraint is varied,  $U$  will be minimized at the equilibrium constraint value. See the figure below (K&T 6.1). Constant-energy entropy maximization is a practical reality in many situations. Constant-entropy energy minimization tends to be important as a mathematical and conceptual tool.
- By virtue of its definition, the entropy  $S(U, V, N)$  can be shown to be a concave function of all of its extensive variables – negative (downward) curvatures. Similarly, the internal energy  $U(S, V, N)$  is a convex function of its extensive variables – positive (upward) curvatures.
- Extrema with respect to internal-constraint variables are very important in thermodynamics.

The equilibrium value of a constraint variable  $X$  maximizes the entropy, so that  $\left(\frac{\partial S}{\partial X}\right)_U = 0$  and  $\left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0$ . This implies that  $\left(\frac{\partial U}{\partial X}\right)_S = -\left(\frac{\partial U}{\partial S}\right)_X \left(\frac{\partial S}{\partial X}\right)_U = -T \cdot 0 = 0$ , so that internal energy is also at an extreme value. By showing that  $\left(\frac{\partial^2 U}{\partial X^2}\right)_S / \left(\frac{\partial^2 S}{\partial X^2}\right)_U = -T < 0$ , one can prove that entropy maximization implies energy minimization and vice versa. The actual proof is fairly involved.



- 3) Legendre transforms provide a systematic way to exchange two conjugate variables without information loss. In thermodynamics, they allow us to convert between two fundamental relations expressed in terms of different members of a conjugate-variable pair (e.g.  $V$  and  $P$  or  $S$  and  $T$ ). For any monotonically-increasing function  $y(x)$ , it's local slope  $m$  is the variable conjugate to  $x$ , so that  $(x, m)$  form a conjugate pair. Furthermore, there exists another function  $b(m)$  of the conjugate slope variable, which effectively contains all of the information contained in the original function  $y(x)$ . The Legendre transform allows one to convert and forth between  $y(x)$  and  $b(m)$ .
- a. Forward transform:
    - i. Start with monotonically-increasing function  $y(x)$ .
    - ii. Define  $m(x) \equiv y'(x)$  to be the slope of the tangent line of  $y(x)$  at point  $x$ .
    - iii. Define the y-intercept of the tangent line,  $b(x) \equiv y(x) - m(x)x$ , as a function of  $x$ .
    - iv. Invert  $m(x)$  to obtain  $x(m)$ .
    - v. Substitute  $x(m)$  into both  $y(x)$  and  $b(x)$  to obtain  $y(m) \equiv y(x(m))$  and also  $b(m) \equiv b(x(m))$ , which are functions of  $m$  rather than of  $x$ .
    - vi. We can then write  $b(m) = y(m) - x(m)m$ . Observe that  $-x(m)$  is the slope of the tangent line of curve  $b(m)$  and that  $y(m)$  is the y-intercept of  $b(m)$  at point  $m$ .
  - b. Inverse transform (same thing as before but with less explanation):
    - i. Starting with  $b(m)$ , define  $x(m) \equiv -b'(m)$  and  $y(m) \equiv b(m) + x(m)m$ . Invert  $x(m)$  to obtain  $m(x)$ , and substitute it in  $y(m)$  to obtain  $y(x) = m(x)x + b(x)$ .
  - c. Summary:
    - i.  $x$  and  $m$  are conjugate variables
    - ii.  $y(x)$  and  $b(m)$  are Legendre transforms of one another.
    - iii.  $y = b + mx$  and  $b = y - xm$
    - iv.  $dy = db + m dx + x dm$  and  $db = dy - x dm - m dx$
    - v. Together, the slope function  $m(x)$  and intercept function  $b(x)$  can be used to reconstruct the original function  $y(x)$ . They contain all of the same information. Because both  $m(x)$  and  $b(x)$  can be recovered from  $b(m)$ , it also encodes the same information as  $y(x)$ . The transformation is entirely lossless!
    - vi. It's very *important* to appreciate that we *cannot* recover  $y(x)$  from the variable substituted function  $y(m)$  alone. The function  $y(m)$  inherently contains less information than  $y(x)$ . There is no way to recover  $y(x)$  starting from  $y(m)$  alone.
  - d. Forward Legendre transform example starting with  $y(x) = x^{1/2}$ 
    - i.  $m(x) = y'(x) = \frac{1}{2x^{1/2}} \rightarrow x(m) = \frac{1}{4m^2}$
    - ii.  $b(x) = y(x) - m(x)x = x^{1/2} - \left(\frac{1}{2x^{1/2}}\right)x = \frac{1}{2}x^{1/2}$
    - iii.  $b(m) = b(x(m)) = \frac{1}{2}\left(\frac{1}{4m^2}\right)^{1/2} = \frac{1}{4m}$
  - e. Inverse Legendre transform example starting with  $b(m) = 1/4m$ 
    - i.  $x(m) = -b'(m) = \frac{1}{4m^2} \rightarrow m(x) = \frac{1}{2x^{1/2}}$
    - ii.  $y(m) = b(m) + x(m)m = \frac{1}{4m} + \left(\frac{1}{4m^2}\right)m = \frac{1}{2m}$
    - iii.  $y(x) = y(m(x)) = \left\{2\frac{1}{2x^{1/2}}\right\}^{-1} = x^{1/2}$
  - f. Consider the Legendre transform  $F(T, V, N) = U(S, V, N) - TS$ . The analogy is as follows:  $U \leftrightarrow y$ ,  $S \leftrightarrow x$ ,  $T \leftrightarrow m$ ,  $F \leftrightarrow b$ . In this example,  $V$  and  $N$  are just constants. We know that  $U(S, V, N)$  is an FR with natural variables  $S$ ,  $V$ , and  $N$ . Because  $F(T, V, N)$  is the Legendre

transform of an FR, it is also an FR, but with natural variables  $T$ ,  $V$ , and  $N$ . It still contains all of the same information as the original function. It is easy to transform back to the form  $U(S, V, N) = F(T, V, N) + TS$ .

- g. Recall there is no way to get back to  $y(x)$  again starting from  $y(m)$ . Similarly,  $U(T, V, N)$  is obtained from  $U(S, V, N)$  by simple variable substitution rather than a full Legendre transformation, and so is not an FR. It remembers the slope function  $T(S, V, N)$ , but not the intercept function, and so can't be used to reconstruct  $U(S, V, N)$ .

#### 4) Thermodynamic potentials

- a. Thermodynamic potentials are Legendre transforms of the internal energy in which one or more independent extensive variables are replaced by their conjugate intensive variables. They are still fundamental relations of their natural variables, meaning that no information was lost in the Legendre transform. For example, the Helmholtz potential function  $F(T, V, N)$  is an FR.
- b. For a system with 3 independent state variables, one can define  $2^3 = 8$  different thermodynamic potentials -- see the table of potentials in the glossary.
- c. The other thermodynamic potentials don't contain any new information beyond that contained in  $U(S, V, N)$ , though they are very convenient for systems with reservoir contact.

#### 5) Generalized extremum principle for thermodynamic potentials

- a. For a system with intensive variables that are fixed through reservoir contact, the appropriate thermodynamic potential is minimized *locally* (i.e. within the system itself) rather than globally over the manifold of internally constrained states.
- b. Before introducing this principle, we had only learned about entropy maximization at constant internal energy and internal energy minimization at constant entropy in isolated systems.
- c. Important related fact: each thermodynamic potential is a convex (positive or upward curvature) function of its natural extensive variables and a concave (negative or downward curvature) function of its natural intensive variables. In this sense, the thermodynamic potentials and the thermodynamic entropy have opposite curvature patterns.

$$\left( \frac{\partial^2 \Phi}{\partial (\text{natural extensive var})^2} \right) > 0 \quad \text{and} \quad \left( \frac{\partial^2 \Phi}{\partial (\text{natural intensive var})^2} \right) < 0$$

You can browse graduate thermo books (e.g. Callen) for proofs and more information.

- d. One can similarly prepare Legendre transforms of the entropy (called Mattieu functions) and discuss their extrema over internally constrained states. We will not consider them.

#### 6) Isolation of work and heat terms

- a. Upon fixing its natural intensive variables (the reservoir-contact variables), the differential thermodynamic potential isolates a useful heat or work-energy transfer. Let's assume a reversible process in what follows, so that we can define  $dQ = TdS$ ,  $dW_{mech} = -PdV$ ,  $dW_{chem} = \mu dN$ , and  $dW_{all} = dW_{mech} + dW_{chem}$ . You're already familiar with mechanical work. Chemical work is the type of work a battery does.
- b.  $dU(S, V, N) = TdS - PdV + \mu dN = dQ + dW_{mech} + dW_{chem} = dQ + dW_{all}$ . This would be true even if the process were not reversible because energy must be conserved. The internal energy accounts for all types of energy transfer -- nothing is isolated.

- c.  $dF(T, V, N) = d(U - TS) = -SdT - PdV + \mu dN \rightarrow dW_{all}$  at constant temperature. The change in Helmholtz potential isolates the total work, meaning that  $\Delta F = \Delta W_{all}$ . If the system is also closed ( $dN = 0 \rightarrow \Delta W_{chem} = 0$ ), then  $\Delta F$  further isolates mechanical work ( $\Delta F = \Delta W_{mech}$ ), so that we no longer need to integrate  $-\int PdV$  along a process curve; the calculation of  $\Delta F$  only requires the endpoint states. Very convenient!
- d.  $dL(T, V, \mu) = d(U - TS - \mu N) = -SdT - PdV - Nd\mu \rightarrow dW_{mech}$  at constant temperature and chemical potential. See that the Grand (Landau) potential isolates mechanical work ( $\Delta L = \Delta W_{mech}$ ), even for open systems.
- e.  $dH(S, P, N) = d(U + PV) = TdS + VdP + \mu dN \rightarrow dQ + dW_{chem}$  at constant pressure. Thus enthalpy isolates the combination of heat transfer and chemical work ( $\Delta H = \Delta Q + \Delta W_{chem}$ ). If the system is also closed ( $dN = 0 \rightarrow \Delta W_{chem} = 0$ ), the enthalpy change isolates heat transfer alone ( $\Delta H = \Delta Q$ ), which can be very convenient.
- f.  $dG(T, P, N) = d(U - TS + PV) = -SdT + VdP + \mu dN \rightarrow dW_{chem}$  at constant temperature and pressure. The Gibbs potential isolates chemical work ( $\Delta G = W_{chem}$ ) under these conditions, which include reactions conducted under ambient (room temperature and pressure) conditions.
- g. Thermodynamic potentials that don't isolate heat transfer (no factor of  $dQ$  in the differential form), are called "free energies". The change in free energy that occurs during a process is the maximum amount of work that can be done by the process. Of course, an irreversible process can waste ("degrade") all or part of this opportunity.

## Lecture 13: Applications of thermodynamic potentials and free energies

- 1) Helmholtz free energy ( $F = U - TS$ ) of an ideal gas at constant temperature
  - a. Consider the reversible expansion of an ideal-gas system in contact with a thermal reservoir of temperature  $T$ .
  - b.  $dF(T, V, N) = -SdT - PdV + \mu dN = -SdT + dW_{mech} + dW_{chem}$ .
  - c. For a closed system in contact with a reservoir at fixed temperature  $T$ ,  $dW_{chem} = \mu dN = 0$  and  $-SdT = 0$ , so that  $\Delta F = \Delta W_{mech}$ . In other words, the change in Helmholtz potential isolates mechanical work on a closed system at constant temperature.
  - d.  $F(T, V, N) = U(T, V, N) - TS(T, V, N) = cNRT - NRT \left\{ \ln \left[ \left( \frac{V}{V_0} \right) \left( \frac{T}{T_0} \right)^c \left( \frac{N_0}{N} \right)^{c+1} \right] + (c+1) \right\}$
  - e. Previously, we used determined mechanical work by integrating in the  $P - V$  plane:  

$$\Delta W_{mech} = - \int P(V) dV = - \int \frac{NRT}{V} dV = -NRT \ln \left( \frac{V_f}{V_i} \right).$$
  - f. Now, for a closed system ( $N = \text{const}$ ) in contact with a temperature reservoir ( $T = \text{const}$ ), we can simply declare that  $\Delta W_{mech} = \Delta F = -NRT \ln \left( \frac{V_f}{V_i} \right)$ .
  - g. If the process had been irreversible in any degree, then we would have  $(-\Delta W) < (-\Delta F)$ , and the work done would be non-maximal (or even zero in the case of free expansion).
  - h. To refer to a thermodynamic potential as a *free energy* implies that its change measures only the work available to be done, and never the heat transferred. This can only apply to a thermodynamic potential for which temperature is a natural variable.
  
- 2) Enthalpy ( $H = U + PV$ , never called a free energy) of an ideal gas at constant pressure
  - a.  $dH(S, P, N) = TdS + VdP + \mu dN = dQ + dW_{chem}$  at constant  $P$ .
  - b. Further assume a closed system ( $W_{chem} = \mu dN = 0$ ) so that  $\Delta H = \Delta Q$ . In other words, the change in enthalpy isolates heat transfer in a closed system at constant pressure.
  - c. Enthalpy is commonly used to quantify the heats of formation of chemical compounds at ambient pressure, because  $dH = dU + VdP + PdV = dU + PdV$  accounts for both the change in internal energy and the work required to push surrounding material out of the way to make room for the evolution of the reaction products. Enthalpy is also important to many other processes (e.g. gas cooling and liquification via Joule-Thompson throttling).
  - d. Consider the reversible expansion of a closed ideal-gas system at constant pressure, where we can express the enthalpy as a simple function of  $P$  and  $V$ .
    - i.  $H = U + PV = cPV + PV = (1+c)PV = \left( \frac{1+c}{c} \right) U = \gamma U$
    - ii. This state equation is not an FR, but is still useful for quantifying heat transfer.
    - iii.  $\Delta Q = \Delta H = (c+1)P\Delta V$
  - e. Of course, we can also express enthalpy in terms of its natural variables.
    - i.  $H(S, P, N) = (1+c)P_0V_0 e^{\{S/(c+1)NR+1\}} \left( \frac{P}{P_0} \right)^{1/(c+1)} \left( \frac{N}{N_0} \right)$
    - ii. Because this is an FR, it has broader applications than the state equation above it.

- 3) Gibbs free energy ( $G = U - TS + PV = \sum \mu_i N_i$ ) of an ideal gas at constant temperature and pressure
  - a.  $dG(T, P, N) = -SdT + VdP + \mu dN = \mu dN = dW_{chem} \rightarrow \Delta W_{chem} = \Delta G$
  - b. The Gibbs potential isolates chemical work at constant temperature and pressure and is widely used throughout the physical sciences. Many of the chemical processes on Earth take place at constant temperature and pressure due to contact with thermal and mechanical reservoirs such as the atmosphere or some other fluid.
  - c. It is relevant to vapor pressure (with or without solute), droplet formation (critical radius, energy barrier), osmotic pressure, chemical reactions in batteries, gas dissolved in liquid, etc.
  
- 4) The Grand potential or Landau free energy ( $L = U - TS - \mu N = -PV$ ) of an ideal gas
  - a.  $dL = -SdT - PdV - Nd\mu = dW_{mech} \rightarrow \Delta W_{mech} = \Delta L$  at constant  $T$  and  $\mu$ .
  - b.  $\Delta L = \Delta(-PV) = -P \Delta V = \Delta(-NRT) = -\Delta N RT$  at constant  $T$  and  $\mu$ .
  - c. Reversibly compress the gas in a porous diathermal cylinder that is bathed in the same gas.
  - d. By the Gibbs-Duhem relation, the pressure must also be in equilibrium with the outside.
  
- 5) Total potential ( $K = U - TS + PV - \mu N = 0$ )
  - a.  $dK = -SdT + VdP - Nd\mu = 0$  at constant  $T$ ,  $P$ , and  $\mu$ .
  - b. Identically zero.
  - c. It's zero differential yields the Gibbs-Duhem relation.
  
- 6) Other potentials:  $\Phi_\mu$  and  $\Phi_{P,\mu}$  don't have traditional names because it is less common to encounter physical situations that hold only these intensive parameters equal; but they still have applications.
  
- 7) Joule-Thomson throttling (K&T 6.3)
  - a. A simple constant-enthalpy process for gas cooling and liquefaction, where  $N$  moles of an a gas are forced adiabatically through a porous plug at constant high pressure  $P_i$ , and recovered on the other side at constant low pressure  $P_f$ . See K&T Fig 6.3.
  - b. The work done by the pressure source on a specific amount  $N$  of the gas in pushing it through the plug is  $-\int_{V_i}^0 P_i dV = P_i V_i$ . The work done by the gas in clearing out space for itself on the other side is similarly  $P_f V_f$ . The change in internal energy will then be the difference in these two work amounts, which is  $\Delta U = U_f - U_i = P_i V_i - P_f V_f$ .
  - c. If we rearrange this expression as  $U_i + P_i V_i = U_f + P_f V_f$ , we find that the enthalpy of the gas ( $H = U + PV$ ) is conserved. This is a constant-enthalpy process, regardless of how it proceeds microscopically.
  - d. For an ideal gas, it's easy to show that  $H = (c + 1)PV = \gamma U$ , so that  $H$  and  $U$  and  $PV = NRT$  are each conserved individually. Thus an isenthalp is also an isotherm for an ideal gas.
  - e. Because  $\Delta U = \Delta Q = 0$ ,  $\Delta W = 0$  as well.
  - f. For a non-ideal gas modeled by a van der Waals state equation, an isenthalp is not a flat horizontal line in the  $T$  vs  $P$  plane (K&T Fig 6.4). At high and low temperatures,  $T(P)$  is slightly but monotonically decreasing. At intermediate temperatures, there's a bump in the isenthalp, so that adding some pressure heats the gas, but adding more pressure cools it again. This bump, which is absent in an ideal gas is essential to the JT-liquefaction process. We ideally want to operate right at this peak on the high-pressure side of the plug and well below the peak on the low-pressure side of the plug (K&T Figs 6.5 and 6.6).



- g. There's a max inversion temperature above which the process doesn't work for lack of a  $T$  vs  $P$  peak. To liquify helium, for example, the helium gas must be pre-cooled below its 43 K inversion temperature. Each cycle then cools the gas a little more.
- h. Patent by Linde and Hampson in 1895. Nobel prize for Onnes in 1895 for liquefaction of  $^4\text{He}$ . This is still a very effective way to cool and liquefy air. Common refrigerator compressors involve a throttling process that expands a liquid on one side into a gas on the other side. The effect is very similar, though I don't know whether it's appropriate to call this Joule-Thompson throttling.
- 8) Joule-Thompson throttling of a van der Waals gas (follow Callen 6-3)
- $dT = \frac{(-T)(-V\alpha)+V}{Nc_p} dP = \frac{v}{c_p} (T\alpha - 1) dP$
  - K&T derive this important expression for the slope of a constant enthalpy curve in the  $PT$  plane, which includes molar volume ( $v = V/N$ ), the coefficient of thermal expansion ( $\alpha$ ), and the molar heat capacity at constant pressure ( $c_p$ ). We'll only learn the tools to motivate the derivation in the next lecture. For now, just accept the result as is. Remarkably, it is true for any system – not only gasses! Note that the expression and its derivation do assume a closed system ( $dN = 0$ ).
  - Joule-Thompson throttling can either heat or cool a gas, depending on the sign of the slope  $dT/dP$  of the isenthalp. To cool the gas, we need a positive slope (i.e.  $T\alpha > 1$ ) so that  $dP$  and  $dT$  have the same sign.
  - A  $TP$  isenthalp always has a negative slope at high temperature. But for some systems, the isenthalps develop a peak at sufficiently low temperature, below which the slope becomes positive. For any given isenthalp, the location of the peak on the temperature axis is called the inversion temperature:  $T_{inv} = 1/\alpha$ .
  - For an ideal gas,  $\alpha = 1/T$ , so that  $T\alpha = 1$  and  $dT/dP = 0$  under all circumstances. The  $TP$  isenthalps are perfectly horizontal. There is no inversion! Joule-Thompson throttling just doesn't work for an ideal gas.
  - The van der Waals gas model is much more interesting. In the homework assignment, you'll show that  $\frac{1}{\alpha} = \frac{Tv}{v-b} - \frac{2a(v-b)}{Rv^2}$ . Define small unitless parameters  $\epsilon_1 = \frac{b}{v}$  and  $\epsilon_2 = \frac{a}{RTv}$  and show that  $\frac{1}{\alpha} = T \left( \frac{1}{1-\epsilon_1} - 2(1-\epsilon_1)\epsilon_2 \right) \approx T(1 + \epsilon_1 - 2\epsilon_2)$ . The condition  $T_{inv}\alpha = 1$  then implies that  $\epsilon_1 = 2\epsilon_2$ , which gives us  $T_{inv} = \frac{2a}{bR}$ .
  - The idea that  $T < T_{inv}$  makes  $T\alpha > 1$  is frankly counterintuitive! K&T and other textbooks quietly ignore this problem in hopes that we won't notice. The resolution is for  $\alpha$  to increase faster than temperature decreases along the isenthalp. But does it? We can demonstrate that it does for a van der Waals gas. Allow temperature to deviate from the inversion temperature according to  $T = \frac{2a}{bR} (1 + \epsilon_3)$ , where  $\epsilon_3$  is another small unitless parameter. To first order in the small parameter, we find that  $T\alpha - 1 \approx A\epsilon_3$  where  $A = \frac{b(v-b)^2v^2}{b^3-2b^2v+bv^2-v^3}$ . This expression is always negative because  $v > b$  for a van der Waals gas. Thus,  $dT < 0 \rightarrow \epsilon_3 < 0 \rightarrow T\alpha - 1 \approx A\epsilon_3 > 0 \rightarrow \frac{dT}{dP} > 0 \rightarrow dP < 0$ . This was the desired result: lower pressure is associated with a lower temperature. Even for the simplest possible non-ideal gas model, this was complicated. But it does work. We cool and liquefy many gasses with this process.

## 9) Formation enthalpy and Gibbs free energy of a chemical reaction

- a. Consider a chemical reaction with  $0 \rightleftharpoons \sum \nu_i A_i$  (products minus reactants) where we start with just the right amount of each gas for a complete reaction. Let reaction variable  $\Delta N$  be the change in the number of moles expected for a species with  $\nu = 1$ . Assume the system is closed during the reaction, so the mole-number change of each species is  $\Delta N_i = \nu_i \Delta N$ .
- b. The Gibbs free energy change is  $\Delta G = \sum \mu_i \Delta N_i = \sum \nu_i \mu_i \Delta N$  and the molar Gibbs free energy change is  $\Delta g = \sum \mu_i \Delta N_i = (\sum \nu_i \mu_i) \Delta N$ .
- c. Chemical reactions introduce a subtlety into the Euler equation ( $U = TS - PV + \sum \mu_i N_i$ ). If the reaction has  $\Delta G < 0$ , energy that was previously stored in chemical bonds is released into the system. But if the system is isolated overall, one would expect the total energy to remain constant. The problem here is that the chemical potential is defined in terms of an arbitrary reference state, which gets altered during the species transformation. The difference between the energies of the reference states is the energy released, which can raise the temperature, pressure, internal energy, and entropy of an isolated system, or else be exchanged as work or heat energy into external reservoirs. Most textbooks avoid the issue; they simply mention the energy released or consumed by a reaction as though it came from somewhere else, without worrying about how to account for it in the Euler equation.
- d. At a given temperature and pressure, let the reference state of any chemical compound be a stoichiometric collection of the stable forms (gas, liquid, solid, etc) of each of the individual elements of the compound at that temperature and pressure. So carbon monoxide CO at room temperature and pressure shall be compared against solid carbon graphite and molecular O<sub>2</sub> gas. The molar enthalpy ( $\Delta h_f^\circ = \Delta H_f^\circ / N$ ) and Gibbs free energy ( $\Delta g_f^\circ = \Delta G_f^\circ / N$ ) of formation are the changes in enthalpy and Gibbs potential per mole that occur in producing the compound from its stable elements. For a reaction, the total change in molar enthalpy is computed as the stoichiometric sum of the molar enthalpies of formation of the products minus the reactants:  $\Delta h = \sum \nu_i \Delta h_{fi}^\circ$ . Remember that the  $^\circ$  and  $f$  in  $\Delta h_f^\circ$  indicate “standard” and “of formation”, respectively. Ditto for the molar Gibbs free energy change, which is  $\Delta g = \sum \nu_i \Delta g_{fi}^\circ$ .
- e. We view  $\Delta h$  as the energy invested in or recovered from changing chemical bonds. However, some of the heat transferred into a system to facilitate a chemical reaction at constant temperature and pressure actually contributes to the reaction (like loan premium), while the rest is spent doing mechanical work ( $-\Delta w_{mech}$ ) on the external pressure reservoir (like loan interest). The enthalpy change,  $\Delta h = \Delta q = \Delta u + (-\Delta w_{mech})$ , sums up all of this heat (like the whole loan payment).
- f. If the reaction enthalpy  $\Delta h$  is positive, the reaction removes energy from the system as it moves forward, which must be paid for with heat from the reservoir if the temperature is to remain constant; we call such a reaction endothermic because it imports heat energy. If the reaction enthalpy  $\Delta h$  is negative, the reaction releases energy into the system as it moves forward; we call such a reaction exothermic because it exports energy.
- g. A positive reaction enthalpy encourages a reaction to move forward, though it alone is not enough to ensure that it does so. Entropy increase and enthalpy decrease are competing driving forces in chemical reactions. At constant temperature and pressure, the molar Gibbs free energy and enthalpy changes of reaction are related as  $\Delta g = \Delta(h - Ts) = \Delta h - T\Delta s$ , where  $\Delta s$  is the molar difference in system entropy (products – reactants). The molar Gibbs free energy of reaction is a weighted sum over the chemical potentials of the products and

reactants, and accounts for both their changes in intrinsic chemical-bond energy ( $\Delta h$ ) and entropy ( $\Delta s$ ); the sign of  $\Delta g$  alone determines whether or not a reaction proceeds spontaneously. If the products have lower chemical potentials than the reactants, so that  $\Delta g < 0$ , the reaction will proceed spontaneously until the chemical potentials of the two sides equilibrate ( $\sum v_i \mu_i = 0$ ) or the reactants are spent. Otherwise it must be forced.

- h. Tables of standard enthalpies of formation ( $\Delta h_f^\circ$ ) and Gibbs free energies of formation ( $\Delta g_f^\circ$ ) are usually presented with absolute standard-state molar entropies  $s^\circ$ . Because these are absolute entropies rather than entropy changes, we expect that  $\Delta g_f^\circ \neq \Delta h_f^\circ - Ts^\circ$ .
  - i. The relative signs and magnitudes of enthalpy and entropy change are important.
    - i. If  $\Delta h > 0$  and  $T\Delta s < 0$ , then  $\Delta g > 0 \rightarrow$  endothermic and not spontaneous.
    - ii. If  $\Delta h < 0$  and  $T\Delta s > 0$ , then  $\Delta g < 0 \rightarrow$  exothermic and spontaneous.
    - iii. If  $\Delta h > 0$  and  $T\Delta s > 0$ , then  $\Delta g$  might be either positive or negative depending on which term is larger. An endothermic reaction can be spontaneous. Cool☺
    - iv. If  $\Delta h < 0$  and  $T\Delta s < 0$ , then  $\Delta g$  might be either positive or negative depending on which term is larger. An exothermic reaction doesn't have to be spontaneous.
    - v. In summary, if  $\Delta h$  and  $T\Delta s$  are both positive or both negative,  $\Delta g$  could be either positive or negative depending on which term is larger. Thus, an endothermic reaction can be spontaneous and an exothermic reaction can be non-spontaneous.
  - j. Explore examples.
    - i. Here's a simple [discussion](#) of formation enthalpy and Gibbs free energy.
    - ii. Browse some online data tables of formation enthalpies and Gibbs free energies. Search for and substantiate a few uncommon examples of endothermic spontaneous and exothermic non-spontaneous formation reactions.
    - iii. For a reactions involving non-elemental compounds, compute the stoichiometry-weighted sums of their their formation enthalpies and Gibbs free energies.
- 10) Consider an osmotic pressure cell at room temperatures and pressure, initially both the left side ( $l$ ) and the right side ( $r$ ) contain pure water ( $w$ ). Then sugar ( $s$ ) is added to the left side, reducing the chemical potential of water only on the left. The barrier is permeable only to water (not to sugar), so that water passes from right to left, until the pressure differential due the differing water-column heights  $\Delta P = P_l - P_r$  matches the osmotic pressure. See K&T Fig 6.8.
- a. Define  $x_s = N_s/(N_w + N_s)$  as the mole fraction of sugar on the left side.
  - b. Assume that  $x_s$  and  $\Delta P = P_l - P_r$  are both small quantities.
  - c. The molar concentration (moles per liter) of solute is  $n_s = \frac{N_s}{V} = \frac{x_s(N_s + N_w)}{V} \approx \frac{x_s N_w}{V} = x_s n_w$ , where  $n_w$  is the molar concentration of water.
  - d. Let  $\mu_w^0(P, T)$  be the chemical potential of pure water, which depends on  $P, T$ .
  - e. The chemical potential of water on the left (high-pressure) side is  $\mu_w^0(P_l, T) + \Delta\mu$ , while that on the right (low-pressure) side is  $\mu_w^0(P_r, T)$ . Here,  $\Delta\mu$  will turn out to be negative, which then drives the osmosis.
  - f. Minimizing  $G$  equalizes the chemical potential for water:  $\mu_w^0(P_l, T) + \Delta\mu = \mu_w^0(P_r, T)$ , so that  $-\Delta\mu = \mu_w^0(P_l, T) - \mu_w^0(P_r, T) \approx \left(\frac{\partial \mu_w^0}{\partial P}\right)_{T, N_w} \Delta P = \frac{1}{N_w} \left(\frac{\partial G}{\partial P}\right)_{T, N_w} \Delta P = \frac{V_w}{N_w} \Delta P = \frac{\Delta P}{n_w}$

- g. Though not an ideal gas, water has a similar state equation of the form  $\frac{\mu}{T} = s + \text{const}$ , so that the change in entropy due to solute mixing will be of the form  $\Delta\mu = -T\Delta s = x_l \ln(x_l) RT = (1 - x_s) \ln(1 - x_s) RT \approx -x_s RT$  when  $x_s$  is small.
- h. Thus  $\Delta P = -\Delta\mu n_w = x_s n_w RT \approx n_s RT$  – the van't Hoff relation for osmotic pressure.
- i. Hydrostatic pressure difference is  $\Delta P = \rho g \Delta h$ , which will equal the osmotic pressure.

11) Water droplet formation [Skip this content in the interest of time.]

- a. The derivation in K&T 6.4.1 is really hard to follow due to unexplained steps and undefined quantities. In comparison, K&T 10.4 is fairly simple; focus on that instead.
- b. For a given temperature, water liquid and vapor can coexist at sufficiently high partial pressure ( $P_g$ ) in air. When  $P_g$  of the water vapor surpasses the saturation vapor pressure  $P_\infty$ , the vapor would naively be expected to liquefy because the chemical potential becomes lower in the liquid state by an amount  $\Delta\mu = \mu_g - \mu_l > 0$ , which provides a free-energy benefit per mole of liquid.
- c. The liquid initially forms in the vapor as droplets, which have a costly gas-liquid interface that opposes formation, so that  $\Delta P = P_g - P_\infty$  must become substantially positive to overcome this barrier.
- d. Consider a single droplet of radius  $r$  and its surrounding vapor, and let  $\gamma$  be the surface tension of the droplet. Solve for the critical radius in terms of a small but finite  $\Delta P$ .
- e. At constant  $T$  and  $P$ , the free energy change is  $dG = (\sum \mu_i dN_i) + \dots = dW_{chem} + dW_{misc}$ , which ignores heat and mechanical work, but accounts for chemical and other non-mechanical forms of work (e.g. the formation of the interface).
- f.  $\Delta G(r) = \mu_l \Delta N_l + \mu_g \Delta N_g + 4\pi r^2 \gamma = (\mu_l - \mu_g) \Delta N_l + 4\pi r^2 \gamma = -\Delta\mu \left( \frac{4}{3} \pi r^3 n_l \right) + 4\pi r^2 \gamma = 4\pi r^2 \left( \gamma - \frac{1}{3} n_l \Delta\mu r \right)$ . The first term is the liquid-phase advantage, which scales with the droplet volume; the greater the droplet volume the better. The second term is surface-tension disadvantage; the smaller the droplet area the better. For small  $r$ , the area terms wins, discouraging growth. For large  $r$ , the volume term wins, encouraging growth. Thus, there is a critical radius that must be surpassed by a fluctuation in order to obtain a stable droplet. Graph this function to see the barrier height and critical radius.
- g.  $\frac{\partial[\Delta G(r)]}{\partial r} = 4\pi r (2\gamma - \Delta\mu n_l r) = 0 \rightarrow r_c = \frac{2\gamma}{\Delta\mu n_l}$  and  $\Delta G_c = \frac{16}{3} \pi \frac{\gamma^3}{(\Delta\mu n_l)^2}$
- h. Treat supersaturated vapor as an ideal gas, so that 
$$\Delta\mu = (\mu_g - \mu_l) = RT \ln \left[ \left( \frac{P_r}{P_\infty} \right) \left( \frac{T}{T} \right)^{c+1} \right] = RT \ln \left[ \left( \frac{P_\infty + \Delta P}{P_\infty} \right) \right] \approx RT \frac{\Delta P}{P_\infty} \approx \frac{V_g}{N_g} \Delta P = \frac{\Delta P}{n_g}.$$
- i. The critical radius is then  $r_c = \frac{2\gamma n_g}{\Delta P}$ , which is associated with a fairly large energy fluctuation  $\Delta G_c = \frac{16}{3} \pi \frac{\gamma^3}{\Delta P^2} \left( \frac{n_g}{n_l} \right)^2$ . This energy barrier tends to make the vapor metastable.

## Lecture 14: Maxwell Relations and partial derivative reduction

- 1) From multi-variable calculus, **second-order mixed partial derivatives are equivalent**, meaning that it doesn't matter in what order the two partial derivatives are applied ( $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ ). In other words, the functional operations  $\frac{\partial}{\partial x}$  and  $\frac{\partial}{\partial y}$  *commute*.
- 2) The first and second-order partial derivatives of thermodynamic potentials can be classified to clarify what makes a given partial derivative Maxwellian or non-Maxwellian. Here, I provide my own custom set of acronyms for this classification. Abbreviate thermodynamic potential as TDP.
  - a. First order partial derivatives of TDPs
    - i. First order partial derivatives of TDPs are called FOPs, e.g.  $\left(\frac{\partial G}{\partial T}\right)_{P,N}$ .
    - ii. The *inverse* of a FOP is called an iFOP, e.g.  $\left(\frac{\partial T}{\partial G}\right)_{P,N}$ .
    - iii. A *permutation* of a FOP is called a pFOP, e.g.  $\left(\frac{\partial P}{\partial T}\right)_{G,N}$ .
    - iv. A FOP involving only *natural variables* of a TDP needs no special prefix. But a FOP involving *unnatural* (i.e. non-natural) variables of a TDP is called a uFOP, e.g.  $\left(\frac{\partial G}{\partial V}\right)_{P,N}$ .
    - v. In a similar fashion, we can define iuFOPs and puFOPs.
  - b. Second-order partials of TDPs are called SOPs.
    - i. Second-order *mixed* partials of TDPs are called SOMP, e.g.  $\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial^2 G}{\partial P \partial T}\right)_N$ .  
Second-order *unmixed* partials of TDPs are called SOUPs, e.g.  $\left(\frac{\partial S}{\partial T}\right)_{P,N} = \left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N}$ .
    - ii. An inverse of a SOMP is called an iSOMP, e.g.  $\left(\frac{\partial P}{\partial S}\right)_{T,N} = \left(\frac{\partial^2 G}{\partial P \partial T}\right)_N^{-1}$ , and an inverse of a SOUP is called an iSOUP, e.g.  $\left(\frac{\partial T}{\partial S}\right)_{P,N} = \left(\frac{\partial^2 G}{\partial T^2}\right)_N^{-1}$ .
    - iii. A permutation of a SOMP is called a pSOMP, e.g.  $\left(\frac{\partial T}{\partial P}\right)_{S,N}$ . And the inverse of a pSOMP, e.g.  $\left(\frac{\partial P}{\partial T}\right)_{S,N}$ , is called an ipSOMP.
    - iv. One could call a permuted SOUP a pSOUP, e.g.  $\left(\frac{\partial P}{\partial T}\right)_{S,N}$ , though such derivatives are already covered by the classifications above. This example is an ipSOMP.
- 3) Maxwellian vs non-Maxwellian SOPs
  - a. Maxwellian SOPs
    - i. Only a SOMP can be described as a Maxwellian partial derivative.
    - ii. **To be Maxwellian, a SOMP must be presented as a first-order partial of a state variable obtained as a FOP.** Thus, though  $\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial^2 G}{\partial P \partial T}\right)_N$ , we say that  $\left(\frac{\partial S}{\partial P}\right)_{T,N}$  is Maxwellian, while the equivalent explicit second-order partial  $\left(\frac{\partial^2 G}{\partial P \partial T}\right)_N$  is not.

- iii. A Maxwellian partial always contains one pair of conjugate variables, one being in the numerator of the derivative, and the other being held fixed.
  - iv. For a simple system with three independent state variables, there are  $2^3 - 1 = 7$  thermodynamic potentials (not including the total potential  $K$ ). For each potential, there are three variable choices for the first derivative, and two choices for the second, providing a total of  $7 \cdot 6 = 42$  Maxwellian partials.
- b. Non-Maxwellian SOPs
- i. A conjugate pair of state variables appear in the wrong place
    1. Both appear inside the derivative, one in the numerator and one in the denominator. In  $\left(\frac{\partial S}{\partial T}\right)_{P,N} = -\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N}$ , the conjugate pair  $(S, T)$  appear inside the derivative. These cases turn out to be SOUPs or iSOUPs.
    2. One appears in denominator and the other is held constant, e.g.  $\left(\frac{\partial P}{\partial S}\right)_{T,N} = \left(\frac{\partial S}{\partial P}\right)_{T,N}^{-1} = -\left(\frac{\partial^2 G}{\partial P \partial T}\right)_N$ . These cases turn out to be iSOMPs.
    3. Both are simultaneously held constant, e.g.  $\left(\frac{\partial P}{\partial N}\right)_{S,T}$  or  $\left(\frac{\partial T}{\partial \mu}\right)_{\mu,N}$ . These cases turn out to be pSOMPs or ipSOMPs.
  - ii. If we consider partials involving more than one thermodynamic potential, e.g.  $\left(\frac{\partial F}{\partial V}\right)_{U,N}$ , the possibilities really start to proliferate! There are tens of thousands of possible derivatives involving thermodynamic potentials if we allow arbitrary combinations of extensive variables, intensive variables, and thermodynamic potentials. Note one limitation: the four parameters in the partial derivative must be functionally relatable; otherwise, the partial derivative is not valid.
- 4) Maxwell relations
- a. By virtue of the general equivalence of SOMPs with differently ordered derivatives, these 42 Maxwellian partials can be partitioned into 21 equivalent pairs. The equality of such a pair is called a **Maxwell relation**.
  - b. Example with  $V$  and  $S$  active in  $U$ :  $\left(\frac{\partial T}{\partial V}\right)_{S,N} = \left(\frac{\partial^2 U}{\partial V \partial S}\right)_N = \left(\frac{\partial^2 U}{\partial S \partial V}\right)_N = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$
  - c. Example with  $P$  and  $T$  active in  $G$ :  $\left(\frac{\partial V}{\partial T}\right)_{P,N} = \left(\frac{\partial^2 G}{\partial T \partial P}\right)_N = \left(\frac{\partial^2 G}{\partial P \partial T}\right)_N = -\left(\frac{\partial S}{\partial P}\right)_{T,N}$
  - d. Characterizing a Maxwell relation (assume a simple system with 3 independent variables)
    - i. No TDP appears explicitly in the relation.
    - ii. The variables in the numerators are first derivatives of the same TDP; the denominator variable and two constant variables on either side readily identify the TDP with its corresponding natural variables.
    - iii. Each side of the relation will feature a distinct conjugate variable pair, wherein one variable sits in the numerator and its conjugate is held constant. The natural variable in the denominator on one side of the relation is the conjugate variable held constant on the other side of the relation.
    - iv. Of the three natural variables in the relation, two are active (i.e. appear in denominators), and one is inactive (constant on both sides, its conjugate not present).
    - v.  $d\Phi = A'dA + B'dB \Rightarrow \left(\frac{\partial A'}{\partial B}\right)_A = \left(\frac{\partial B'}{\partial A}\right)_B$  is the corresponding Maxwell relation.

- e. Review the K&T table of Maxwell relations. Our K&T errata list points out a few errors.
    - i. The  $SN$  square of  $U$  should have  $\left(\frac{\partial T}{\partial N}\right)_{S,V}$  rather than  $\left(\frac{\partial T}{\partial N}\right)_{S,N}$ .
    - ii. The differential FR of  $\Phi_\mu$  should include  $-PdV$  rather than  $VdP$ .
    - iii. The  $TP$  square of  $G$  needs a  $-$  sign in front of  $\left(\frac{\partial S}{\partial P}\right)_{T,N}$ .
    - iv. It would be nice to refer to  $\Phi_{T,\mu}$  as  $L$  (Landau or Grand potential).
  - f. Subtleties involving SOMP's of the *total* thermodynamic potential  $K = 0$ 
    - i. The six SOMP's of  $K$  are zero, and the corresponding Maxwell relations are useless.
    - ii.  $K$  is a function of all three intensive variables, but must itself be extensive. The only way that this can be true is for the system size to be exactly zero (no system at all)!
    - iii. Any Maxwellian partial of  $K$  appears as a derivative of an extensive variable with respect to an intensive variable while holding two intensive variables constant, which implies that the extensive variable is expressible solely in terms of intensive variables, which is impossible.
    - iv. Meaningful Maxwellian derivatives (not based on  $K$ ) involving all three intensive parameters  $T, P, \mu$  must hold an extensive variable constant. This effectively holds the system size constant, which is fine.
- 5) The reduction of partial derivatives.
- a. For a closed system, it is possible to express any valid first or second derivative involving TDP's and/or state variables in terms of three specially-designated SOMP's of the Gibbs potential ( $\alpha$ ,  $\kappa_T$  and  $c_P$ ) and other state variables. Recall their respective definitions.
    - i.  $\alpha_P = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,N} = \frac{1}{V} \left( \frac{\partial^2 G}{\partial P \partial T} \right)_N$
    - ii.  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N} = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial P^2} \right)_{T,N}$
    - iii.  $c_P = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_{P,N} = -\frac{T}{N} \left( \frac{\partial^2 G}{\partial T^2} \right)_{P,N}$
  - b. What's the big deal about reduction? First,  $\alpha_P$ ,  $\kappa_T$ , and  $c_P$  (or  $c_V$ ) are easy to measure experimentally. Once they are known as empirical functions of the natural variables of the system, we can calculate any other 2<sup>nd</sup>-order derivative quantity without additional experiments, even if we don't know the FR. This is actually quite a big deal!
  - c. There is a simple 5-step process for reducing any thermodynamic first or second derivative to the desired form. First work through some examples below and then come back to this.
    - i. Eliminate each potential one at a time by inverting or permuting it into the numerator and applying its differential fundamental relation.
    - ii. Eliminate the chemical potential -- bring it to the numerator and apply the Gibbs-Duhem relation ( $d\mu = -sdT + vdP$ ). This leaves only  $S, T, P, V, N$ .
    - iii. Eliminate the entropy -- bring it to the numerator and either use a Maxwell relation or substitute a heat capacity ( $c_P$  or  $c_V$ ).
    - iv. Eliminate volume -- bring it to the numerator and substitute for  $\alpha_P$  or  $\kappa_T$ .
    - v. Eliminate any factors of  $c_V$  via the relation  $c_V = c_P - Tv \frac{\alpha_P^2}{\kappa_T}$ .

- 6) Reduction of  $\left(\frac{\partial P}{\partial U}\right)_{T,N}$  (K&T examples 7.1 and 7.4 in section 7.2)
- $\left(\frac{\partial P}{\partial U}\right)_{T,N} = \left(\frac{\partial U}{\partial P}\right)_{T,N}^{-1}$
  - The energetic FR is  $dU = TdS - PdV + \mu dN$ , which simplifies to  $TdS - PdV$  for a closed system, so that differentiating with respect to  $P$  yields  $\left(\frac{\partial U}{\partial P}\right)_{T,N} = T\left(\frac{\partial S}{\partial P}\right)_{T,N} - P\left(\frac{\partial V}{\partial P}\right)_{T,N}$ .
  - Use Maxwell relation  $\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$  to eliminate  $S$ .
  - $\left(\frac{\partial U}{\partial P}\right)_{T,N} = \left(\frac{\partial U}{\partial P}\right)_{T,N}^{-1} = \left[-T\left(\frac{\partial V}{\partial T}\right)_{P,N} - P\left(\frac{\partial V}{\partial P}\right)_{T,N}\right]^{-1}$
  - Use definitions of  $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$  and  $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$  to eliminate volume.
  - $\left(\frac{\partial U}{\partial P}\right)_{T,N} = [T\{-V\alpha_P\} - P\{-V\kappa_T\}]^{-1} = \frac{1}{V(P\kappa_T - T\alpha_P)}$
  - Also see the other K&T reduction examples (7.1-7.6).
- 7) Famous heat-capacity relation:  $c_P - c_V = Tv\frac{\alpha_P^2}{\kappa_T}$
- For the reduction of some partial derivatives, the use of  $c_V$  is a lot cleaner rather than  $c_P$ . One can then convert from  $c_V$  to  $c_P$  with this relation (reduction step 5). The process is as follows, where we assume a closed system ( $dN = 0$ ).
  - $c_V = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N} = -\frac{T}{N}\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N}$  and  $c_P = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{P,N} = -\frac{T}{N}\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N}$
  - Start with state equation  $S(T, P, N)$ , find its differential.  

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P,N} dT + \left(\frac{\partial S}{\partial P}\right)_{T,N} dP + \left(\frac{\partial S}{\partial N}\right)_{P,T} dN$$
  - Now take its partial with respect to  $T$  at constant  $V$  and  $N$ .  

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial T}\right)_{P,N} + \left(\frac{\partial S}{\partial P}\right)_{T,N} \left(\frac{\partial P}{\partial T}\right)_{V,N}$$
  - Apply Maxwell relation  $\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$  and permutation rule  $\left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{-\left(\frac{\partial P}{\partial V}\right)_{T,N}}{\left(\frac{\partial T}{\partial V}\right)_{P,N}}$   
 to obtain 
$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial T}\right)_{P,N} + \left(-\frac{\partial V}{\partial T}\right)_{P,N} \left[\frac{-\left(\frac{\partial P}{\partial V}\right)_{T,N}}{\left(\frac{\partial T}{\partial V}\right)_{P,N}}\right].$$
  - Invoke the definitions of  $\alpha_P$ ,  $\kappa_T$ ,  $c_P$ , and  $c_V$  to obtain the final result.
  - Remarkably, this is true for any system regardless of the FR, not just ideal gasses!
  - Because  $c_P > c_V$ , steam cooking is more efficient at constant volume (pressure cooker); it takes less heat to get a finite temperature increase.



## 8) Other reduction examples:

- a. K&T explore several interesting derivative-reduction examples for general systems (not just ideal gasses). These are worth a look.
- b. Adiabatic-expansion  $TP$  isentrope:  $\left(\frac{\partial T}{\partial P}\right)_{S,N} = \frac{T v \alpha_P}{c_P}$ , where  $v = \frac{V}{N}$ .
- c. Free expansion isoenergetic curve:  $\left(\frac{\partial T}{\partial V}\right)_{U,N} = \frac{1}{N c_V} \left(P - \frac{T \alpha_P}{\kappa_T}\right)$
- d. Joule-Thompson  $TP$  isenthalp:  $\left(\frac{\partial T}{\partial P}\right)_{H,N} = \frac{V}{N c_P} (T \alpha_P - 1)$
- e. Heating a leaky room:  $c_{PV} = \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_{P,V} = c_P - T \alpha_P s$ , where  $s = \frac{S}{N}$ .

## 9) Heating a room full of an ideal gas

- a. Robert Emden, Nature **141**, 908–909 (1938). “Why do we have Winter Heating? The layman will answer: ‘To make the room warmer.’ The student of thermodynamics will perhaps express it thus: ‘To import the lacking internal thermal energy.’ If so, then the layman’s answer is right, the scientist’s is wrong.” <https://www.nature.com/articles/141908a0>
- b. At constant  $P$  and  $V$ ,  $N$  must decrease when  $T$  increases. Thus,  $U$  stays constant inside, while both air and energy escape through leaks (heating the whole neighborhood).
- c.  $S = N \left( s_0 + R \ln \left[ \left( \frac{P}{P_0} \right)^c \left( \frac{V}{V_0} \right)^{c+1} \left( \frac{N_0}{N} \right)^{c+1} \right] \right) = \frac{PV}{RT} \left( s_0 + R \ln \left[ \left( \frac{P_0}{P} \right) \left( \frac{T}{T_0} \right)^{c+1} \right] \right)$ , so that the entropy in the room actually decreases upon heating.
- d.  $c_{PV} = \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_{P,V} = \frac{T}{N} \left(\frac{\partial S}{\partial T}\right)_{U,V} = \frac{T}{N} \left(\frac{\partial S}{\partial N}\right)_{U,V} \left(\frac{\partial N}{\partial T}\right)_{U,V} = \frac{T}{N} \left(-\frac{\mu}{T}\right) \left(\frac{\partial(U/cRT)}{\partial T}\right)_{U,V} = \frac{\mu}{T} < 0$  because  $U = cNRT$  and  $\mu < 0$  for an ideal gas.
- e. The heat capacity is negative, and heat must be removed from the room to warm it!

## Lecture 15: Phase Equilibria

### 1) Energy vs entropy:

- a. The internal energy has both kinetic and electric potential energy contributions in non-ideal gas systems. A thermodynamic system seeks to minimize its free energy rather than its internal energy. At constant temperature and pressure, this is the Gibbs free energy. At high temperatures (and/or low pressures), the entropy term in the free energy dominates, leading to highly disordered atomic configurations. At low temperature (and/or high pressure), interatomic [Coulomb] interactions dominate, leading to more ordered atomic configurations. Phase transitions between distinct atomic configurations occur when there is a change in dominance among various competing entropic and interaction terms in the free energy.
- b. Ice is crystalline phase and is therefore more ordered than water. Ice crystals certainly have impressive symmetries. Is crystalline ice more symmetric than liquid water? No! Water is vastly more symmetric. No matter how you rotate or translate water, it looks the same. In general, the more disordered a phase is the more symmetric it is. As temperature decreases, disorder and symmetry both tend to decrease, though there are exceptions.

### 2) Gibbs Phase rule:

- a. The Gibbs-Duhem relation tells us that the chemical potential is function  $\mu(T, P)$  of the other intensive system variables. Imagine the surface formed by a 3D plot of this function above the  $TP$  plane. In order for multiple phases to coexist in equilibrium, their distinct chemical potentials must be equal, which requires that their  $\mu_i(T, P)$  surfaces intersect. The intersection of two such functions will form a one-dimensional line in the  $TP$  plane. The intersection of three such functions can only occur at a single  $TP$  point. Thus, the dimensionality of the coexistence region depends on the number of phases present – each additional coexisting phase eliminates one dimension. See mathematica-based illustrations.
- b. For a closed system ( $N$  fixed) of one species and one phase, the system can have any combination of pressure and temperature in principle, so that the dimension of the state space is effectively two dimensional (the  $PT$  plane). Adding an additional atomic or molecular species at fixed system size adds a new state variable (a relative mole fraction  $x_i = N_i/N_{total}$ ), whereas requiring the coexistence of an additional phase eliminates a state variable. This concept is neatly summarized by the Gibbs phase rule:
- c. Gibbs phase rule:  $F = C - \phi + 2$ , where  $C$  is the number of distinct species,  $\phi$  is the number of coexisting phases, and  $F$  is the dimensionality of the coexistence region in state space.
  - i. Coexisting  $H_2O$  liquid water and steam: We have  $C = 1$  species and  $\phi = 2$  coexisting phases, yielding an  $F = 1$  dimensional coexistence line in the  $PT$  plane.
  - ii. Gas, liquid, and solid  $H_2O$  all coexist at the triple-point. We have  $C = 1$  species and  $\phi = 3$  phases, so that  $F = 0$ . Because the region of coexistence is zero-dimensional, it makes sense to call it a “point” in the  $PT$  plane.
  - iii. For a binary alloy, the molar ratios of  $C = 2$  species differ in the coexisting liquid and solid phases ( $\phi = 2$ ). The coexistence state space has dimension  $F = 2$ . If we then fix the pressure, thereby reducing the dimensionality further, we can still trace out a 1-dimensional liquidus-solidus curve for temperature vs mole fraction:  $T(x)$ .
  - iv. K&T Figs. 10.4 and 10.5 illustrate coexistence lines and points, and terms like boiling and condensation, melting and freezing, sublimation and deposition.

## 3) Lever rule

- a. The extent of a transition across a two-phase coexistence line obeys the volume “lever rule” which relates the mole fractions ( $x_i = N_i/N$ ) and molar volumes ( $v_i = V_i/N_i = 1/n_i$ ) of the two phases to the overall molar volume  $v = \frac{V}{N} = \sum V_i / \sum N_i$ .
- b.  $v = \frac{V}{N} = \frac{V_1+V_2}{N_1+N_2} = \frac{V_1}{N} + \frac{V_2}{N} = \frac{N_1 v_1}{N} + \frac{N_2 v_2}{N} = x_1 v_1 + x_2 v_2$  and  $x_1 + x_2 = 1$ .
- c. For a liquid-gas coexistence, this has the form  $v = x_g v_g + x_l v_l = x_g v_g + (1 - x_g) v_l$ , where  $v_l$  is usually well known,  $v_g$  can be obtained from the known vapor pressure at the specified temperature, and  $v$  is set by the experimenter. Finally, solve for  $x_g = \frac{v-v_l}{v_g-v_l}$ , and  $x_l = \frac{v_g-v}{v_g-v_l}$ .

## 4) Latent heat

- a. To cross a coexistence line from a lower-entropy phase (e.g. liquid water) to a higher-entropy phase (e.g. steam), heat must be imported (or exported to proceed in the opposite direction).
- b. The molar Gibbs free energy  $g = GN = h - Ts$  is the chemical potential  $\mu(P, T)$ , which must be equal for two coexisting phases in equilibrium, so that  $\Delta g = \Delta h - T\Delta s = 0$ .
- c. Thus,  $\Delta h = T\Delta s$ . For a closed system, you already knew that enthalpy change isolates heat transfer. Here, we see that all of the heat imported into the system is used move material through the transition, thereby increasing its molar enthalpy.
- d. We refer to the difference in molar enthalpy  $\Delta h$  between the two phases as the “latent heat of the transition”. This is the amount of heat required to move 1 mole of material through the transition (towards the high entropy side) at constant  $T$  and  $P$  in a closed system.

## 5) Clausius-Clapeyron equation

- a. Along a coexistence line in the  $PT$  plane, there is only one independent variable, so that we can use absolute rather than partial derivatives with respect to  $P$  and  $T$ .
- b.  $\frac{d\mu_2}{dT} = \frac{d\mu_1}{dT} = \left(\frac{\partial\mu_1}{\partial T}\right)_P + \left(\frac{\partial\mu_1}{\partial P}\right)_T \frac{dP}{dT} = \left(\frac{\partial\mu_2}{\partial T}\right)_P + \left(\frac{\partial\mu_2}{\partial P}\right)_T \frac{dP}{dT} = -s_1 + v_1 \frac{dP}{dT} = -s_2 + v_2 \frac{dP}{dT}$
- c. Then solve for  $\frac{dP}{dT} = \frac{s_2-s_1}{v_2-v_1} = \frac{\Delta h}{T(v_2-v_1)}$  to obtain the famous Clausius-Clapeyron equation.
- d. If the higher-entropy phase also has a higher volume, the slope of the  $P(T)$  coexistence line is positive. This is the normal situation. But there are unusual cases, such as the liquid-solid transition of  $\text{H}_2\text{O}$ , where the slope of the  $P(T)$  coexistence curve is negative. This is caused by the non-linear shape of the water molecule and the relative weakness of hydrogen bonds. Because ice has a greater molar volume than water (i.e. ice is less dense), ice floats. This phenomenon is essential to life on earth. Ice sheets on a lake or ocean thermally insulate the water underneath. Otherwise, lakes and oceans would freeze solid from the bottom up.
- e. For gasses,  $v_g \gg v_l$  so that we neglect  $v_l$  and let  $v_g = RT/P$ . Then  $\frac{dP}{dT} = \frac{\Delta h P}{RT^2}$ , the solution of which is  $P = P_\infty e^{-\Delta h/RT}$ . It is obvious that the slope of such a  $P(T)$  coexistence line is always positive for a liquid-gas transition.

## 6) Liquid-gas transition in a van der Waals gas:

- a. The non-zero size of an individual atom or molecule reduces the effective molar volume. And interactions between particles either increase ( $a > 0$ , repulsion) or decrease ( $a < 0$ , attraction) the effective pressure. Such a non-ideal gas can be described using the van der Waals equation of state:  $\left(P + \frac{a}{v^2}\right)(v - b) = RT$
- b. Or equivalently,  $P = \frac{RT}{v-b} - \frac{a}{v^2} \rightarrow Pv^3 - (Pb + RT)v^2 + av - ab = 0$ , where  $v = V/N$  is the molar volume, which is inverse proportional to the molar density.
- c. Consider the  $PV$  isotherms. At high temperatures, there is only one solution for  $v$  at a given pressure. But below a critical temperature, the  $PV$  isotherms develop a dip, and therefore have three solutions for  $v$ , which correspond to three different densities (liquid, gas, and something unstable in between). To follow an isotherm from one state to the other, the system must cross a phase transition. Similarly, below a critical pressure, the  $TV$  isobars develop a dip.
- d. This would not happen with an ideal gas. It's the non-ideal terms of the van der Waals equation of state that give rise to this phase transition.
- e. Reduced VDW state equation: The VDW-gas critical pressure and temperatures are  $P_c = \frac{1}{27} \frac{a}{b^2}$  and  $RT_c = \frac{8}{27} \frac{a}{b}$ , which is associated with a unique critical molar volume  $v_c = 3b$ . This is the point where  $P(V)$  just begins to form a dip, so that the first and second derivatives are simultaneously zero. If we define reduced parameters  $p = \frac{P}{P_c}$ ,  $t = \frac{T}{T_c}$  and  $v = v/v_c$ , we can rewrite the van der Waals state equation simply as  $\left(p + \frac{3}{v^2}\right)(3v - 1) = 8t$ . Plots of  $p(v)$  or  $v(p)$  at  $t$  values of 0.9, 1.0, and 1.1 are particularly instructive.
- f. At constant temperature and pressure, a system will seek to minimize its Gibbs free energy. If we could artificially vary the molar volume at a given temperature and pressure in order to see the effect on the molar Gibbs free energy,  $g(p, t, v) = f(t, v) + pv$ , we would find a potential well for which the equilibrium state lies at the bottom, thereby minimizing  $\mu$ . Though we can't explore this space, nature does so, and faithfully finds the minimum-free-energy volume, which we know to depend on pressure according to the state equation. To be clear, we fix  $p$  in  $f(t, v) + pv$  to arrive at a concave function of  $v$ , the minimum of which yields the state equation  $v(p)$ . This is an instructive way to think about the state equation.
- g. Below the critical temperature and pressure, the non-ideal terms in the equation of state then give rise to a bump at the bottom of the potential well, and hence a double minimum, so that there are two rather than one valid densities. We refer to the higher density as the liquid phase and the lower density as the gas phase. If the two minima are equally deep at a given  $PT$  point, the two phases will coexist. Away from the liquid-gas coexistence line in the  $PT$  plane, the lower of the two minima will correspond to the stable phase.
- h. Coming up from low pressure or down from high temperature, where the low-density minimum (gas phase) is globally stable, the high-density local minimum (liquid phase) gets deeper and deeper until its bottom eventually meets and descends below that of the low-density minimum, thereby becoming the stable phase. At the coexistence line, the chemical potentials of the two minima are equal, and the system makes its transformation from one phase to the other. Traversing the coexistence line involves a discontinuous change in molar enthalpy (the latent heat) at constant temperature and pressure, which either releases or consumes heat.

- i. Recall the Gibbs-Duhem relation:  $d\mu = -sdT + vdP$ . The change in chemical potential (molar Gibbs free energy) experienced while traversing the coexistence line along an isotherm ( $dT = 0$ ) is obtained via integration as  $\Delta\mu = \int v(P)dP$ , which can be interpreted as the area underneath the  $v(P)$  isotherm.
- j. In the region where  $v(P)$  is multivalued, pressure  $P$  first increases along the isotherm, eventually doubles back in the negative direction, and then finally increases again. Because  $d\mu/dP$  slope is positive,  $\Delta\mu$  also experience a double reversal along the isotherm. Over the course of the double reversal,  $\Delta\mu(P)$  traces out a counter-clockwise triangle, and thereby intersects itself. In the vicinity of this triangle, there are three values of  $\mu$  for a given value of  $P$ : one for the liquid-phase minimum, one for the gas-phase minimum, and an unstable value for the hump separating the two minima.
- k. Carefully compare the isotherms in K&T Figs. 9 and 10 as pressure increases. At any given pressure, the lowest value of  $\Delta\mu$  indicates the stable phase. Observe that  $\Delta\mu$  intersects itself where points D and O meet, marking the coexistence pressure. To the left of this mark (points A to D), the gas phase is stable. To the right of this mark (points O to S), the liquid phase is stable. K&T 9 illustrates the idea that two phases coexist where the integrated areas of the left dip (D-F-K) and right peak (K-M-O) are equal – the Maxwell construction.
- l. The F to M segments are strictly unstable, though some of them are metastable, meaning that they correspond to the local (but not global) free-energy minimum. The segment from D to F is the metastable region of supercooled or supersaturated gas, wherein the gas will readily condense to the more stable liquid phase if given a little energy overcome the barrier between the two minima. Similarly, the segment from M to O is the metastable region of superheated liquid, wherein the liquid will readily boil to the more stable gas phase if given a little energy to overcome the barrier. Supersaturation and superheating examples also include sodium acetate hand warmers, Mentos in Coca-Cola drinks, decompression sickness, cloud chambers, the explosion of distilled water in the microwave.
- m. Traversing the liquid-gas coexistence line involves a discontinuous change in molar volume as the system transitions from one free-energy minimum to another. Above the critical point, however, the two free-energy minima coalesce into a single minimum, thus terminating the coexistence line. Remarkably, by going around the critical point rather than over the coexistence line, it is possible to evolve a fluid from the liquid to the gas phase (or vice versa) without a volume (or density) discontinuity. Read about supercritical water reactors.

7) Critical phenomena (optional)

- a. When a phase transition occurs, it is always possible to quantify the change that occurs in terms of some *order parameter*. Group theory allows us to choose parameters that break the parent symmetry (the symmetry of the phase above the transition) in a certain way.
- b. At an arbitrary point along a critical line or plane, the order parameter makes a discontinuous jump (e.g. density at a liquid-gas transition). However, at a critical point (e.g. the Curie point of a ferromagnet), the free-energy potential well has a single very flat bottom, so that the order parameter starts at zero and evolves continuously as a positive fractional power of  $\Delta T = (T_{crit} - T)$  below the transition.
- c. Various 2<sup>nd</sup>-derivative quantities such as heat capacity and compressibility, diverge as power laws with negative exponents just above or below  $T_{crit}$ . The exponents of these power-laws are known as *critical exponents*.
- d. *Universality* describes the remarkable fact that the critical exponents of a particular phase transition depend only on the macroscopic dimensionality and the symmetry of a system, taking no account of the local interactions. Dramatically different physical systems can belong to the same universality class, and therefore exhibit identical critical behaviors near their critical points.

8) Several well-known types of phase transitions (among a virtually infinite variety)

- a. Liquid-gas (boiling, condensation)
- b. Liquid-solid (melting, freezing)
- c. Solid-gas (sublimation, deposition)
- d. Gas-plasma
- e. Magnetic phase diagrams (paramagnetic ferromagnetic, canted ferromagnetic, collinear anti-ferromagnetic, helical, cycloids, conic, etc).
- f. Displacive phase diagrams (paraelectric, ferroelectric, anti-ferroelectric, relaxor)
- g. Elastic (paraelastic, ferroelastic)
- h. Multiferroic (two or more simultaneous ferroic order parameters)
- i. Superconductivity and superfluidity
- j. Liquid-crystalline orders (nematic, smectic, chiral, conic, etc)
- k. Binary phase diagrams (liquidus-solidus, eutectic, etc)
- l. Solid-solid phase transitions are incredibly diverse
- m. Orderings on surfaces (surface reorderings, adsorbates, electrolyte double layers, etc)

## Lecture 16: Exam Review

## Lecture 17: Probability and mutiplicity

### 1) Introductory definitions and ideas

- a. **Random variables:** When we say that  $X$  is a *random variable*, we mean that it has a variety of possible values or outcomes, each with well-defined probability. If the symbol  $A$  represent one of the possible outcomes or values of random variable  $X$ . Then  $P(A)$  is the probability of that outcome. We can also think of  $A$  as a logical or Boolean quantity (True if outcome  $A$  of random variable  $X$  is realized or False if some other outcome is realized).
- b. **Independent probabilities:** In the following discussion, let  $A$ ,  $B$ , and  $C$  be specific outcomes three distinct and independent random variables  $X$ ,  $Y$ , and  $Z$ . Here, “independent” means that the outcome of one variable is completely uncorrelated to the outcomes of the others.
- c. **Logical operations:** The symbols  $\cap$  and  $\cup$  mean AND and OR, respectively, so that  $P(A \cap B)$  is the probability that both  $A$  and  $B$  occur, and  $P(A \cup B)$  is the probability that either  $A$  or  $B$  will occur. In boolean-logic theory, an overbar (e.g.  $\bar{A}$ ) means NOT or COMPLEMENT, so that  $P(\bar{A})$  refers to the probability that the outcome of  $X$  will be something other than  $A$ . The symbol  $\underline{\cup}$  means XOR (exclusive or), so that  $P(A \underline{\cup} B)$  indicates the probability exactly one of  $A$  and  $B$  will occur, or in other words, that either  $A$  or  $B$  but not both  $A$  and  $B$  will occur.
- d. **Frequency:** The probability of outcome  $A$  can be interpreted as the number of times that it occurs (i.e. the frequency of the outcome) in a statistical sample divided by the number of samples, or other words, as the fraction of samples that yield that outcome.
- e. Well-known probability relationships (based on Boolean algebra) for independent events.
  - i.  $P(\bar{A}) = 1 - P(A)$
  - ii.  $P(A \cap B) = P(A) P(B)$
  - iii.  $P(A \cup B) = P(A) + P(B) - P(A \cap B)$
  - iv.  $P(A \underline{\cup} B) = P(A \cup B) - P(A \cap B) = P(A) + P(B) - 2P(A \cap B)$
  - v.  $P(A \cap B \cap C) = P((A \cap B) \cap C) = P(A) P(B) P(C)$
  - vi.  $P(A \cup B \cup C) = P((A \cup B) \cup C) = P(A)P(B)P(C) - (P(A)P(B) + P(B)P(C) + P(C)P(A)) + (P(A) + P(B) + P(C))$
  - vii.  $P(\overline{A \cap B}) = P(\bar{A} \cup \bar{B}) = 1 - P(A)P(B)$
  - viii.  $P(\overline{A \cup B}) = P(\bar{A} \cap \bar{B}) = (1 - P(A))(1 - P(B))$
- f. The same relationships for cases where  $A$ ,  $B$ , and  $C$  all have the same probability  $p$ .
  - i.  $P(\bar{A}) = 1 - p$
  - ii.  $P(A \cap B) = p p = p^2$
  - iii.  $P(A \cup B) = p + p - p^2 = p(2 - p)$
  - iv.  $P(A \underline{\cup} B) = p + p - 2p^2 = 2p(1 - p)$
  - v.  $P(A \cap B \cap C) = p^3$
  - vi.  $P(A \cup B \cup C) = p^3 - 3p^2 + 3p$
  - vii.  $P(\overline{A \cap B}) = P(\bar{A} \cup \bar{B}) = 1 - p^2$
  - viii.  $P(\overline{A \cup B}) = P(\bar{A} \cap \bar{B}) = (1 - p)^2$
- g. Birthday example: Events  $A$  and  $B$  indicate that two unrelated students have January birthdays, respectively. Both events have the same probability  $P(A) = P(B) = p = 1/12$ .
  - i. Both students have January birthdays:  $P(A \cap B) = p^2 = 1/144$
  - ii. At least one student has birthday in January  $P(A \cup B) = p(2 - p) = 23/144$
  - iii. Exactly one student has a birthday in January:  $P(A \underline{\cup} B) = 2p(1 - p) = 22/144$



## 2) Conditional probabilities:

- a. **Joint probability:** The joint probability  $P(A|B) \equiv P(A \cap B)/P(B)$  is the probability of A given B, which is the probability that A is true among all instances where B is true.
- b. Using this definition, it is clear that  $P(A \cap B) = P(A|B) P(B) = P(B|A) P(A)$ .
- c. This yields **Bayes' theorem for conditional probabilities:**  $\frac{P(A|B)}{P(B|A)} = \frac{P(A)}{P(B)}$ .
- d. Independent events:  $P(A \cap B) = P(A) P(B)$ , so that  $P(A|B) = P(A)$  and  $P(B|A) = P(B)$ . Thus, *independent* means the probability of A is unaffected by assuming B and vice versa.
- e. Example 1: independent eye color and binary gender

- i. Two random variables: binary gender (male, female) and three eye colors (blue, green, and brown).
- ii. Assume them to be independent, so the probability of finding a male in the population of individuals with a given eye color is the same as the probability of finding a male in the overall population.

$$P(M) = 60/100 = 60\%; P(F) = 40/100 = 40\%$$

$$P(Bl) = 40/100 = 40\%; P(Gr) = 10/100 = 10\%; P(Br) = 50/100 = 50\%$$

- iii. Fill in rest of the grid assuming independence of gender and eye color. For example, multiply  $(60\%)(40\%)=24\%$  for the probability of a blue-eyed male.

	M	F	
Bl			40
Gr			10
Br			50
	60	40	

## f. Example 2: correlated eye color and binary gender

- i. Now suppose there are no green-eyed men in the population, though the number of brown-eyed men is the same as before. This leads to complicated conditional probabilities. Fill in the rest of the chart.
- ii. Observe that the fraction of blue-eyed people who are male is now different from the overall fraction of blue-eyed men:

$$P(M|Bl) = \frac{P(M \cap Bl)}{P(Bl)} = \frac{30}{40} = \frac{3}{4} \quad P(Bl|M) = \frac{P(M \cap Bl)}{P(M)} = \frac{30}{60} = \frac{1}{2}$$

	M	F	
Bl			40
Gr	0		10
Br	30		50
	60	40	

## g. Example 3: general correlations between eye color and binary gender

- i. Any conceivable correlations between gender and eye color in this example can be encoded by specific values of two parameters,  $x$  and  $y$ , in the middle grid below. Do not let any of the probabilities become negative, which would make it impossible to preserve the overall row and column sums.

	M	F	
Bl	$24+x+y$	$16-x-y$	40
Gr	$6-2x$	$4+2x$	10
Br	$30+x-y$	$20-x+y$	50
	60	40	

1. For variable independence, assume  $x = y = 0$ .
2. The example with no green-eyed men was constructed by setting  $x = y = 3$ . This altered the blue-eyed and green-eyed probabilities, but left the brown eye color independent of gender.
3. Setting  $x = 3$  and  $y = -3$  leaves the blue eye color independent of gender, while the green and brown eye colors becomes correlated to gender.

## h. Key to examples above

	M	F		M	F		M	F	
Bl	24	16	40	30	10	40	$24+x+y$	$16-x-y$	Bl
Gr	6	4	10	0	10	10	$6-2x$	$4+2x$	Gr
Br	30	20	50	30	20	50	$30+x-y$	$20-x+y$	Br
	60	40		60	40		60	40	

3) Binary diagnostic tests (e.g. cancer screening)

- a. No diagnostic test is perfect. There are a variety of quantitative measures that capture different types of diagnostic quality. Consider the following measures, each of which reach 100% for a perfect test with no false positives or negatives. As a radiologist reading mammograms, if your hospital administration says you will be fired if your tests miss even one true cancer case, what will likely happen to each of these measures? Would this change be good for patients? For the cancer-screening homework problem, consider which of these quality measures has the most surprising value.
  - i. Positive Predictive Value:  $P(\text{condition} + | \text{test} +) = \text{truepos}/(\text{truepos}+\text{falsepos})$
  - ii. Negative Predictive Value:  $P(\text{condition} - | \text{test} -) = \text{trueneg}/(\text{trueneg}+\text{falseneg})$
  - iii. Sensitivity:  $P(\text{test} + | \text{condition} +) = \text{truepos}/(\text{truepos}+\text{falseneg})$
  - iv. Specificity:  $P(\text{test} - | \text{condition} -) = \text{trueneg}/(\text{trueneg}+\text{falsepos})$
- b. See [https://en.wikipedia.org/wiki/Sensitivity\\_and\\_specificity](https://en.wikipedia.org/wiki/Sensitivity_and_specificity).

4) Monty Hall problem (host of the “Let’s Make a Deal” game show)

- a. There’s a new car behind one of three doors, and goats behind the other two doors. You initially select a door, which you don’t get to open yet. The host then opens a second door, one revealing a goat. You now have another decision to make. You can either keep your first selection, or change your selection to the remaining unopened door.
- b. Does either strategy improve your chances of winning? In fact, it’s always better to switch your selection. Doing so doubles your chances of winning.
- c. But how is that possible, when it seems obvious that there’s a 50/50 chance that one of the two remaining doors conceals a goat? Let  $W$  represent a win,  $G$  represent a good first guess, and  $B$  represent a bad first guess. The key to the puzzle is simple: a never-switch strategy wins whenever the initial selection is correct, which is  $P(G) = 1/3$  of the time, while an always-switch strategy wins whenever the initial selection is incorrect, which is  $P(B) = 2/3$  of the time! Subsequently opening a goat door doesn’t change these probabilities.
- d. Probability of a win is  $P(W) = P(W \cap G) + P(W \cap B) = P(W|G)P(G) + P(W|B)P(B) = \frac{1}{3}P(W|G) + \frac{2}{3}P(W|B)$ , where the conditional probabilities depend on strategy.  
 For never switch,  $P(W|G) = 1$  and  $P(W|B) = 0$ , so that  $P(W) = \frac{1}{3}(1) + \frac{2}{3}(0) = \frac{1}{3}$ .  
 For always switch,  $P(W|G) = 0$  and  $P(W|B) = 1$ , so that  $P(W) = \frac{1}{3}(0) + \frac{2}{3}(1) = \frac{2}{3}$ .
- e. Still seems weird? Consider that if the host were to open a door first, your chance of success would be  $\frac{1}{2}$  as expected. But when you guess first, it limits the host’s subsequent choice. That’s where the weirdness lies. The hosts selection provides new information – it shifts all of the probability that was originally associated with the goat door to the unselected doors.

## 5) Probability distributions

- a. Let  $X$  be a *random variable*. This means that if you sample (i.e. measure) it over and over again, the results will show some scatter.
- b. Let  $P(x)$  be a *probability distribution function (pdf)* associate with random variable  $X$ , so that  $P(x)dx$  yields the probability that the measured value of  $X$  will fall between  $x$  and  $x + \Delta x$ . In this sense,  $P(x)$  is also the *probability density* at  $x$ .
- c.  $P(x)$  is said to be *continuous or discrete* depending on whether the variable  $X$  can take on a continuum of values or a set of discrete values (e.g. integers).
- d. *The total probability that a sample of  $X$  will yield any possible outcome is 1.* For continuous distributions, we express this as  $\int P(x)dx = 1$ . For continuous distributions,  $\sum P(x_i) = 1$ . The range of the sum or integral is the full range of  $X$ .
- e. Quantities commonly used to describe a distribution include the following:
  - i. **Mean:**  $\mu \equiv \int x P(x)dx$  or  $\sum x_i P(x_i)$ . This measures the average value of  $X$  and will correspond loosely to the position of a single well-defined peak if one exists.
  - ii. **Variance:**  $V \equiv \int (x - \langle x \rangle)^2 P(x)dx$  or  $\sum (x_i - \langle x \rangle)^2 P(x_i)$ . This is the average squared deviation from the mean, which is a measure of how wide the distribution is.
  - iii. **Standard deviation:**  $\sigma \equiv \sqrt{V}$ . Measure of distribution width; has the same units as  $X$ .
  - iv. **Median:** The value of  $X$  for which half of the accumulated probability lies below it.
  - v. **Maximum:** The most probable value of  $X$  (i.e. the exact location of the highest peak).
  - vi. **Skewness:** A measure of the asymmetry of the peak (positive skew leans forward).
- f. *The mean value of any function  $f(x)$  is computed as  $\langle f \rangle = \frac{\int f(x)P(x)dx}{\int P(x)dx}$  or  $\frac{\sum f(x_i)P(x_i)}{\sum P(x_i)}$ .* If we assume a normalized probability distribution, the denominator is equal to 1. When all values of  $x$  are equally probable, this simplifies to the well-known formula  $\langle f \rangle = \frac{\int_a^b f(x)dx}{b-a}$ .

## 6) Continuous probability distributions [mostly for reference, don't memorize]

- a. **Normal (Gaussian) distribution:**  $P(x) = e^{-(x-\mu)^2/2\sigma^2} / \sqrt{2\pi\sigma^2}$ 
  - i. In an unspecified experiment, suppose that you measure a value of  $\mu \pm \sigma$ . What distribution is typically used to describe this uncertainty?
  - ii. Continuous with two parameters ( $\mu$  is peak position,  $\sigma$  is peak width)
  - iii. Mean:  $\mu = \mu$ , Variance:  $V = \sigma^2$
  - iv. Various distributions approximate a normal distribution in the limit of large  $\mu$ . Furthermore, the central limit theorem says that if we repeatedly take finite samples from any distribution, their estimated means exhibit a normal distribution. The uncertainties of normal distributions propagate in a very nice way.
  - v.  $\mu = \langle x \rangle = \int_{-\infty}^{\infty} x \frac{e^{-(x-\mu)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}} dx = \mu + \int_{-\infty}^{\infty} (x - \mu) \frac{e^{-(x-\mu)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}} dx + \mu = \mu$  as expected. Here, we employed the fact that the integrand is odd and therefore integrates to zero, and also the fact that  $\int P(x)dx = 1$ .
  - vi.  $V = \langle (x - \langle x \rangle)^2 \rangle = \int_{-\infty}^{\infty} (x - \mu)^2 \frac{e^{-(x-\mu)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}} dx = \int_{-\infty}^{\infty} \frac{s^2 e^{-s^2/2\sigma^2}}{\sqrt{2\pi}\sigma} ds = \frac{\sqrt{2\pi}\sigma^3}{\sqrt{2\pi}\sigma} = \sigma^2$
- b. **Exponential distribution:**  $P(x) = \frac{1}{\lambda} e^{-x/\lambda}$ 
  - i. Consider a sequence of random events (in space or time). What is the probability that two adjacent events will be separated by a distance  $x$ ? What is the probability that 2.134 minutes will separate the next two spontaneous claps?
  - ii. Continuous with one parameter, where  $\lambda$  (the decay constant of the distribution) is the mean event separation and  $1/\lambda$  is the event density.
  - iii. Mean:  $\mu = \lambda$ , Variance:  $V = \lambda^2$

## 7) Discrete probability distributions [mostly for reference, don't memorize]

- a. Poisson distribution:  $P(x) = e^{-\lambda} \frac{\lambda^x}{x!}$ 
  - i. What is the probability of counting  $x$  random events within a finite window of time or space. What is the probability that  $x = 10$  students will visit my office today when an average of  $\lambda = 8$  students usually visit in a day?
  - ii. Discrete with one parameter:  $\lambda$  is the average number of events per window.
  - iii. Mean:  $\mu = \lambda$ , Variance:  $V = \lambda$
  - iv. If we measure  $X = N$ , we assume that this is the mean and estimate that  $\sigma = \sqrt{N}$ , so that the relative uncertainty is  $\frac{\sigma}{\mu} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$ , which gets smaller with increasing  $N$ .
- b. Bernoulli distribution:  $P(x) = p^x(1-p)^{1-x} = \begin{cases} p & \text{for } x = 1 \\ 1-p & \text{for } x = 0 \end{cases}$ 
  - i. What is the probability of success if we flip a coin? Call a Heads (or 1) a success and a Tails (or 0) a failure. This distribution applies even for a biased  $p \neq 1/2$  coin.
  - ii. Discrete with one variable  $p$  and limited two-state range:  $x \in \{0, 1\}$ .
  - iii. Mean:  $\mu = p$ , Variance:  $V = p(1-p)$
  - iv.  $\mu = \langle x \rangle = \sum_0^1 x p^x(1-p)^{1-x} = 0 * p^0(1-p)^1 + 1 * p^1(1-p)^0 = p$
  - v.  $V = \langle (x - \langle x \rangle)^2 \rangle = \sum_0^1 (x-p)^2 p^x(1-p)^{1-x} = (-p)^2(1-p) + (1-p)^2p = p(1-p)$
  - vi. For a balanced coin, we have  $p = 1/2$  and  $P(0) = P(1) = 1/2$ .
  - vii. This distribution also applies to a balanced die with  $1/p$  sides, so that  $p$  is the probability of rolling a 1 (or some other specified value), and  $1-p$  is the probability of rolling any other value.
- c. Binomial distribution:  $P(x) = \binom{N}{x} p^x(1-p)^{N-x}$  for  $x \geq 0$ 
  - i. Given  $N$  Bernoulli trials, what is the probability of  $x$  successes. Equivalently, if we flip a collection of  $N$  possibly-unbalanced coins (probability of heads is  $p$  for a given coin), what is the chance of having exactly  $x$  coins land on heads?
  - ii. Discrete distribution with two variables:  $N$  is the number of trials, and  $p$  is the single-trial probability of success.
  - iii. Mean:  $\mu = Np$ , Variance:  $V = Np(1-p)$
  - iv. For a balanced coin, we have  $p = \frac{1}{2}$  and  $P(x) = \frac{1}{2^N} \binom{N}{x}$ . Remember this!
  - v. This distribution also applies to a collection of  $N$  balanced dice with  $1/p$  sides each, so that  $P(x)$  is the probability of having exactly  $x$  of the dice land with a given value.
- d. Negative Binomial:  $P(x) = \binom{x-1}{s-1} p^s(1-p)^{x-s}$  for  $x \geq s$ 
  - i. If we want  $s$  successful Bernoulli trials, what is the probability that it will take  $x$  trials in order to obtain them? If we repeatedly flip a coin until we get  $s = 3$  heads, what is the probability that it will take  $x = 5$  flips to get them? (12/32).
  - ii. Discrete distribution with two variables:  $s$  is the # of successes,  $x$  is the # of trials.
  - iii. Mean:  $\mu = \frac{s}{p}$ , Variance:  $V = \frac{s(1-p)}{p^2}$
  - iv. For a balanced coin ( $p = 1/2$ ),  $p(x) = \frac{1}{2^x} \binom{x-1}{s-1}$
- e. Geometric distribution:  $P(x) = p(1-p)^{1-x}$ 
  - i. What is the probability that the separation between adjacent random discrete events will be  $x$ . What is the probability that there will be exactly two empty seats between neighboring students on any given row in the room?
  - ii. Discrete version of the exponential distribution – one parameter, where  $p$  is the event density and  $1/p$  is the average event separation.
  - iii. Mean  $\mu = 1/p$ , Variance  $V = (1-p)/p^2$

## Lecture 18: Counting problems, microstates, and macrostates

### 1) Permutations and combinations, ordered and unordered sets

- a. Ordered arrangements of  $n$  objects:  $n! = n(n-1)(n-2) \dots 3 \cdot 2 \cdot 1$ 
  - i. How many ways can we arrange 3 distinctly colored marbles? We have 3 choices for the first one, 2 choices for the second one, and 1 choice for the third one. So the number of arrangements is  $3! = 3 \cdot 2 \cdot 1 = 6$ .
  - ii. How many permutations of the integers (1,2,3,4) are there?  $4! = 4 \cdot 3 \cdot 2 \cdot 1 = 24$ .
- b. Ordered  $k$  subsets of  $n$  objects:  $\frac{n!}{(n-k)!} = n(n-1) \dots (n-k+1)$ 
  - i. How many ways are there to form a quorum presidency (president and 1<sup>st</sup> and 2<sup>nd</sup> counselors) from among 6 individuals? We have 6 choices for the president, 5 choices for 1<sup>st</sup> counselor and 4 choices for 2<sup>nd</sup> counselor.  $\frac{6!}{(6-3)!} = 6 \cdot 5 \cdot 4 = 120$ .
- c. Unordered  $k$  subsets of  $n$  objects:  $\binom{n}{k} = \frac{n!}{k!(n-k)!}$ 
  - i. How many unordered ways are there to pick 2 marbles from a bag of 6? If we cared about the order of selection, there would be  $\frac{6!}{(6-2)!} = 30$  ways. But since we don't, the permutations of each pair are equivalent, and we need to further divide by  $2! = 2$ . As a result, there are  $\binom{6}{2} = \frac{6!}{4!2!} = \frac{(6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1)}{(4 \cdot 3 \cdot 2 \cdot 1)(2 \cdot 1)} = \frac{6 \cdot 5}{2 \cdot 1} = 15$  ways.
  - ii. Among 3 single men and 3 single women, how many unordered double dates can be set up? There are  $m = \binom{3}{2}$  unordered ways to choose two men and  $w = \binom{3}{2}$  unordered ways to choose two women. For a pair of men and a pair of women, there are  $p = 2!$  possible matchups. Total number is  $m \cdot w \cdot p = \binom{3}{2} \binom{3}{2} (2!) = 18$ .

### 2) Microstates of a system comprised of multiple random variables

- a. When a system is comprised of multiple random variables, a specific outcome for each variable combine to form a single *microstate*. The set of all possible microstates can be constructed by systematically forming all possible combinations of the outcomes of each of the random variables, where the value of each variable spans its full range.
- b. If a family has  $N = 3$  children, each of which is either a boy (B) or a girl (G), the biological gender of each child is an independent random variable with  $t = 2$  possible outcomes. The possible microstates are GGG, GGB, GBG, GBB, BGG, BGB, BBG, BBB.
- c. The number  $\Omega$  of microstates of a system is referred to as its *multiplicity*.
- d. The microstate multiplicity (number of microstates) of a system consisting of  $N$  independent variables is the product of their individual multiplicities:  $\Omega_{\text{tot}} = \Omega_1 \Omega_2 \dots \Omega_N$ . So if, for example, we have  $N$  independent and nominally identical random variables, each of which has  $\Omega_i = t$  possible outcomes, there will be a total of  $\Omega_{\text{tot}} = t^N$  joint microstates.
- e. For a microstate constructed from multiple independent random variables, the individual-outcome probabilities multiply to yield the joint probability of the microstate, just as the individual-variable multiplicities multiply to yield the joint multiplicity of the system!

### 3) Macrostates

- a. A *macrostate* is a collection of microstates that all share a macroscopic property. The multiplicity of a macrostate is the number of microstates in its collection.
- b. The macroscopic property that defines a macrostate is a function of the microscopic random variables of a system. Such a function is also a random variable with many possible values.
- c. In families with multiple children, associate biological gender with random variable  $x$ , where  $x = 1$  indicates a girl and  $x = 0$  indicates a boy. One macroscopic property of interest is the total number of girls  $g = \sum x_i$ . For the case of three children, there are four possible girl-

- number macrostates: 0, 1, 2, and 3. The total system multiplicity is  $2^3 = 8$ , as listed in the previous section. The  $g = 0$  macrostate contains only the BBB microstate and therefore has a multiplicity of 1. Similarly, the  $g = 3$  macrostate contains only the GGG microstate and so multiplicity 1. The  $g = 1$  (GBB, BGB, BBG) and  $g = 2$  (BGG, GBG, GGB) macrostates each contain three microstates and so have multiplicity 3.
- d. The probability of a specific macrostate is the sum of the probabilities of its microstates! When microstates are equally probable, the probability of observing a given macrostate is equal to the fraction of all possible microstates in the macrostate:  $P_m = \Omega_m / \Omega_{tot}$ .
- e. In the three-child family above, each microstate has probability  $1/\Omega_{tot} = 1/8$ , so that the girl-number macrostate probabilities are  $P(0) = P(3) = 1/8$  and  $P(1) = P(2) = 3/8$ .

4) Flipping  $N$  distinguishable coins

- Equally probable microstates represented by strings of heads (H) and tails (T).
- Given  $N$  flips of a balanced coin, the probability of the macrostate with  $n$  successes (heads flips) will be a binomial distribution  $P(n) = \frac{1}{2^N} \binom{N}{n}$ .
- For 4 coin flips, there are  $2^4 = 16$  microstates:
 

TTTT	THTT	HTTT	HHTT
TTTH	THTH	HTTH	HHTH
TTHT	THHT	HTHT	HHHT
TTHH	TTHH	HTHH	HHHH
- Let the total number of heads ( $n_H$ ) define the macrostate. The macrostates are then  $n_H \in \{0, 1, 2, 3, 4\}$ , which have respective degeneracies of  $\{1, 4, 6, 4, 1\}$  and respective probabilities of  $\{\frac{1}{16}, \frac{4}{16}, \frac{6}{16}, \frac{4}{16}, \frac{1}{16}\}$ . The most probable macrostate is  $n_H = 2$ .

## Lecture 19: The most probable macrostate, statistical entropy and the thermodynamic fundamental relation, microstate ensembles, multi-parameter macrostates

### 1) Stirling's theorem:

- In statistical mechanics, we frequently need to compute  $\ln(N!)$ , which can be nicely approximated by the simple analytical expression  $\ln(N!) \approx N \ln(N) - N$ . This is often called the **Sterling approximation or Sterling's theorem**.
- G&W Fig 1.1 motivates the approximation in terms of the area under the curve  $y = \ln(x)$ , which is  $A(N) = \int_1^N \ln(x) dx = N \ln(N) - N + 1$ .
- This area is also roughly the average of the stair-case functions above and below the curve, so that  $A(N) \approx \frac{1}{2} \{ \sum_2^N \ln(n) + \sum_2^{N-1} \ln(n) \} = \frac{1}{2} \{ \ln(N!) + \ln((N-1)!) \} = \ln((N!)^2 / N) = \ln(N!) - \frac{1}{2} \ln(N)$ .
- Equate these expressions to obtain  $\ln(N!) \approx N \ln(N) - N + \frac{1}{2} \ln(N) + 1$ .
- For large values of  $N$ , only the largest terms matter, so that  $\ln(N!) \approx N \ln(N) - N$ .

### 2) The most probable macrostate

- Consider the probability of obtaining  $x$  successes  $N$  flips of an unbiased coin ( $p = 1/2$ ), which is governed by the binomial probability distribution:  

$$P(n) = \binom{N}{x} p^x (1-p)^{N-x} \rightarrow \binom{N}{x} \left(\frac{1}{2}\right)^x \left(\frac{1}{2}\right)^{N-x} = \frac{1}{2^N} \frac{N!}{x!(N-x)!}$$
- Plan to reproduce G&W Fig 1.2 in the HW.
- To determine the most probable number of successes, observe that  $P(x)$  and  $\ln[P(x)]$  will both peak (have zero slope) at the same place. Treat  $x$  as the variable and  $N$  as a constant.
- $\ln[P(x)] = \ln \left[ \frac{1}{2^N} \frac{N!}{x!(N-x)!} \right] \approx \text{const} - [x \ln(x) - x] - [(N-x) \ln(N-x) - (N-x)]$
- $d \ln[P(x)] = -[\ln(x) + 1 - 1] - [-\ln(N-x) - 1 + 1] = \ln(N-x) - \ln(x) = 0$
- $N - x = x \rightarrow x = N/2$  is the most probable macrostate.
- The FWHM (call it  $\Delta$ ) of this peak is of order  $N^{1/2}$ . Take the natural log of both sides of  $P\left(\frac{N}{2} + \frac{\Delta}{2}\right) = \frac{1}{2} P\left(\frac{N}{2}\right)$  and assume that  $\Delta/N$  is small in order to prove that  $\Delta \propto N^{1/2}$ .
- The relative width is then  $\frac{\Delta}{N} \propto N^{-1/2}$ , so that the peak gets exceedingly sharp as  $N$  grows to a scale comparable to Avagadro's number.

### 3) Statistical entropy

- For the sake of notational convenience, we'll often refer to the probability of the  $s^{\text{th}}$  microstate as  $P_s$  rather than  $P(s)$ . The meaning is the same either way.
- We define **statistical entropy** as  $S/k_B = -\sum P_s \ln(P_s)$ , where the sum is over microstates of the system or some macrostate of the system. This "Shannon entropy" arises from information theory. You might want to browse the Wikipedia pages on "information theory" and "Claude E. Shannon".
- The average value of any function  $f_s$  over the microstates of a system can be calculated as  $\langle f \rangle = \sum P_s f_s$ . The quantity  $\ln(1/P_s)$  is called the *information content* or *surprisal* of the  $s^{\text{th}}$  microstate. Rare (improbable) microstates are more informative or suprising than common ones and so have a higher information content; they carry more weight. The statistical entropy can be expressed as  $S/k_B = -\sum P_s \ln(P_s) = \sum P_s \ln(1/P_s) = \langle \ln(1/P) \rangle$ , which is the average amount of information required to describe an arbitrary microstate of the system.



- d. The famous Boltzmann entropy function,  $S = k_B \ln(\Omega)$ , applies to the situation where all microstates of the system are equally probable, so that  $P_s = 1/\Omega$ , wherein the entropy summation is simply  $S/k_B = -\sum P_s \ln(P_s) = -\sum_1^\Omega \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = -\frac{\Omega}{\Omega} \ln\left(\frac{1}{\Omega}\right) = \ln(\Omega)$ . See that the concept of statistical entropy is not identical to that of multiplicity (also called degeneracy), but is clearly a measure of multiplicity.
- e. Think of a numerical digit as a quantum of information. Consider a system of 7 people, each of whom has 365 birthday options, so that  $\Omega = 365^7 \approx 8.63 \times 10^{17}$  is the system multiplicity. If it were common to express the statistical entropy in terms of decimal (base 10) numbers, we could write  $S_{(\text{base } 10)}/k_B = \log_{10}(8.63 \times 10^{17}) \approx 17.94$ , implying that one needs almost 18 decimal digits of information to communicate an arbitrary set of seven distinct birthdays. In base 365, we need  $S_{(\text{base } 365)}/k_B = \log_{365}(365^7) = 7$  digits for the same purpose. In base 2, it would  $S_{(\text{base } 2)}/k_B = \log_2(8.63 \times 10^{17}) \approx 59.58$  binary digits, which is a string of almost 60 zeros and ones. Which of these is the real statistical entropy? In practice, we use the less familiar but more natural base  $e \approx 2.71828$ , wherein the statistical entropy of this system is quantified as  $S/k_B = \ln(8.63 \times 10^{17}) \approx 41.30$ .
- f. By equating this statistical entropy with the thermodynamic entropy, we obtain a fundamental relation (FR) for the system. This equivalence is the “deep magic” of statistical mechanics.
- g. The statistical entropy has all of the properties we required of the thermodynamic entropy. For example, when we combine two isolated (and hence constant-energy) systems with microstate multiplicities of  $\Omega_1$  and  $\Omega_2$ , respectively, the resulting multiplicity is  $\Omega_1 \Omega_2$ , and the resulting entropy is  $S = k \ln(\Omega_1 \Omega_2) = k \ln(\Omega_1) + k \ln(\Omega_2) = S_1 + S_2$ . Thus, statistical entropy is additive and therefore homogeneous in the extensive system variables. It will also prove to be continuous, differentiable, and monotonically increasing with respect to each extensive system variable.
- h. Most importantly, the equilibrium macrostate is the most probable one, which also has the greatest microstate multiplicity, and hence the greatest information content and entropy. When dealing with a system possessing a macroscopic number of microscopic variables, the most probable macrostate is vastly more probable than most other macrostates, so that the chances of observing the system in macrostates far from equilibrium becomes negligible. This is the statistical origin of the 2<sup>nd</sup> law of thermodynamics!
- i. The 2<sup>nd</sup> law of thermodynamics is not a fundamental physical law, but is rather a very strong statement about the statistics of large systems. Through it, classical thermodynamics can be reduced to the study of the most probable macrostate.

#### 4) Microstate ensembles

- a. Statistical mechanics provides a method for deriving the fundamental relation (FR) of a thermodynamic system based on the probabilities its microstates.
- b. The FR of a system and its natural variables depend on which reservoirs a system is in contact with. Similarly, the physically-accessible microstates and their probabilities depend on which reservoirs are employed. The collection of physically-accessible microstates and their probabilities is referred to as a thermodynamic *ensemble*.
  - i. The *microcanonical* ensemble assumes an isolated system. The calculation yields the fixed internal energy  $U(S, V, N)$ . All microstates are equally probable:  $P_s = 1/\Omega$ .
  - ii. The *canonical* ensemble assumes a closed system and contact with a temperature reservoir. The calculation yields the Helmholtz free energy  $F(T, V, N)$ . The



microstates have non-uniform probabilities  $P_s \propto e^{-E_s/k_B T}$ , which depend on energy. Internal energy is a statistical rather than fixed variable:  $U = \langle E \rangle = \sum E_s P_s$ , so that it can *fluctuate* over time as the system explores different microstates of the fixed-temperature macrostate.

- iii. The *grand canonical* ensemble assumes contact with both temperature and chemical reservoirs. Calculations yield  $L(T, V, \mu)$ . The microstates have non-uniform probabilities  $P_s \propto e^{-(E_s - \mu N_s)/k_B T}$ , which depend on energy and chemical potential.
- iv. One can similarly define ensembles for each of the other thermodynamic potentials.
- c. The details of a stat-mech calculation depend strongly on which ensemble we are using. Many of the most beloved equations of stat mech are specific to one type of ensemble.
- d. The choice of ensemble is purely a matter of convenience. When calculating the FR of a given system, however, one ensemble may be vastly more convenient than another.
- e. Once the FR has been determined using any ensemble, we can apply Legendre transforms to obtain other thermodynamic potentials appropriate to other types of reservoir contact.

#### 5) Multi-parameter macrostates (leads towards the next topic)

- a. Consider a set of  $N$  dice with  $t$  equally probable faces, numbered from 0 to  $t - 1$ . The microstate that results from rolling them all, will be a string of  $N$  integers  $\{q_1, q_2, \dots, q_N\}$  between 0 and  $t - 1$ . There are  $t^N$  possible microstates.
- b. Define  $n_i$  as the number of dice with the  $i^{\text{th}}$  face up so that for any microstate,  $\sum n_i = N$ . An important type of macrostate definition involves specifying the value of each of the  $n_i$ . The resulting collection of integers  $m = \{n_0, n_1, \dots, n_{t-1}\}$  constitutes a multi-parameter macrostate. One can often use a function with a single parameter to specify the values of every integer in the collection, which is vastly simpler than specifying a microstate.
- c. The multiplicity of macrostate  $m = \{n_0, n_1, \dots, n_{t-1}\}$  is the product of the number of ways to choose the locations of  $n_0$  dice among  $N$  slots, the number of ways to choose the locations of the  $n_1$  dice amongst the remaining  $N - n_0$  slots, and so on until the number of ways to choose the locations of the  $n_{t-1}$  dice among the remaining  $N - \sum_{i=0}^{t-2} n_i$  slots. It's very easy to show that this product simplifies to the following form:

$$\Omega_m = \binom{N}{n_0} \binom{N - n_0}{n_1} \binom{N - n_0 - n_1}{n_2} \dots \binom{N - n_0 - \dots - n_{t-2}}{n_{t-1}} = \frac{N!}{\prod n_i!}$$

Recall that microstates involving many “equivalent but independent random variables” multiply just like independent probabilities!

- d. Example of two three-sided dice ( $N = 2, t = 3$ ): Macrostate  $m = \{n_0, n_1, n_2\}$  can be 110, 101, 011, 002, 020, 200. This is a complete list of the three-digit partitions of the number 2. The first three macrostates have  $\Omega_m = \frac{2!}{1!1!0!} = 2$  microstates each while the last three have  $\Omega_m = \frac{2!}{2!0!0!} = 1$  each. The total number of microstates is  $\Omega = \sum_m \Omega_m = 3 * 2 + 3 * 1 = 9$  which is  $t^N = 3^2$  as expected.

## Lecture 20: The 1D Einstein solid – a microcanonical analysis

- 1) In the context of statistical mechanics, we are **changing notation** so that  $N$  now refers to the number of particles rather than the number of moles in a system. Try not to get confused over this change.
- 2) Describing an Einstein solid
  - a. We're ready to do our first serious statistical-mechanical calculation of a fundamental relation. Our target is the Einstein solid, which is simpler than a real solid due to three assumptions. (1) In a real solid, neighboring atoms exert forces on one another and thereby *interact*, which causes their motions to become *correlated*. Random variable correlations complicate statistics. The forces exerted by its neighbors create a potential well around an atom, in which it can oscillate. In an Einstein solid, **we assume/pretend that each potential well is independent of the others in order to avoid correlated motion**; this approximation is useful, but not good for everything. (2) In an Einstein solid, we assume **the potential well experienced by each atom is harmonic (quadratic), so its quantum-mechanical energy levels are equally spaced**, which is often but not always a good approximation. (3) In an Einstein solid, **we assume every atom has an identical potential well**, so there is only one type of atomic site, which is true only for the simplest of real crystals.
  - b. **As for any solid, the atoms of an Einstein solid are identifiable or distinguishable by their individual locations.** However, because the atoms of an Einstein solid don't push against or otherwise interact with each other with each other, it doesn't really matter exactly how they are arranged in space. **For this reason, the concepts of pressure  $P$  and volume  $V$  play no role in the thermodynamics of an Einstein solid.**
  - c. Each atom is an independent harmonic oscillator; **the  $a^{\text{th}}$  atom has energy  $E_a = \left(Q_a + \frac{1}{2}\right)\Delta\epsilon$ , where index  $a$  runs over all  $N$  atoms,  $Q_a$  is the number of energy quanta stored on a given atom, and  $\Delta\epsilon$  is the energy-level spacing (i.e. the size of each energy quantum, G&W simply call it  $\epsilon$ ). The factor of  $\frac{1}{2}$  represents the quantum-mechanical zero-point energy of a harmonic oscillator. **A system microstate is defined by the energies  $E_a$  (or quanta counts  $Q_a$ ) of each of the atoms in the solid.** Important extensive variables include the number of atoms,  $N$ , the number of energy quanta,  $Q = \sum Q_a$ , and the internal energy,  $U = \sum E_a = \sum \left(\frac{1}{2} + Q_a\right)\Delta\epsilon$ , which are all related as  **$U = \left(\frac{N}{2} + Q\right)\Delta\epsilon$ .****
  - d. The probability of a macrostate is determined by the ratio of its multiplicity over the total number of microstates of the system. It is important to appreciate that **a physical constraint on the system can limit the number of microstates that are physically accessible, and hence belong in the denominator** of such a probability:  $P_{\text{macrostate}} = \frac{\Omega_{\text{macrostate}}}{\Omega_{\text{accessible}}}$ . For example, if we constrain the total internal energy  $U$ , which also fixes  $Q$ , only the finite set of microstates with the requisite total number of quanta  $Q$  are physically accessible.
  - e. In contrast to an atom-based indexing, it is also useful to index by energy level. We define  **$\epsilon_i = \left(\frac{1}{2} + i\right)\Delta\epsilon$  as the energy stored in the  $i^{\text{th}}$  energy level**, summed over all atoms, where index  $i$  runs from 0 to  $Q$  over each of the  $Q + 1$  sequential energy levels. We don't need more levels than this because no atom can store more than the total number of quanta. **We can also define  $n_i$  to be the number of atoms in energy level  $\epsilon_i$ , such that  $\sum_{i=0}^Q n_i = N$  is the total number of atoms.** Do not confuse the  $a$  and  $i$  indices!

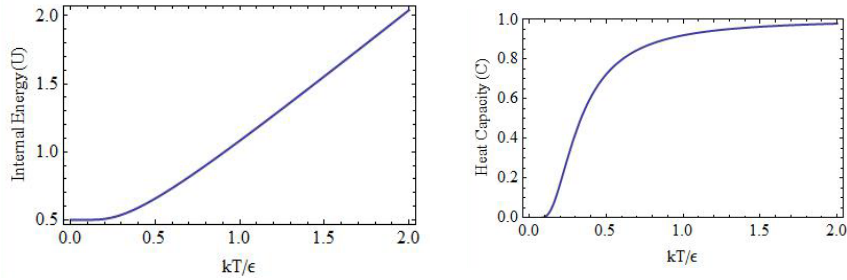
- f. The multi-parameter macrostates of an Einstein solid can be defined by the numbers of atoms  $\{n_0, n_1, \dots, n_i, \dots, n_Q\}$  occupying each of the available energy levels. Remarkably, this scenario turns out to be perfectly analogous to rolling  $N$  dice with  $Q + 1$  sides each, while requiring the sum of their values to be  $\sum_{i=0}^Q i n_i = Q$ .
- g. Because  $n_i/N$  is the fraction of atoms in the  $i^{\text{th}}$  energy level, a multi-parameter macrostate of the form  $\{n_0, n_1, \dots, n_i, \dots, n_Q\}$  is an energy partition or distribution. Consider an example: if we have  $N = 5$  atoms and  $Q = 3$  energy quanta, possible partitions of the energy into energy levels are  $\{n_0, n_1, n_2, n_3\} = \{4, 0, 0, 1\}$ ,  $\{3, 1, 1, 0\}$ , and  $\{2, 3, 0, 0\}$ .
- h. For a given value of  $Q$  (based on the fixed-energy constraint), we'll use the symbol  $m(Q)$  to index the compatible multi-parameter macrostates. With the analogy to dice rolls in mind, the microstate multiplicity must be  $\Omega_{m(Q)} = \left( \frac{N!}{\prod n_i!} \right)_{m(Q)}$ , where the  $m(Q)$  subscript implies that  $\sum_{i=0}^Q i n_i = Q$ . The total number of physically-accessible microstates can then be expressed as  $\Omega_{\text{access}} = \sum_{m(Q)} \Omega_{m(Q)} = \sum_{m(Q)} \left( \frac{N!}{\prod n_i!} \right)_{m(Q)}$ . For the example above, this would be  $\frac{5!}{4!0!0!1!} + \frac{5!}{3!1!1!0!} + \frac{5!}{2!3!0!0!} = 5 + 20 + 10 = 35$ .
- i. Alternatively, we can recognize this scenario as equivalent to the general problem of partitioning  $Q$  indistinguishable objects into  $N$  distinguishable bins, some of which may remain empty. This number is well known to be  $\Omega_{\text{access}} = \binom{Q + N - 1}{Q} = \frac{(Q + N - 1)!}{Q! (N - 1)!}$ . For the example above, this is  $\frac{(3 + 5 - 1)!}{3! (5 - 1)!} = \frac{7!}{3! 4!} = 35$ , as expected. Impressive correspondence!
- j. A more practical analogy might help. At the grocery checkout counter, imagine partitioning the conveyor belt up into  $N = 3$  bins by laying  $N - 1 = 2$  foot-long hot dogs across the belt. If you have  $Q = 3$  tomatoes, the unique tomato-hotdog arrangements include:  
 $\{\{T, T, T, H, H\}, \{T, T, H, T, H\}, \{T, T, H, H, T\}, \{T, H, T, T, H\}, \{T, H, T, H, T\},$   
 $\{T, H, H, T, T\}, \{H, T, T, T, H\}, \{H, T, T, H, T\}, \{H, T, H, T, T\}, \{H, H, T, T, T\}\}$   
 This is also the number of ways to obtain  $Q = 3$  tails from  $Q + N - 1 = 3 + 2 = 5$  flips of a coin:  $\binom{Q + N - 1}{Q} = \binom{5}{3} = 10$ .
- k. We started with distributing energy quanta amongst atoms, recast the problem as partitioning indistinguishable objects into distinguishable bins, morphed it into rolling dice, and then reinterpreted it again as flipping coins. There's real power in being able to view the same problem from multiple perspectives.

### 3) Entropy, internal energy, and heat capacity of a 1D Einstein solid

- a. Define the average number of quanta per atom as  $q = Q/N$ , and the average internal energy per atom as  $u = U/N$ , which is equal to  $\left(q + \frac{1}{2}\right) \Delta\epsilon$ . Or equivalently,  $Q = \frac{U}{\Delta\epsilon} - \frac{N}{2}$ . Also remember that volume has no influence in an Einstein solid.
- b. Assume an isolated system, so that the total internal energy  $U$  is fixed, and we work in the microcanonical ensemble, where every microstate has equal probability  $1/\Omega_{\text{access}}$ .
- c. Hang on tight. Here we go. The fundamental relation  $S(U, N)$  or  $S(u, N)$  is
- $$\frac{S}{k_B} = \ln(\Omega_{\text{access}}) = \ln \left[ \frac{(Q + N - 1)!}{Q! (N - 1)!} \right] \approx \ln \left[ \frac{(Q + N)!}{Q! N!} \right]$$
- $$\approx (Q + N) \ln(Q + N) - (Q + N) - Q \ln(Q) + Q - N \ln(N) + N$$

$$\begin{aligned}
 &= (Q + N) \ln(Q + N) - Q \ln(Q) - N \ln(N) \\
 &= N(q + 1) \ln(N(q + 1)) - Nq \ln(Nq) - N \ln(N) \\
 &= N(q + 1) \ln(q + 1) - Nq \ln(q) \\
 &= S(u, N)/k_B = N \left\{ \left( \frac{u}{\Delta\epsilon} + \frac{1}{2} \right) \ln \left( \frac{u}{\Delta\epsilon} + \frac{1}{2} \right) - \left( \frac{u}{\Delta\epsilon} - \frac{1}{2} \right) \ln \left( \frac{u}{\Delta\epsilon} - \frac{1}{2} \right) \right\}
 \end{aligned}$$

- d. Temperature is computed as  $\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_N = \frac{k_B}{\Delta\epsilon} \ln \left( \frac{\frac{u}{\Delta\epsilon} + \frac{1}{2}}{\frac{u}{\Delta\epsilon} - \frac{1}{2}} \right) = \frac{k_B}{\Delta\epsilon} \ln \left( \frac{2u + \Delta\epsilon}{2u - \Delta\epsilon} \right)$ .
- e. Internal energy: algebraically invert this expression to obtain  $U(T, N) = \frac{N}{2} \Delta\epsilon \coth \left( \frac{\Delta\epsilon}{2k_B T} \right)$ .
- f. Heat capacity is  $C(T, N) = \left( \frac{\partial U}{\partial T} \right)_N = Nk_B \left( \frac{\Delta\epsilon}{2k_B T} \right)^2 \text{csch}^2 \left( \frac{\Delta\epsilon}{2k_B T} \right)$ .
- g. By counting hot dogs and tomatoes, we bridged statistical mechanics and thermodynamics!



#### 4) Limiting cases of the 1D Einstein solid

- a. The low-temperature limit ( $T \rightarrow 0$ ) of the internal energy includes only quantum zero-point energy, so that  $\frac{u}{\Delta\epsilon} = \frac{1}{2}$ ,  $U = \frac{1}{2} N \Delta\epsilon$ ,  $C = 0$ ,  $Q = 0$  and  $S = 0$ . Einstein developed this model to improve the less accurate Dulong-Petit heat capacity, which doesn't go to zero at  $T = 0$ .
- b. In the high-temperature limit ( $kT \gg \Delta\epsilon$ ), define small parameter  $z = \Delta\epsilon/k_B T$  and expand the energy to lowest order in  $z$ , which yields  $U = Nk_B T$  and  $C = Nk_B$ . In this limit,  $Q \gg N$ , and zero point energy is unimportant, so that temperature becomes a measure of how many quanta  $q$  we have per oscillator:  $U = Nk_B T = \left( \frac{N}{2} + Q \right) \Delta\epsilon \approx Q \Delta\epsilon$  and  $u = k_B T \approx q \Delta\epsilon$ . The entropy then becomes  $\frac{S}{k_B} \approx N \left( 1 + \ln \left( \frac{u}{\Delta\epsilon} \right) \right) = N(1 + \ln(q))$ .

#### 5) 3D Einstein solid

- a. The dimension of a 3D Einstein-solid doesn't refer to the spatial arrangement of the atoms, but rather assumes that each atom is a 3D harmonic potential well that can oscillate in all three directions. This effectively gives us three oscillators per atom instead of one.
- b.  $U = \left( \frac{3}{2} N + Q \right) \Delta\epsilon$  and  $q = \frac{Q}{N} = \frac{u}{\Delta\epsilon} - \frac{3}{2}$  and  $q + 3 = \frac{u}{\Delta\epsilon} + \frac{3}{2}$
- c.  $\frac{S}{k_B} = \ln \left[ \frac{(Q+3N-1)!}{Q! (3N-1)!} \right] = N \left\{ \left( \frac{u}{\Delta\epsilon} + \frac{3}{2} \right) \ln \left( \frac{u}{\Delta\epsilon} + \frac{3}{2} \right) - \left( \frac{u}{\Delta\epsilon} - \frac{3}{2} \right) \ln \left( \frac{u}{\Delta\epsilon} - \frac{3}{2} \right) \right\} \rightarrow 3N \left( 1 + \ln \left( \frac{u}{\Delta\epsilon} \right) \right)$  at high temperature.
- d.  $\frac{1}{T} = \frac{k_B}{\Delta\epsilon} \ln \left( \left( \frac{u}{\Delta\epsilon} + \frac{3}{2} \right) / \left( \frac{u}{\Delta\epsilon} - \frac{3}{2} \right) \right)$
- e.  $U_{3D} = 3U_{1D}$  and  $C_{3D} = 3C_{1D}$

## Lecture 21: Boltzmann statistics, statistical temperature, and the canonical ensemble

### 1) Boltzmann statistics

- a. Consider an  $N$ -atom 1D Einstein solid. Place one quantum of energy on each atom, so that  $Q = N = 10^4$ . This is the initial model.
- b. To simulate the effect of being in contact with a temperature reservoir, the model is evolved in a series of random moves, where a move consists of selecting two atoms at random and moving one quantum from the first atom to the second atom if the first bin has at least one quantum. The number of move attempts will be referred to as  $Y$ .
- c. In the evolved model, the occupancies ( $n_i$ ) of each of the energy levels ( $\epsilon_i$ ) comprise the energy distribution. As the number of moves (the extent of thermalization) increases, the limiting form of the energy distribution is an exponential decay of the form curve  $n_i \propto e^{-\beta \epsilon_i}$ . This limit is called the *Boltzmann macrostate*. Why does an exponential distribution emerge from shifting energy around in a purely random fashion? Because this distribution of energy is far more probable than any other, as we'll demonstrate via both derivation and simulation. Once the Boltzmann macrostate is realized, the probability of evolving substantially away from it again is very small.
- d. In the homework, you assume  $N = 10^4$  atoms, and run simulations for each of  $Y = 10^2, 10^3, 10^4$  and  $10^5$  move attempts. For visual convenience, let the atoms be arranged on a two-dimensional  $\sqrt{N} \times \sqrt{N}$  grid. For each case, make an array plot of the evolved model and a list plot of the resulting energy distribution. You should find that the Boltzmann macrostate is achieved when  $Y \gtrsim 10 N$ .
- e. G&W compute the differential macrostate multiplicity  $d \ln(\Omega_m) = d \ln \left( \frac{N!}{\prod n_i!} \right) = 0$  in terms of all of the  $dn_i$ , in order to show that if we simultaneously maximize  $\Omega_m$  with respect to each of the  $n_i$ , we obtain a distribution of the form  $n_i = A e^{-\beta \epsilon_i}$ . This formalizes what we saw with our own eyes. They used the coefficient  $\beta$  to define a *statistical temperature*  $k_B T = 1/\beta$ . Statistical temperature is meaningful in the information-theoretic sense, even in situations like our simulation, where nothing is actually moving. For large systems, this statistical quantity turns out to be our thermodynamic temperature.
- f. If  $k_B T \gg \Delta \epsilon$ , the Boltzmann distribution is approximately flat at low energies. To be "hot" means that the high-energy states are almost as probable as the low-energy states. This trend holds true even for weird systems that only have two energy levels.
- g. Fit an exponential-decay function of the form  $n_i = A e^{-\beta \epsilon_i}$  to the  $Y = 10^5$  energy distribution, and check that  $A \approx N/2$  and  $\beta = 0.69 \approx \ln(2)$ .
- h. Let's try to explain why  $\beta = \ln(2)$  here. Recalling that  $\epsilon_i = \left(\frac{1}{2} + i\right) \Delta \epsilon$  and  $n_i \propto e^{-\epsilon_i/k_B T}$ , we can express the dependence of occupancy on energy level as  $n_i \propto e^{-(\Delta \epsilon/k_B T)i}$ . Note that the zero-point energy was factored out into the proportionality constant. Because the internal energy is  $U = N \left(\frac{1}{2} + \frac{Q}{N}\right) \Delta \epsilon$ , and because we assumed that  $Q = N$  in the simulation, we have  $\frac{U}{\Delta \epsilon} = \frac{3}{2}$ , and the temperature state equation is  $\frac{\Delta \epsilon}{k_B T} = \ln \left( \frac{2U + \Delta \epsilon}{2U - \Delta \epsilon} \right) = \ln \left( \frac{2U/\Delta \epsilon + 1}{2U/\Delta \epsilon - 1} \right) = \ln(2)$ . This yields  $n_i \propto e^{-\ln(2)i}$ , implying that  $\beta = \ln(2)$ , which agrees perfectly with our simulation.

## 2) The canonical ensemble of microstates

- a. Because the Boltzmann energy distribution references energy levels rather than atoms, it can be applied to either a single atom or the entire system. A given microstate  $s$  assigns a different energy level  $i$  to each atom in the system, which makes formulas based on atom index vs energy-level index interchangeable:  $Q_{s,a} \leftrightarrow i$  and  $E_{s,a} \leftrightarrow \epsilon_i$  and  $P_{s,a} \leftrightarrow P_i = n_i/N$ .
- b. The probability of seeing a given atom in a given energy level is proportional to the occupancy of that energy level, which obeys Boltzmann statistics. Thus, for microstate  $s$ , the probability of finding the  $a^{\text{th}}$  atom with energy  $E_{s,a} = \left(\frac{1}{2} + Q_{s,a}\right) \Delta\epsilon$  is  $P_{s,a} \propto e^{-E_{s,a}/k_B T}$ .
- c. For the entire system, the probability of the  $s^{\text{th}}$  microstate of a Boltzmann macrostate is equal to  $P_s = \prod_a P_{s,a} \propto \prod_a e^{-E_{s,a}/k_B T} = e^{-(\sum_a E_{s,a})/k_B T} = e^{-E_s/k_B T}$ . The set of all microstates exhibiting such Boltzmann statistics are referred to as the *canonical ensemble*. I prefer to refer to it as the fixed-temperature (as opposed to constant energy) ensemble. In the fixed-temperature ensemble, the microstates are NOT all equally probable.
- d. Because  $E_s$  and  $Q_s$  vary from one microstate to the next, total energy and total quantum number which will fluctuate over time as energy quanta are randomly transferred to and from the reservoir in equilibrium. This means that the macroscopic internal energy of a system in contact with a temperature reservoir is actually a statistical mean quantity:  $U = \langle E \rangle = \sum P_s E_s$ . The size of these fluctuations is computed as an rms deviation from the mean, according to  $\Delta E = \langle (E - \langle E \rangle)^2 \rangle^{1/2}$ . For a single-particle system, the relative size of the energy fluctuations,  $\Delta E/E$  can be very large. But for a large system ( $N \rightarrow \infty$ ), relative energy fluctuations are proportional to  $N^{-1/2}$ . Remember that the peak centered at the most probable macrostate gets very narrow. In other words,  $E_s$  is very close to  $U$  for all microstates of the Boltzmann macrostate. All other microstates are physically inaccessible by virtue of their low probability. From a statistical point of view, this is what it means to be in contact with a thermal reservoir.
- e. Subtlety Alert: In section 2.4, G&W say that  $S/k_B = \ln(\Omega_B)$ , where  $\Omega_B = \frac{N!}{\prod n_i!}$  is the multiplicity of the Boltzmann macrostate. We previously introduced  $S/k_B = \ln(\Omega)$  for an isolated system, which employs a fixed energy  $U$  and  $Q$  (the microcanonical ensemble), so that  $\Omega$  was the total number of microstates, and the microstates are all equally probable. However, in a constant- $T$  (canonical) ensemble, the microstates are not equally probable. What is going on here? IMHO, this slipping back and forth between two ensembles in the same derivation is unnecessarily confusing and should be avoided. G&W are implicitly using the facts that only the microstates of the Boltzmann macrostate are physically accessible and that all microstates of the Boltzmann macrostate have the same internal energy,  $U = \langle E \rangle$ .

## Lecture 22: The canonical partition function of a 1D Einstein solid

### 1) More on the 1D Einstein solid

- a. We continue our analysis of the 1D Einstein solid, single harmonic oscillator in contact with a reservoir (canonical ensemble). Because the microstates of the constant-temperature (canonical) ensemble are not equally probable, we need a new method of determining their probabilities. We continue to assume that each atom is an independent vibrational harmonic oscillator. Now, however, we assume that each atom randomly exchanges energy with a reservoir of temperature  $T$ , thus introducing Boltzmann statistics.

### 2) Single-particle canonical partition function

- a. Assume a system size of 1 atom. In the fixed-energy (microcanonical) ensemble, we would have multiplicity  $\Omega = 1$  and entropy  $S = k_B \ln(1) = 0$ . However, when in contact with a temperature reservoir, there are many physically-accessible microstates for a single atom, the probabilities of which comprise a Boltzmann distribution. The probability of an atom being in the  $i^{\text{th}}$  energy level is proportional to its occupancy:  $P_i = \frac{n_i}{N} \propto e^{-\epsilon_i/k_B T}$ .
- b. We define the *single-particle canonical partition function* to be the sum of these unnormalized probabilities over all relevant energy levels:  $Z_{sp} \equiv \sum e^{-\epsilon_i/k_B T}$ .
- c. The probability of finding the system in the  $i^{\text{th}}$  energy level is then  $P_i = \frac{n_i}{N} = \frac{e^{-\epsilon_i/k_B T}}{Z_{sp}}$ , which is properly normalized so that  $\sum P_i = \sum \frac{e^{-\epsilon_i/k_B T}}{Z_{sp}} = \frac{Z_{sp}}{Z_{sp}} = 1$  and  $\sum_i n_i = \sum_i N P_i = N$ .
- d. For a 1D harmonic oscillator of infinite extent,  $\epsilon_i = (1/2 + i)\Delta\epsilon$  for all  $i$  from 0 to  $\infty$ . The single-particle canonical partition function evaluates as follows:

$$\begin{aligned} Z_{sp} &= \sum_{i=0}^{\infty} e^{-(1/2+i)\Delta\epsilon/k_B T} = \sum_{i=0}^{\infty} e^{-(\frac{1}{2}+i)\alpha} = (e^{-\alpha})^{1/2} \sum_{i=0}^{\infty} (e^{-\alpha})^i = x^{1/2} \sum_{i=0}^{\infty} x^i \\ &= \frac{x^{1/2}}{1-x} = \frac{e^{-\alpha/2}}{1-e^{-\alpha}} = \frac{1}{2} \frac{2}{e^{\alpha/2} - e^{-\alpha/2}} = \frac{1}{2 \sinh(\alpha/2)} = \frac{1}{2} \operatorname{csch}\left(\frac{\alpha}{2}\right) = \frac{1}{2} \operatorname{csch}\left(\frac{\Delta\epsilon}{2k_B T}\right) \end{aligned}$$

- e. The G&W section 3.3 on the Einstein solid use somewhat different notation. With a nod to quantum physics, they use  $h\nu$  rather than  $\Delta\epsilon$  as the energy-level spacing. They use  $n$  rather than  $i$  to index energy levels, which is not consistent with their notation in chapter 2. I sweep the whole exponential argument into a unitless parameter  $\alpha = \Delta\epsilon/k_B T$ , while they define a parameter  $\theta = \Delta\epsilon/k_B$  (with Kelvin temperature units) and refer to the argument as  $\theta/T$ . I prefer more the compact  $\operatorname{csch}(\alpha/2)$  function, whereas they use the equivalent exponential form in Eq. 3.5. I also find it convenient to define convenience variable  $x = e^{-\alpha}$  for summing the geometric series.



- 3) A system of  $N$  distinguishable atoms in contact with a temperature reservoir
- G&W use  $m$  as the microstate index, and refers to the particle energies as  $\{\epsilon_i, \epsilon_j, \epsilon_k, \dots\}$ . Instead of this, we will use  $s$  for microstates and refer to the individual atom energies as  $\{E_{s,1}, \dots, E_{s,a}, \dots, E_{s,N}\}$ , so that  $E_s = \sum_a E_{s,a} = \sum_a \left(\frac{1}{2} + Q_{s,a}\right) \Delta\epsilon = \frac{N}{2} + Q_s$ .

- Because Boltzmann statistics yields  $P_s \propto e^{-E_s/k_B T}$ , we also define an  $N$ -atom partition function  $Z_N$  that yields a microstate probability of  $P_s = \frac{1}{Z_N} e^{-E_s/k_B T}$ .

$$Z_N \equiv \sum_s e^{-E_s/k_B T} = \sum_s e^{-(\sum_a E_{s,a})/k_B T} = \sum_s \left\{ \prod_a e^{-E_{s,a}/k_B T} \right\} = \prod_a \left\{ \sum_i e^{-\epsilon_i/k_B T} \right\} = (Z_{sp})^N$$

We just converted a sum of products into a product of sums – an important mathematical operation! It works because the energy levels are the same for each atom.

- Think of each energy level in the inner sum as a different type of breakfast cereal (there are  $t$  varieties), and let each atom be one of the  $N$  cereal boxes that any given grocery store must keep on the shelf. Each of the  $t^N$  microstate-products in the outer sum represents one possible way for the store manager to stock the shelf (i.e how many of each type of cereal to display and in which order). Suppose that we have  $t = 3$  varieties of breakfast cereal [Apple Jacks (A), Bran Flakes (B), and Cap'n Crunch (C)] and need to display exactly  $N = 2$  boxes of cereal on the shelf. The  $3^2 = 9$  microstates are  $(A + B + C)^2 = AA + BB + CC + AB + BA + BC + CB + AC + CA$ . If we assume that A is the ground state, B the first excited state, and C the 2<sup>nd</sup> excited state. The term AB, a product of two Boltzmann factors, puts the first box in the ground state and the other box in the first excited state, which will have a total energy of  $E_A + E_B$ .

- 4) The canonical partition function as a bridge to classical thermodynamics:

- It is instructive to start with the Shannon entropy.

$$\begin{aligned} \frac{S}{k_B} &= -\sum P_s \ln(P_s) = -\sum P_s \ln\left(\frac{1}{Z_N} e^{-E_s/k_B T}\right) = \sum P_s \{E_s/k_B T + \ln(Z_N)\} \\ &= \frac{1}{k_B T} \sum P_s E_s + \sum P_s \ln(Z_N) = \frac{U}{k_B T} + \ln(Z_N) \end{aligned}$$

which can be rearranged to isolate energy on the left:  $U = TS - k_B \ln(Z_N)$ .

- $U(T, V, N)$  is not a fundamental relation. But  $U - TS$  yields the Helmholtz potential,  $F(T, V, N) = -k_B T \ln(Z_N)$ , in terms of its natural variables,  $N, V$ , and  $T$ . This is a very general expression and also a fundamental relation. When working in the fixed- $T$  ensemble, we normally calculate  $F(T, V, N)$  directly rather than starting with the entropy.

- $F(T, N) = -k_B T \ln(Z_N) = -N k_B T \ln(Z_{sp}) = -N k_B T \ln\left(\frac{1}{2} \text{csch}\left(\frac{\Delta\epsilon}{2k_B T}\right)\right)$  for Einstein solid.

- $\beta = \frac{1}{k_B T}$  or  $T = \frac{1}{k_B \beta}$  implies that  $\frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta} \frac{\partial}{\partial T} = -\frac{1}{k_B \beta^2} \frac{\partial}{\partial T} = -k_B T^2 \frac{\partial}{\partial T}$ . This allows us to obtain the internal energy  $U$  directly from  $Z_N$ . The algebraic steps involved may seem unintuitive, but do take us where we want to go

$$k_B T^2 \frac{\partial \ln(Z_N)}{\partial T} = -\frac{\partial \ln(Z_N)}{\partial \beta} = -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = -\frac{1}{Z_N} \frac{\partial (\sum e^{-\beta E_s})}{\partial \beta} = \sum E_s \frac{e^{-\beta E_s}}{Z_N} = \sum P_s E_s = \langle E \rangle = U$$

- $U(T, V, N) = k_B T^2 \left(\frac{\partial \ln(Z_N)}{\partial T}\right)_{V, N}$  is a very convenient and very general expression we can use with the canonical (fixed- $T$ ) ensemble. Remember it! Alternatively, we could perform a Legendre transform on  $F(T, V, N)$  to obtain  $U(S, V, N)$  as an FR. Or, we could calculate  $S(T, V, N) = -\left(\frac{\partial F}{\partial T}\right)_{V, N}$  and substitute it into  $U = F + TS$ .

- Applying this relation to the single-particle canonical partition function, we obtain

$$U = \frac{N}{2} \Delta\epsilon \coth\left(\frac{\Delta\epsilon}{2k_B T}\right) \text{ for the 1D Einstein solid, which is exactly what we got previously}$$

when working with the microcanonical (fixed  $U$ ) ensemble. As we said before, the choice of ensemble is a matter of convenience. Any microstate ensemble should deliver the same physics for the same system.



- g. Take home message: In the microcanonical ensemble, the magic of statistical mechanics arises from counting microstate and macrostate probabilities, which are often analogous to combinatorial problems involving coin flips or dice rolls. In the canonical ensemble, these probabilities are obtained via the partition function, which is often easier to calculate.

5) Partition functions with degeneracy

- a. The  $d$ -shell of an iron atom has five orbitals and  $5 * 2 = 10$  available states with the same energy (i.e. energy degenerate states). In an iron-oxide material, some iron atoms have an octahedral arrangement of neighboring oxygen atoms, the influence of which splits these five  $d$  orbitals between a low-energy triplet of energy  $\epsilon_0$  and degeneracy  $g_0 = 3 * 2 = 6$ , and a high-energy doublet of energy  $\epsilon_1$  and degeneracy  $g_1 = 2 * 2 = 4$ . This is not like an Einstein solid. How does one define a single-particle partition function over degenerate energy levels?
- b. We could simply write  $Z_{sp} = \sum_{i=1}^{10} e^{-\epsilon_i/kT}$  without making the degeneracy explicit in the expression. While this isn't wrong, it would prevent us from assuming that  $\epsilon_i = \left(\frac{1}{2} + i\right) \Delta\epsilon$ . If we want each energy to appear only once, we make the degeneracy explicit by expressing the partition function as  $Z_{sp} = 6e^{-\epsilon_0/kT} + 4e^{-\epsilon_1/kT}$ .
- c. In general, if  $g_i$  is the degeneracy of level  $\epsilon_i$ , then  $Z_{sp} = \sum g_i e^{-\epsilon_i/k_B T}$  and  $P_i = \frac{g_i}{Z_{sp}} e^{-\epsilon_i/k_B T}$ .
- d. This formula defines the fraction of the atomic population in a specific degenerate energy level, or the relative fractions in two degenerate energy levels.
- e. Of course, we can also treat the degeneracy at the microstate level:  $Z_N = \sum g_s e^{-E_s/k_B T}$ , where  $g_{s,a}$  is the degeneracy of the energy level occupied by atom  $a$  in microstate  $s$  and where  $g_s = \prod_a g_{s,a}$ . Note that we probably won't use this approach because it is easier to treat the degeneracy within  $Z_{sp}$  and simply use  $Z_N = Z_{sp}^N$ .

## Lecture 23: Statistical mechanics of a two-state quantum paramagnet

### 1) Magnetic materials

- a. Adding magnetic degrees of freedom to the system introduces a new term in the internal energy. The differential form of the energetic fundamental relation becomes  $dF(T, V, N, B) = -SdT - PdV + \mu dN - MdB$ , where magnetic moment  $M$  and magnetic field  $B$  are a new pair of conjugate variables.
- b. If we continue to treat each atom as independent of (i.e. uncorrelated to) its neighbors (an OK approximation in a paramagnet), the system volume  $V$  has no influence so that  $P$  is zero. We then focus on free energy  $F(T, N, B)$ .
- c. The dependence of the magnetic moment on  $N$  and  $T$  can be obtained as a partial derivative of the free energy in the usual way:  $M(T, N, B) = -\left(\frac{\partial F}{\partial B}\right)_{N,T}$ . We could do the same thing with respect to  $T$  to obtain  $S(T, N, B)$ .

### 2) Introduce the two-state ( $J = 1/2$ ) paramagnet:

- a. The energy of vector magnetic moment  $\boldsymbol{\mu}$  in magnetic field  $\mathbf{B}$  is  $E = -\boldsymbol{\mu} \cdot \mathbf{B}$ . Classically, the angle between them can be anything. In a quantum system, the component of the moment parallel to the field can only take on quantized values.
- b. An atom with only one unpaired  $s$ -shell electron atom has spin quantum number  $J = 1/2$ , the component of the magnetic moment along the field direction is one of  $\pm\mu_B$ , where  $\mu_B = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24}$  J/T is the Bohr magneton.
- c. There are only two single-particle magnetic states, which have energies:  $\pm\mu_B B$ .
- d. The single-particle partition function has only two terms, one for each state:  $Z_{sp} = \sum e^{-\epsilon_i/k_B T} = e^{\mu_B B/k_B T} + e^{-\mu_B B/k_B T} = 2 \cosh(\mu_B B/k_B T)$ .
- e. Define unitless factor  $\alpha \equiv \mu_B B/k_B T$  for convenience in order to simplify many of our equations.  $\alpha \rightarrow 0$  as  $T \rightarrow \infty$  and  $\alpha \rightarrow \infty$  as  $T \rightarrow 0$ .
- f. G&W define a characteristic temperature:  $\theta \equiv \frac{\mu_B B}{k_B}$ , so that  $\alpha = \theta/T$ .
- g. Single particle partition function:  $Z_{sp} = 2 \cosh(\alpha)$

### 3) Free energy:

- a.  $F(T, N, B) = -k_B T \ln(Z_N) = -Nk_B T \ln(Z_{sp}) = -Nk_B T \ln(2 \cosh(\alpha))$ . This is a fundamental relation for the magnetic two-state system!

### 4) Magnetic moment and magnetic susceptibility

- a. Magnetic moment:  $M = -\left(\frac{\partial F}{\partial B}\right)_{N,T} = N\mu_B \tanh(\alpha)$
- b. Magnetic susceptibility:  $\chi = \frac{dM}{dB} = N\mu_B \frac{\alpha/B}{\cosh^2(\alpha)}$
- c. Low-temperature limit:  $\tanh(\alpha) \rightarrow 1$  as  $\alpha \rightarrow \infty$ 
  - i.  $M \rightarrow M_{sat} = N\mu_B$  and  $\chi \rightarrow 0$
  - ii. There is no random thermal misalignment at  $T = 0$ . All atomic moments are aligned with the external field. The total magnetic moment is saturated at its maximum value, so that it doesn't change with  $B$ .
- d. High-temperature limit:  $\tanh(\alpha) \rightarrow \alpha$  as  $\alpha \rightarrow 0$

- i.  $M \rightarrow N\mu_B\alpha = N\frac{\mu_B^2}{k_B}\left(\frac{B}{T}\right)$  and  $\chi \rightarrow N\frac{\mu_B^2}{k_BT}$
- ii. This is Curie's law.  $B$  and  $T$  have opposite effects.  $B$  brings order, while  $T$  disorders. When fully disordered, random vector spins sum to zero.

5) Internal energy:

- a. Specifically, we're referring to the magnetic component of the internal energy, while ignoring the vibrations that we considered in previous lectures.
- b.  $U = Nk_BT^2 \left( \frac{\partial \ln(Z_{sp})}{\partial T} \right) = -N\mu_B B \tanh(\alpha)$
- c. Compare to the expression for  $M$  above and see that  $U = -MB$ , as expected.
- d. Low-temperature limit:  $\tanh(\alpha) \rightarrow 1$  as  $\alpha \rightarrow \infty$ 
  - i.  $U \rightarrow -N\mu_B B = -M_{sat}B$ .
  - ii. The interaction energy of the saturated magnetic moment and the field.
- e. High-temperature limit:  $\tanh(\alpha) \rightarrow \alpha$  as  $\alpha \rightarrow 0$ 
  - i.  $U \rightarrow -N\mu_B B \alpha = -N\mu_B B \left( \frac{\mu_B}{k_B} \right) \left( \frac{B}{T} \right)$
  - ii. Random spins with balanced populations  $\parallel$  and  $\perp$  to field sum to zero.
  - iii. Because  $M \propto B$ , we can see that  $U = -MB \propto B^2$  (quadratic in  $B$ ).
  - iv. Energy is negative and maxes out at zero at high  $T$ . This is a different kind of energy (energy of alignment rather than energy of motion).

6) Entropy:

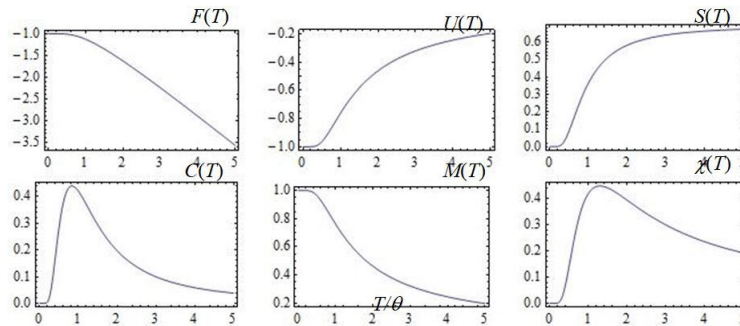
- a.  $S = (U - F)/T = Nk_B(-\alpha \tanh(\alpha) + \ln(2 \cosh(\alpha)))$
- b. High-temperature limit:  $\tanh(\alpha) \rightarrow \alpha$  and  $\cosh(\alpha) \rightarrow 1$  as  $\alpha \rightarrow 0$ 
  - i.  $S \rightarrow Nk_B\{-\alpha^2 + \ln(2)\} \rightarrow Nk_B \ln(2)$
  - ii.  $S/Nk_B = -\sum P_i \ln(P_i)$  can only equal  $\ln(2)$  if the two states are equally probable ( $P_+ = P_- = 1/2$ ). This is a high-temperature characteristic.
- c. Low-temperature:  $\tanh(\alpha) \rightarrow 1 - 2e^{-2\alpha}$ ;  $\ln(2 \cosh(\alpha)) \rightarrow \alpha + e^{-2\alpha}$  as  $\alpha \rightarrow \infty$ 
  - i.  $S \rightarrow Nk_B\{-\alpha(1 - 2e^{-2\alpha}) + (\alpha + e^{-2\alpha})\} \rightarrow 2Nk_B\alpha e^{-\alpha} \rightarrow 0$
  - ii. Only the low-energy state populated at low  $T$ :  $P_+ = 1$  and  $P_- = 0$ .

7) Heat capacity:

- a.  $C = T \left( \frac{\partial S}{\partial T} \right)_N = \left( \frac{\partial U}{\partial T} \right)_N = Nk_B\alpha^2 \operatorname{sech}^2(\alpha)$
- b. High-temperature limit:  $\operatorname{sech}(\alpha) \rightarrow 1$  as  $\alpha \rightarrow 0$ 
  - i.  $C \rightarrow Nk_B\alpha^2 = Nk_B \left( \frac{\mu_B}{k_B} \right)^2 \left( \frac{B}{T} \right)^2 \rightarrow 0$ .
  - ii. Unlike the heat capacity of an ideal gas, which stays constant, we can raise  $T$  for a paramagnetic solid without changing  $U$ ! Heat capacity is a measure of the number of active modes available to store energy. At high  $T$ , when the energy has reached its maximum value, the heat capacity goes to zero.
- c. Low-temperature limit:  $\operatorname{sech}(\alpha) \rightarrow 2e^{-\alpha}$  as  $\alpha \rightarrow \infty$ 
  - i.  $C \rightarrow Nk_B\alpha^2(4e^{-2\alpha}) \rightarrow 0$
  - ii. At low  $T$ , where no modes are accessible (insufficient energy to excite atoms to the upper energy level).
- d. Schottky anomaly: the heat capacity peaks in the middle near  $T = \theta/2$ .

8) Visual intuition

- Graph each of the hyperbolic trig functions as a function of  $\xi$ .
- Graph  $Z_{sp}(T), F(T), U(T), M(T), C(T)$  and develop intuition for them.
- Consider the high and low-temperature limits of each quantity.



## 9) Two-state systems

- Two-state systems appear in many contexts in physics, and often have nothing to do with magnetism. Though their energy splitting may be defined differently (something other than  $\Delta\epsilon = 2\mu_B B$ ), the fundamental relations otherwise has the same form as derived here. The  $J = 1/2$  paramagnetic can be viewed as a model two-state system.

## 10) General multi-state paramagnet

- $U = -MB$  turns out to be a general result for multi-state paramagnets. Prove this for the homework.
- From  $F = -k_B T \ln(Z_N)$ , show that  $M = -\left(\frac{\partial F}{\partial B}\right)_{N,T} = -\frac{U}{B}$ .
- Employ  $U = \langle E \rangle = N\langle\epsilon\rangle = NB \sum P_i \mu_i$ , where  $\epsilon_i = \mu_i B$  is the  $i^{\text{th}}$  energy level of a given atom.

## 11) Negative temperature

- As the temperature of a system increases towards infinity, the relative populations of the two states,  $n_1/n_0 = e^{-(\epsilon_1 - \epsilon_0)/k_B T} \rightarrow e^{-0} = 1$ , meaning that the states tend towards equal occupancy. But at no point should the population of the higher-energy state exceed that of the lower-energy state. If the higher energy level were more populous ( $n_1/n_0 > 1$ ), we could call it an *inverted* population. What are the implications of this situation?
- Switch back to the fixed-energy (microcanonical) ensemble and imagine a two-state paramagnetic with  $N$  atoms and total energy  $U = Q\Delta\epsilon = Q(\epsilon_1 - \epsilon_0)$ . The number  $Q$  of atoms in the upper energy level is proportional to the total energy. The number of ways to choose which atoms to place in the upper level is very simple in this case:  $\Omega = \binom{N}{Q}$ . And we already know from past work that the entropy  $S/k_B = \ln(\Omega)$  peaks in the middle at  $Q = N/2$ . Suppose that we add energy to the system until  $Q > N/2$  and thereby overpopulate the upper level. The slope of  $S(U)$  in that regime is clearly negative on the right-hand side of the entropy peak, meaning that the temperature  $T$  must be negative.
- A negative temperature means that the system must export heat energy in order to increase its entropy. Weird!

- d. Doesn't a negative temperature violate the rule that  $S(U)$  increase monotonically? Yes and no. The fundamental relation only defines the thermodynamic equilibrium states, and this is definitely not an equilibrium state. But if the system is isolated, the energy is constant, so that the state would be stable. Yes and no. The system will inevitably have other types of energy (e.g. thermal atomic vibrations or macroscopic magnetic potential energy due to sample orientation in the external field). The system can equilibrate by exchanging heat energy between the magnetic and motional subsystems within the material. Alternatively, the material could reduce its magnetic internal energy by doing work via macroscopic reorientation in the external field or modification of the external field. Either mechanism allows the system to return to a Boltzmann energy distribution.
- e. Every water-molecule hydrogen atom is a proton with a magnetic  $J = 1/2$  spin. During a medical MRI, some region of the body is subjected to a large magnetic field. At room temperature, most but not all of the proton spins fall to the lower energy level so that their moments align with the field. The application of a brief magnetic field pulse which rotates rapidly in the plane perpendicular to the main magnetic field causes every proton spin to reverse its direction, effectively switching the magnetic energy level of every atom and inverting the population. The instrument then measures the time  $t_1$  required for the population to return to equilibrium, which is different for different types of tissues.

## 12) Magnetic refrigeration

- a. The exchange of energy between the magnetic and motional (translational, rotational, vibrational) subsystems of a magnetic material makes it possible to run a refrigerator cycle. Materials that do this well are called magnetocalorics.
- b. Such a cycle typically has two adiabatic magnetization processes and two isomagnetic heating/cooling processes, and is visualized as a rectangle in the  $BS$  plane. This is loosely analogous to the Brayton cycle, where applying a magnetic field to the material is analogous to applying pressure.
- c. Rapid (adiabatic) application of a magnetic field without external heat transfer occurs at constant system entropy, which implies that  $\alpha = \mu_B B / k_B T$  is constant. The increase in  $B$  must then be accompanied by an increase in  $T$ . Like adiabatic compression, adiabatic magnetization raises the temperature of the magnetic subsystem.
- d. When the temperature of the magnetic subsystem is higher than that of the motional subsystem, heat flows from the magnetic subsystem into the motional subsystem, the magnetic moment of the material increases along the field direction, and the magnetic internal energy and entropy both decrease. During this isomagnetic cooling step, the material is in thermal contact with the warm exterior side of the refrigerator so that the heat leaving the magnetic system is expelled to the outside.
- e. Subsequent adiabatic removal of the field lowers the temperature of the magnetic subsystem, and causes heat to flow from the motional subsystem into the magnetic subsystem. Because this is done while in thermal contact with the cold interior of the refrigerator, heat is drawn away from the inside to replace the heat lost to the magnetic subsystem.

- f. The efficiency of the process depends greatly on the strength of the magnetocaloric effect. The quest for better magnetocaloric materials is an active area of research.

## Lecture 24: Statistical mechanics of a multi-state non-degenerate quantum paramagnet

- 1) Review of multi-electron angular momentum and spin states
  - a. Hydrogen-atom quantum numbers
    - i. Principle quantum number:  $n \in \{1, \dots\}$
    - ii. Orbital quantum number:  $l \in \{0, \dots, n-1\}$ ;  $n$  possible values  
Common symbols:  $0 \rightarrow s$ ,  $1 \rightarrow p$ ,  $2 \rightarrow d$ ,  $3 \rightarrow f$  ...
    - iii. Magnetic quantum number:  $m_l \in \{-l, \dots, +l\}$ ;  $2l+1$  possible values
    - iv. Spin quantum number:  $m_s \in \{-1/2, +1/2\}$ ; 2 possible values
  - b. Degeneracy for a given  $n$  shell:  $\sum_0^{n-1} 2(2l+1) = \frac{4(n-1)(n)}{2} + 2n = 2n^2$
- 2) The multi-electron spin ( $\mathcal{S} = \sum \mathbf{s}_i$ ), orbital ( $\mathcal{L} = \sum \mathbf{l}_i$ ) and total ( $\mathcal{J} = \mathcal{L} + \mathcal{S} = \sum \mathbf{j}_i$ ) angular momentum vectors are sums over the contributing electrons.
  - a. The multi-electron quantum numbers  $S$ ,  $L$ , and  $J$  are obtained from the quantum numbers  $s$ ,  $l$ , and  $j$  of the individual electrons.
    - i. Multi-spin quantum number  $S$  runs in integer steps from  $|s_1 \pm \dots \pm s_t|_{\min}$  to  $|s_1 \pm \dots \pm s_t|_{\max}$ .
    - ii. Multi-orbital quantum number  $L$  runs in integer steps from  $|l_1 \pm \dots \pm l_t|_{\min}$  to  $|l_1 \pm \dots \pm l_t|_{\max}$ .
    - iii. Total quantum number  $J$  runs in integer steps from  $|L - S|$  to  $|L + S|$ .
  - b. The multi-electron quantum numbers  $m_S$ ,  $m_L$ , and  $m_J$  respectively run in integer steps from  $-S$  to  $+S$ ,  $-L$  to  $+L$ , and  $-J$  to  $+J$ , and thereby have respective magnetic multiplicities of  $2S+1$ ,  $2L+1$ , and  $2J+1$ .
  - c. Total number of N-atom spin states ( $2^N$ ) is preserved on the multi-electron-spin basis.  
[https://en.wikipedia.org/wiki/Clebsch-Gordan\\_coefficients#Tensor\\_product\\_space](https://en.wikipedia.org/wiki/Clebsch-Gordan_coefficients#Tensor_product_space)
  - d. The  $\mathcal{S}$ ,  $\mathcal{L}$  and  $\mathcal{J}$  vectors have respective magnitudes of  $\sqrt{S(S+1)}\hbar$ ,  $\sqrt{L(L+1)}\hbar$ , and  $\sqrt{J(J+1)}\hbar$ , and z-axis components of  $m_S\hbar$ ,  $m_L\hbar$  and  $m_J\hbar$ .
  - e. The gyromagnetic ratio,  $\gamma = |\boldsymbol{\mu}|/|\mathcal{J}|$ , indicates how much magnetic moment we get per unit of angular momentum. The Lande factor,  $g_J \equiv \frac{|\boldsymbol{\mu}|/\mu_B}{|\mathcal{J}|/\hbar}$ , is a unitless version of the gyromagnetic ratio. One can show that the Lande factor is computed as  

$$g_J = g_S \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} + g_L \frac{J(J+1)-S(S+1)+L(L+1)}{2J(J+1)} = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)},$$
 where  $g_S = 2$  and  $g_L = 1$ . [https://en.wikipedia.org/wiki/Lande\\_g-factor](https://en.wikipedia.org/wiki/Lande_g-factor)
  - f. For pure-spin systems ( $L = 0$  and  $J = S$ ), the Lande factor is  $g_J = g_S = 2$ . For pure-orbital systems ( $S = 0$  and  $J = L$ ), the Lande factor is  $g_J = g_L = 1$ . In solids, it is common to have  $L = 0$  due to a phenomenon known as orbital quenching.  
<https://www.researchgate.net/post/What-is-quenching-of-orbital-angular-momentum>
  - g. Key result: the quantized energy levels of a multi-state quantum paramagnet are  $E_{m_J} = g_J m_J \mu_B B$ , where  $m_J \in \{-J, \dots, +J\}$ . Knowing  $J$  allows us to list all possible states without reference to the  $s$  and  $l$  values of the individual contributing electrons.
  - h. Don't confuse the Lande factor  $g_J$  with the degeneracy factor  $g_J$ .

3) Spin configurations of  $d$ -shell transition metals

- a. Start by assuming orbital quenching ( $L = 0, J = S$ ).
- b. There are  $2 \cdot 2 + 1 = 5$  degenerate  $d$ -shell orbitals to begin with. The electric fields of the neighboring atoms break the orbital energy degeneracy of the atom by raising some orbital energies and lowering others. The difference between the upper and lower energy levels is called the crystal-field splitting energy ( $\Delta_{cf}$ ).
- c. An octahedral arrangement of neighbors raises two orbitals (called  $e_g$  orbitals) and lowers three orbitals (called  $t_{2g}$  orbitals), whereas a tetrahedral arrangement of neighbors raises the three  $t_{2g}$  orbitals and lowers the two  $e_g$  orbitals. The study of such things is known as *crystal field theory*.
- d. No two electrons can occupy the same quantum state. Two electrons that pair up in the same orbital, must have opposite (antiparallel) spins. There's an energy penalty ( $\Delta_{pair}$ ) for pairing up like this. To avoid this penalty, electrons tend to prefer to be in separate orbitals where they can have mutually parallel spins.
- e. Once the lowest-energy orbitals are each half full, the next electron must decide whether to move up to the higher level or to pair up in the lower level. The outcome depends on which energy penalty ( $\Delta_{cf}$  or  $\Delta_{pair}$ ) is greatest.
- f. This results in a variety of possible spin configurations. For an atom with 6  $d$ -shell electrons and an octahedral environment, the possibilities are
  - i. low-spin ( $t_{2g}^6 e_g^0$ )  $\rightarrow J = 0$
  - ii. intermediate-spin ( $t_{2g}^5 e_g^1$ )  $\rightarrow J = 1$
  - iii. high-spin ( $t_{2g}^4 e_g^2$ )  $\rightarrow J = 2$

## 4) Multi-state quantum paramagnet partition function

- a. Recall from discussion above that  $E_{m_J} = g_J m_J \mu_B B$ , where  $m_J \in \{-J, \dots, +J\}$ .
- b. Use  $\alpha \equiv \frac{g_J \mu_B B}{2k_B T}$  and  $x \equiv e^{-2\alpha}$  so that  $e^{-E_{m_J}/k_B T} = e^{-2\alpha m_J}$  to find  $Z_{sp}$ .
- c. 
$$Z_{sp} = \sum_{-J}^{+J} e^{-m_J 2\alpha} = \sum_{-J}^{+J} x^{m_J} = \left\{ \sum_0^\infty - \sum_{J+1}^\infty + \sum_{-\infty}^0 - \sum_{-\infty}^{-(J+1)} - 1 \right\} x^{m_J}$$

$$= \frac{1}{1-x} - \frac{x^{J+1}}{1-x} + \frac{x}{x-1} - \frac{x^{-J}}{x-1} - 1 = \frac{x^{-J} - x^{J+1}}{1-x} = \frac{e^{2J\alpha} - e^{-2(J+1)\alpha}}{1 - e^{-2\alpha}} = \frac{e^{(2J+1)\alpha} - e^{-(2J+1)\alpha}}{e^{\alpha} - e^{-\alpha}} = \frac{\sinh[(2J+1)\alpha]}{\sinh[\alpha]}$$
- d.  $F(N, B, T) = -Nk_B T \ln(Z_{sp})$
- e.  $M = -\left(\frac{\partial F}{\partial B}\right)_{N,T} = \frac{1}{2} N g_J \mu_B \{(2J+1) \coth((2J+1)\alpha) - \coth(\alpha)\}$ 
  - i. High temperature (small  $\alpha$ ): use  $\coth(\alpha) \rightarrow \frac{1}{\alpha} + \frac{\alpha}{3}$  to show that
 
$$M \rightarrow \frac{1}{3} N \frac{g_J^2 \mu_B^2 J(J+1)}{k_B} \frac{B}{T} = \text{const} \cdot \frac{B}{T}. \text{ This is Curie's law again!}$$
  - ii. Low temperature (large  $\alpha$ ):  $M \rightarrow N g_J J \mu_B$ . All spin  $z$ -components aligned!
- f. Prove that  $M$  reduces to the two-state expression  $N \mu_B \tanh(\alpha)$  when  $J = 1/2$ .
- g. Other thermodynamic quantities (such as internal energy, entropy, heat capacity) also turn out to be generalizations of the simpler two-state quantum paramagnet result, and reduce to the simpler result when  $J = 1/2$ .



## 5) Classical paramagnet

- a. Boltzmann factor:  $e^{-\mu \cdot \mathbf{B}/k_B T} = e^{-\mu B \cos(\theta)/k_B T} = e^{-\alpha \cos(\theta)}$  where  $\alpha \equiv \frac{\mu B}{k_B T}$ .
- b. Partition function:  $Z_{sp} = \iint e^{-\alpha \cos(\theta)} \sin(\theta) d\theta d\phi = 4\pi \frac{\sinh(\alpha)}{\alpha}$ , where the angles are integrated isotropically over a full sphere:  $\theta$  from 0 to  $\pi$  and  $\phi$  from 0 to  $2\pi$ .
- c. Free energy:  $F = -k_B T \ln(Z_N) = -N k_B T \ln\left(4\pi \frac{\sinh(\alpha)}{\alpha}\right)$
- d. Magnetic moment:  $M = -\left(\frac{\partial F}{\partial B}\right)_{N,T} = N\mu \left\{ \coth(\alpha) - \frac{1}{\alpha} \right\}$ 
  - i. Low-temperature limit:  $M \rightarrow N\mu$ . Observe that replacing  $\mu$  with  $g_J \mu_B J$  yields the general quantum case.
  - ii. High-temperature limit:  $M \rightarrow \frac{1}{3} N\mu\alpha = \frac{1}{3} \frac{N\mu^2 B}{k_B T}$ . Note that  $\coth(\alpha) \rightarrow \frac{1}{\alpha} + \frac{\alpha}{3}$ .  
Observe that replacing  $\mu$  with  $g_J \mu_B \sqrt{J(J+1)}$  yields general quantum case.
- e. Internal energy:  $U = -N\mu B \left\{ \coth(\alpha) - \frac{1}{\alpha} \right\}$ 
  - i. Low-temperature limit:  $U \rightarrow -N\mu B$
  - ii. High-temperature limit:  $U \rightarrow -\frac{1}{3} N\mu B\alpha = -\frac{1}{3} \frac{N\mu^2 B^2}{k_B T}$
- f. Entropy:  $S = (U - F)/T$ 
  - i. Low-temperature limit:  $S \rightarrow -\infty$ . Not an acceptable low-temperature FR.
  - ii. High-temperature limit:  $S \rightarrow N k_B \ln(4\pi)$ . Effectively counts the possible directions over the surface of a sphere.
- g. Heat capacity:  $C = N k_B \{1 - \alpha^2 \text{csch}^2(\alpha)\}$ 
  - i. Low-temperature limit:  $C \rightarrow N k_B$  (doesn't go to zero!)
  - ii. High-temperature limit:  $C \rightarrow \frac{1}{3} N k_B \alpha^2 = \frac{1}{3} \frac{N\mu^2 B^2}{k_B T^2}$
- h. Why are the thermodynamic properties of quantum and classical paramagnets the same in the high-temperature limit? At high temperature, the quantum-mechanical energy-level spacing  $\mu B$  is so much smaller than the thermal energy scale  $k_B T$  that it can be treated as differentially small, which is essentially the classical picture.

## Lecture 25: Statistical mechanics of the ideal gas

### 1) Quantum concentration for a monatomic ideal gas

- a. We prefer to use particular rather than molar quantities for statistical mechanics. We'll use the symbol  $n_{conc} = N/V$  to indicate particle concentration, or number of particles per unit volume. Similarly,  $v = V/N$  is the volume per particle.
- b. The quantum mechanical wavelength of a matter wave is called the de Broigle wavelength, and is calculated as  $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m\epsilon}} = \frac{2\pi\hbar}{\sqrt{2m(\frac{3}{2}k_B T)}} = \sqrt{\frac{2\pi}{3}} \left( \frac{2\pi\hbar^2}{mk_B T} \right)^{1/2} \approx \left( \frac{2\pi\hbar^2}{mk_B T} \right)^{1/2}$ .
- c. The quantum concentration  $n_Q = \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} = \frac{1}{\lambda^3}$  is the maximum concentration beyond which the quantum-mechanical matter waves of nearby gas molecules begin to overlap one another, so that we then have to worry about how many molecules are allowed to occupy the same state (quantum statistics). This is a very high concentration, where the average molecular volume  $v_Q = \frac{1}{n_Q} \approx \lambda^3$  has a diameter of one deBroigle wavelength. In contrast, an ideal gas operates in the low-concentration limit where quantum effects can be neglected.
- d. The quantum concentration only depends on temperature and physical constants; it increases (the deBroigle wavelength decreases) with temperature so that it's more difficult to cross the quantum threshold at high temperature. Quantum statistics apply in the cold dense limit, whereas an ideal gas is warm and dilute.
- e. In past work on ideal gasses (e.g. lecture 5), we mentioned a reference state but never defined it. We'll do that now. At arbitrary temperature  $T_0$ , the ideal-gas reference state has the quantum concentration for that temperature:  $N_0/V_0 = n_Q(T_0)$  and  $U_0 = \frac{3}{2} N_0 R T_0$ .

### 2) Degenerate Boltzmann statistics of a monatomic ideal gas

- a. Let  $n_i$  be the number of particles in the  $\epsilon_i$  energy level, and let  $g_i$  be the number of number of states with that energy (i.e. the degeneracy or the *density of states*).
- b. The number of ways to place  $n_i$  particles in  $g_i$  states that have a given energy is  $\frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$ . We did something very similar with hot dogs and tomatoes; but that was assigning indistinguishable quanta to distinguishable atoms.
- c. Taking a product over all energy levels, the total number of ways to distribute all particles across energy levels is  $\Omega = \prod \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} = \prod \frac{(g_i + n_i - 1) \dots (g_i)}{n_i!}$ .
- d. Simultaneously maximizing this number with respect to all of the energy-level occupancies  $n_i$  (via the method of Lagrange multipliers described in G&W) once again yields Boltzmann statistics:  $n_i \propto g_i e^{-\epsilon_i/k_B T}$ , except that degeneracy is accounted for this time. The single-particle partition function is  $Z_{sp} = \sum g_i e^{-\epsilon_i/k_B T}$ . And because  $\sum n_i = N$ , the energy-level occupancy is  $n_i = \frac{N}{Z_{sp}} g_i e^{-\epsilon_i/k_B T}$ .

## 3) Low-concentration limit for indistinguishable particles

- a. If the number of energy levels is much larger than the number of particles ( $g_i \gg n_i$ ), the probability of two particles competing for the same state is very small (accurate for ideal gas), and we entirely avoid quantum statistics. In this limit, we then have

$$\Omega = \prod \frac{(g_i + n_i - 1) \dots (g_i)}{n_i!} \approx \prod \left( \frac{g_i}{n_i!} \right).$$

$$\begin{aligned} \text{b. } \frac{S}{k_B} &= \ln(\Omega_B) = \ln \left[ \prod \left( \frac{g_i}{n_i!} \right) \right] \approx \sum \{n_i \ln g_i - n_i \ln n_i + n_i\} = \sum n_i \left\{ 1 - \ln \left( \frac{n_i}{g_i} \right) \right\} = \\ &= \sum n_i \left\{ 1 - \ln \left( \frac{N}{Z_{sp}} e^{-\frac{\epsilon_i}{k_B T}} \right) \right\} = \sum n_i \left\{ 1 - \ln(N) + \frac{\epsilon_i}{k_B T} + \ln(Z_{sp}) \right\} \\ &= N - N \ln(N) + \frac{U}{k_B T} + N \ln(Z_{sp}) \approx \frac{U}{k_B T} + \ln(Z_{sp}^N) - \ln(N!) \approx \frac{U}{k_B T} + \ln \left( \frac{1}{N!} Z_{sp}^N \right) \end{aligned}$$

- c. Helmholtz free energy:  $F = U - TS = -k_B T \ln \left( \frac{1}{N!} Z_{sp}^N \right)$ . Compared to systems studied previously, this has an extra factor of  $N!$  in the denominator of the log. Why?
- d. Unlike the Einstein solid or paramagnetic solid, where each atom had a separate potential well or magnetic moment at a distinguishable location, the particles of an ideal gas operate indistinguishable in the same volume, so that there is no practical way to track them separately. The factor of  $N!$  in the denominator divides out all permutations of the indistinguishable molecules/particles of the same gas species, so that only unordered configurations are counted.
- e. The Helmholtz free energy is  $F(N, V, T) = -k_B T \ln(Z_N)$ , where the partition function for  $N$  indistinguishable particles is  $Z_N = \frac{1}{N!} (Z_{sp})^N$ .

## 4) Single-particle partition function of a monatomic ideal gas

- a. Unlike G&W, we avoid a discussion of the density of states  $g(\epsilon)$  here. It will provide an alternative approach in the next lecture.
- b. Within a box of finite volume, every gas particle has six continuous degrees of freedom, a finite position vector ( $\mathbf{x}$ ) inside a box of volume  $V$  and a momentum vector ( $\mathbf{p}$ ) which runs over an infinite range.
- c. The Boltzmann factor is  $e^{-E(\mathbf{x}, \mathbf{p})/k_B T} = e^{-p^2/2(m k_B T)}$ , which is a Gaussian function in  $p = |\mathbf{p}|$  and doesn't depend on  $\mathbf{x}$  at all.
- d. This state space is quantized into 6D regions of volume  $(\Delta x \Delta p)^3 = \left( \frac{h}{2} \right)^3 = (\pi \hbar)^3$ , which are so small that the sum over states can be treated as an integral.
- e. 
$$\begin{aligned} Z_{sp} &= \sum_s e^{-p_s^2/2(m k_B T)} = \sum_s e^{-p_s^2/2(m k_B T)} \frac{\Delta x_s^3 \Delta p_s^3}{(\pi \hbar)^3} = \frac{1}{(\pi \hbar)^3} \int e^{-p^2/2(m k_B T)} dx^3 dp^3 \\ &= \frac{1}{(\pi \hbar)^3} \int e^{-(p_x^2 + p_y^2 + p_z^2)/2(m k_B T)} dx dy dz dp_x dp_y dp_z \\ &= \frac{1}{(\pi \hbar)^3} \left\{ \int dx dy dz \right\} \left\{ \int_0^{+\infty} e^{-p_z^2/2(m k_B T)} dp_z \right\}^3 = \frac{1}{(\pi \hbar)^3} \{V\} \left\{ \sqrt{(\pi/2) m k_B T} \right\}^3 \\ &= V \left( \frac{m k_B T}{2 \pi \hbar^2} \right)^{3/2}, \text{ so that } Z_{sp} = V n_Q(T). \end{aligned}$$
- f. Here, we used the integral formula  $\int_0^{+\infty} e^{-x^2/2\alpha} dx = \sqrt{\pi\alpha/2}$ .
- g. Because particle-in-a-box states are standing waves, which already consist of equal mixtures of  $-p$  and  $+p$  contributions, we sum/integrate only over the first octant of reciprocal space to avoid overcounting the states.

- h. To recap,  $Z_{sp} = Vn_Q = V/v_Q$  tells us how many quantum volumes fit into the system volume. If you pack a large enough number of particles ( $N$ ) into the system, the volume per particle eventually drops to the level of the quantum volume, so that  $\frac{Z_{sp}}{N} = \frac{n_Q}{n_{conc}} = \frac{v}{v_Q} \rightarrow 1$ , at which point, quantum statistics become relevant and we're not in Kansas anymore (not an ideal gas).

5) Completing the bridge to thermodynamics

- a.  $\ln(Z_N) = N \ln(Z_{sp}) - \ln(N!) = N \ln(Z_{sp}) - N \ln(N) + N = N \left\{ 1 + \ln\left(\frac{Z_{sp}}{N}\right) \right\}$   
 $= N \left\{ 1 + \ln\left(\frac{Vn_Q}{N}\right) \right\} = N \left\{ 1 + \ln\left(\frac{n_Q}{n_{conc}}\right) \right\}$
- b.  $F(T, V, N) = -k_B T \ln(Z_N) = -Nk_B T \left\{ 1 + \ln\left(\frac{n_Q(T)}{n_{conc}}\right) \right\}$ . New fundamental relation!
- c.  $S(T, V, N) = -\left(\frac{\partial F}{\partial T}\right)_{V, N} = Nk_B \left\{ \frac{5}{2} + \ln\left(\frac{n_Q(T)}{n_{conc}}\right) \right\}$
- d. We can easily form the Sackur Tetrode equation as a fundamental relation. Show that  $U(T, V, N) = F(T, V, N) + T S(T, V, N) = \frac{3}{2} Nk_B T$ , and substitute  $T = \frac{2}{3} \frac{U}{Nk_B}$  in  $n_Q$ .  
 Then  $S(U, V, N) = Nk_B \left\{ \frac{5}{2} + \ln\left(\frac{n_Q(U)}{n_{conc}}\right) \right\}$ , where  $n_Q(U) = \left(\frac{mU/N}{3\pi\hbar^2}\right)^{3/2}$ . Only molecular translations have been considered to this point. We'll add complexity in the next lectures.
- e. In the reference state at some temperature  $T_0$ , the concentration is  $n_{conc} = n_Q(T_0)$ , so that the  $\ln\left(\frac{n_Q}{n_{conc}}\right) = \ln(1) = 0$ , and entropy per particle is  $s_0 = \frac{5}{2} k_B$ . This is exactly what we used in thermodynamics for a *monatomic* ideal gas!
- f. Because the Sackur-Tetrode equation breaks down (ceases to be valid) when  $n_{conc}$  is comparable to  $n_Q$ , I'm not sure whether the value  $5/2 \approx \ln(12.18)$  is meaningful; it suggests that the breakdown actually occurs when  $n_{conc} = 12.18 n_Q$ . A higher concentration would yield an impossible negative entropy.
- g. We'll now show that the argument of the natural log in the Sackur-Tetrode equation is the very same argument we were using in thermodynamics. Try to follow each step.
- $$\frac{I}{I_0} = \left(\frac{V}{V_0}\right) \left(\frac{U}{U_0}\right)^{3/2} \left(\frac{N_0}{N}\right)^{5/2} = \left(\frac{V}{V_0}\right) \left(\frac{T}{T_0}\right)^{3/2} \left(\frac{N_0}{N}\right) = \left(\frac{N_0/V_0}{N/V}\right) \left(\frac{T}{T_0}\right)^{3/2} = \frac{n_Q(T_0)}{n_{conc}} \left(\frac{T}{T_0}\right)^{3/2} = \frac{n_Q(T)}{n_{conc}}$$

6) Chemical potential of a *monatomic* ideal gas

- a.  $\frac{\mu}{k_B T} = -\frac{1}{k_B} \left(\frac{\partial S}{\partial N}\right)_{U, V} = -\frac{1}{k_B} \left(\frac{\partial}{\partial N} Nk_B \left\{ \frac{5}{2} + \ln\left(\frac{V}{N} \left(\frac{mU}{3\pi\hbar^2 N}\right)^{3/2} \right) \right\}\right)_{U, V} = -\frac{S}{Nk_B} + \frac{5}{2}$   
 $= -\ln\left(\frac{n_Q}{n}\right)$ , so that  $\frac{\mu}{k_B T} = \ln\left(\frac{n_{conc}}{n_Q}\right)$ .
- b. In thermodynamics, we assumed the chemical potential of an ideal gas to always be negative, except in the reference state, where it equals zero. We now better understand what this means – that the concentration is always less than the quantum concentration ( $n_{conc} \ll n_Q$ ), except in reference state where they are equal.

## Lecture 26: Kinetic theory of a monatomic ideal gas, Gibbs paradox

### 1) Density of states

- a. For a quantum particle in a 1D box, the box width  $a$  is a half-integer multiple of the deBroglie wavelength  $\lambda_n$ , so that  $\lambda_n = \frac{a}{(n/2)} = \frac{2a}{n}$ . The corresponding momentum can be expressed as  $p = \hbar k = \hbar \frac{2\pi}{\lambda_n} = 2\pi\hbar \frac{n}{2a} = n \frac{\pi\hbar}{a} = n \Delta p$ , where quantum number  $n$  is a positive integer and  $\Delta p = \frac{\pi\hbar}{a}$  is the momentum spacing between adjacent states.
- b. One could naively argue that a negative integer  $n$  corresponds to a state in which the momentum is in the negative direction, and should therefore be allowed. But in fact, the state with positive integer  $n$  is a standing wave, and therefore already consists of an equal mixture of waves with momenta  $+n \Delta p$  and  $-n \Delta p$  along each axis. For a box of size  $\Delta x = a$ , we have  $\Delta x \Delta p = \pi\hbar$ , which we used in the previous lecture.
- c. For a 3D box of volume  $V = a^3$ , define a quantized 3D grid of momentum states:  $\mathbf{p} = (p_x, p_y, p_z) = (n_x, n_y, n_z)\Delta p$ , where  $n_x, n_y$ , and  $n_z$  are non-negative integers.
- d. The kinetic energy of a state is  $\epsilon_{(n_x, n_y, n_z)} = \frac{p_{(n_x, n_y, n_z)}^2}{2m} = \frac{\Delta p^2}{2m} (n_x^2 + n_y^2 + n_z^2)$ .
- e. For notational convenience, we'll group states  $(n_x, n_y, n_z)$  with the same energy into energy levels indexed by the letter  $i$ , similar to what we have done previously. We can then use  $\epsilon_i$  and  $p_i$  and  $g_i$  to refer to the respective energy and momentum-vector magnitude and degeneracy (number of states) of the  $i^{th}$  energy level.
- f. States with the same energy  $\epsilon_i$  live on the surface of the positive octant of a sphere in momentum space. The total number of states  $G_i$  with energy less than or equal to  $\epsilon_i$  is the octant volume divided by  $\Delta p^3$ , which is  $G_i = \frac{1}{8} \frac{4\pi}{3} \left(\frac{p_i}{\Delta p}\right)^3 = \frac{p_i^3 a^3}{6\pi^2 \hbar^3} = \frac{(2m\epsilon_i)^{3/2} V}{6\pi^2 \hbar^3}$ .
- g. For a macroscopic system, the momentum states and energy levels are so closely spaced that we can think of momentum and energy as continuous variables:  $\epsilon_i \rightarrow \epsilon$ ,  $G_i(\epsilon_i) \rightarrow G(\epsilon)$ , and  $g_i(\epsilon_i) \rightarrow g(\epsilon)$ .
- h. The state degeneracy can be viewed as the number of states with energies in the range from  $\epsilon$  to  $d\epsilon$ , which is  $dG(\epsilon) = g(\epsilon)d\epsilon$ , where  $g(\epsilon)$  is called the *density of states*.
- i. We then have  $g(\epsilon) = \frac{dG(\epsilon)}{d\epsilon} = \frac{mV(2m\epsilon)^{1/2}}{2\pi^2 \hbar^3}$ . The density of states is an important concept in many systems, not only ideal gasses.

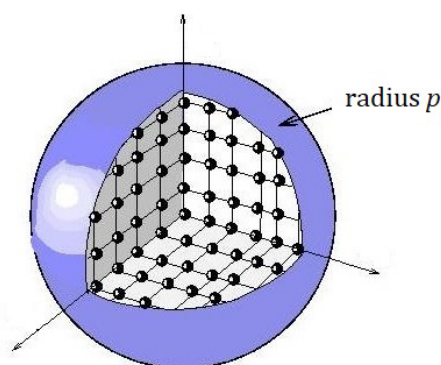
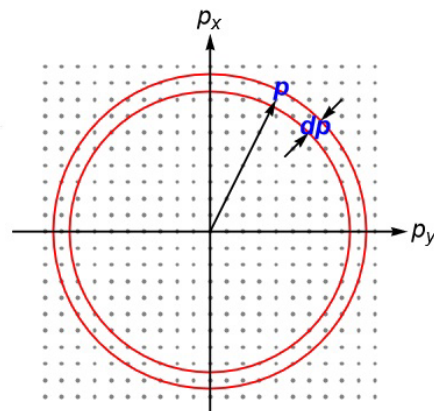


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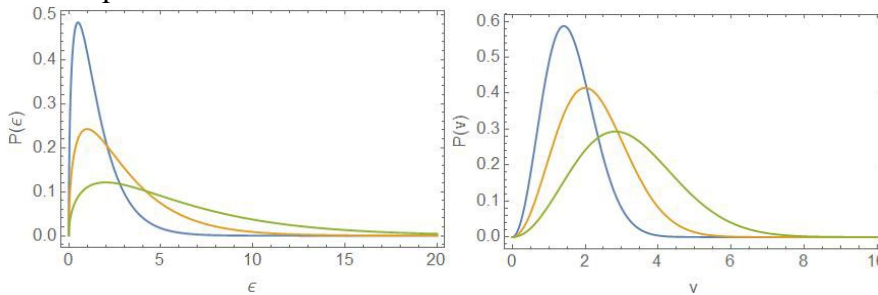
- j.  $Z_{sp} = \sum g_i e^{-\epsilon_i/k_B T} \rightarrow \int g(\epsilon) e^{-\epsilon/k_B T} d\epsilon$  is the continuous form of the single-particle partition function. As a sanity check, let's perform this integral to see if we get the same result as in the previous lecture. Define  $\xi = \epsilon/k_B T$ .

$$\int g(\epsilon) e^{-\epsilon/k_B T} d\epsilon = \int \left( \frac{mV(2m\epsilon)^{1/2}}{2\pi^2 \hbar^3} \right) e^{-\epsilon/k_B T} d\epsilon = \frac{2}{\sqrt{\pi}} V \left( \frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} \int_0^\infty \xi^{1/2} e^{-\xi} d\xi$$

$$= \frac{2}{\sqrt{\pi}} V \left( \frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} \frac{\sqrt{\pi}}{2} = V n_Q. \text{ It worked! We have } Z_{sp} = V n_Q.$$

## 2) Maxwell-Boltzmann distribution (energy, momentum, velocity)

- a.  $P_i = \frac{g_i e^{-\epsilon_i/k_B T}}{Z_{sp}} \rightarrow P(\epsilon) d\epsilon = \frac{g(\epsilon)}{Z_{sp}(\epsilon)} e^{-\epsilon/k_B T} d\epsilon$  is the continuous probability that a particle has an energy between  $\epsilon$  and  $\epsilon + d\epsilon$ .
- b.  $P(\epsilon) d\epsilon = \frac{g(\epsilon) e^{-\epsilon/k_B T}}{Z_{sp}(\epsilon)} d\epsilon = \left\{ \frac{mV(2m\epsilon)^{1/2}}{2\pi^2 \hbar^3} \right\} \frac{e^{-\epsilon/k_B T}}{V n_Q(T)} d\epsilon = \frac{2}{\sqrt{\pi}} \frac{\epsilon^{1/2}}{(k_B T)^{3/2}} e^{-\epsilon/k_B T} d\epsilon$
- c.  $P(p) dp = P(\epsilon) d\epsilon = P(\epsilon(p)) \frac{d\epsilon}{dp} dp = P(\epsilon = p^2/2m) \frac{p}{m} dp =$   
 $2 \left( \frac{p^2/2m}{\pi(k_B T)^3} \right)^{1/2} e^{-p^2/2mk_B T} \left( \frac{p}{m} \right) dp = \left\{ 4\pi p^2 \frac{e^{-p^2/2mk_B T}}{(2\pi mk_B T)^{3/2}} \right\} dp$
- d.  $P(v) dv = P(p) dp = P(p(v)) \left( \frac{dp}{dv} \right) dv = P(p = mv) m dv$   
 $= 4\pi m^2 v^2 \frac{e^{-mv^2/2k_B T}}{(2\pi mk_B T)^{3/2}} m dv = 4\pi v^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} dv$
- e. Recap:  $P(\epsilon) = \frac{2}{\sqrt{\pi}} \frac{\epsilon^{1/2}}{(k_B T)^{3/2}} e^{-\epsilon/k_B T}$  and  $P(v) = 4\pi v^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}$
- f. Each probability density  $P(x)$  has physical units inverse to its argument  $x$ , so that the product  $P(x)dx$  is unitless. The peak in each distribution shifts to the right as temperature increases.



## 3) Maxwell-Boltzmann averages

- a.  $\langle f \rangle = \int f(\epsilon) P(\epsilon) d\epsilon = \int f(p) P(p) dp = \int f(v) P(v) dv$  for any quantity  $f$ .
- b.  $\langle \epsilon \rangle = \int \epsilon P(\epsilon) d\epsilon = \frac{3}{2} k_B T$  for the average single-particle kinetic energy. This yields total internal energy  $U = \frac{3}{2} N k_B T$ , as expected.
- c.  $\langle v^2 \rangle = \int v^2 P(v) dv = \frac{3k_B T}{m}$  for the average squared velocity.
- d.  $v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}$
- e.  $v_{peak} = \sqrt{\frac{2k_B T}{m}}$  is the point of zero slope atop the peak in the distribution.
- f. We have reproduced the basic results of the kinetic theory of a monatomic ideal gas from lecture 1, but also build some useful tools ( $Z_{sp}(\epsilon)$  and  $P(\epsilon)$ ) along the way.



## 4) Gibbs paradox (ideal gas)

- a. In preparation for the four thought experiments below, consider that isothermal entropy change in an ideal gas can be calculated as  $\Delta S = S' - S = \Delta \left( \frac{U-F}{T} \right) = \frac{\Delta U - \Delta F}{T} = -\frac{\Delta F}{T} = k_B \Delta [\ln(Z_N)] = k_B [\ln(Z'_N) - \ln(Z_N)] = k_B \ln \left( \frac{Z'_N}{Z_N} \right)$ . Here, we used the facts that  $U \propto T$  and that  $F = -k_B T \ln(Z_N)$  for an ideal gas.
- b. Experiment #1: Increase the volume of a *single ideal gas species* from  $V$  to  $V' = 2V$  at constant temperature (and hence constant internal energy).

- i. The partition function changes from  $Z_N = Z_{sp}^N / N!$  to  $Z'_N = Z_{sp}'^N / N!$ .

$$\Delta S / k_B = \ln \left( \frac{Z'_N}{Z_N} \right) = \ln \left( \frac{Z_{sp}'^N / N!}{Z_{sp}^N / N!} \right) = N \ln \left( \frac{Z_{sp}'}{Z_{sp}} \right) = N \ln \left( \frac{V'}{V} \right) = N \ln(2).$$

- ii. See that the indistinguishability factor ( $N!$ ) did not affect the result.

- c. Experiment #2: Equal amounts ( $N_A = N_B = N/2$ ) and volumes ( $V$ ) of two *different* gasses (A and B) at same  $T$  mix into their combined volume of  $V' = 2V$ .

$$\begin{aligned} \text{i. } \frac{Z_{tot}'}{Z_{tot}} &= \left( \frac{Z_{N_A}' Z_{N_B}'}{Z_{N_A} Z_{N_B}} \right) = \left( \frac{Z_{spA}'^{N_A} / N_A!}{Z_{spA}^{N_A} / N_A!} \right)^{N_A} \left( \frac{Z_{spB}'^{N_B} / N_B!}{Z_{spB}^{N_B} / N_B!} \right)^{N_B} = \left( \frac{V' n_Q}{V n_Q} \right)^{N_A} \left( \frac{V' n_Q}{V n_Q} \right)^{N_B} = \\ &\left( \frac{V'}{V} \right)^{N_A} \left( \frac{V'}{V} \right)^{N_B} = \left( \frac{V'}{V} \right)^N = 2^N \end{aligned}$$

$$\text{ii. } \frac{\Delta S}{k} = \ln \left( \frac{Z_{tot}'}{Z_{tot}} \right) = \ln(2^N) = N \ln(2). \text{ Entropy of mixing.}$$

- iii. See that the indistinguishability factor ( $N!$ ) did not affect the result.

- d. Experiment #3: Equal amounts ( $N/2$ ) and volumes ( $V$ ) of *distinguishable particles of the same gas* at same  $T$  mix into their combined volume of  $2V$ .

$$\text{i. } Z_{tot} = Z_{sp}^{N/2} Z_{sp}^{N/2} = Z_{sp}^N, \text{ where } Z_{sp} = n_Q V.$$

$$\text{ii. } Z_{tot}' = Z_{sp}'^N = \left( \frac{Z_{sp}}{Z_{sp}} \right)^N = \left( \frac{n_Q V'}{n_Q V} Z_{sp} \right)^N = \left( \frac{V'}{V} Z_{sp} \right)^N$$

$$\text{iii. } \frac{\Delta S}{k} = \ln \left( \frac{Z_{tot}'}{Z_{tot}} \right) = \ln \left( \left( \frac{V'}{V} \right)^N \right) = N \ln \left( \frac{V'}{V} \right) = N \ln(2)$$

- iv. The entropy increases, though the actual state of the system is unchanged. This impossible result is called the Gibbs paradox.

- e. Experiment #4: Equal amounts ( $N/2$ ) and volumes ( $V$ ) of *indistinguishable particles of the same gas* at same  $T$  mix into their combined volume of  $2V$ .

$$\text{i. } Z_{tot} = \frac{Z_{sp}^{N/2}}{(N/2)!} \frac{Z_{sp}^{N/2}}{(N/2)!} = \frac{Z_{sp}^N}{(N/2)!^2}, \text{ where } Z_{sp} = n_Q V.$$

$$\text{ii. } Z_{tot}' = \frac{Z_{sp}'^N}{N!}, \text{ where } Z_{sp}' = n_Q V'.$$

$$\begin{aligned} \text{iii. } \frac{\Delta S}{k} &= \ln \left( \frac{Z_{tot}'}{Z_{tot}} \right) = \ln \left[ \left( \frac{V'}{V} \right)^N \frac{(N/2)!^2}{N!} \right] = N \ln(2) + 2 \ln((N/2)!) - \ln(N!) \\ &\approx N \ln(2) + 2 \left[ \left( \frac{N}{2} \right) \ln \left( \frac{N}{2} \right) - \frac{N}{2} \right] - [N \ln(N) - N] \\ &= N \{ \ln(2) + [\ln(N) - \ln(2) - 1] - [\ln(N) - 1] \} = 0 \end{aligned}$$

- iv. For indistinguishable particles, the entropy doesn't change, which sort of makes sense given that the state of the system is unchanged, though this conflicts with the result of the previous experiment.

- v. The resolution of the Gibbs paradox is to assume that gas particles of the same species in a box are indistinguishable.

## Lecture 27: Complete treatment of the ideal gas

- 1) It's finally time to derive the thermodynamics of a gas of polyatomic molecules, which can not only translate, but also rotate and vibrate. We already have a translational single-particle partition function, which we'll refer to here as  $Z_{\text{trans}}$ . The next steps are to compute the rotational ( $Z_{\text{rot}}$ ) and vibrational ( $Z_{\text{vib}}$ ) single-particle partition functions. Because the state probabilities and Boltzmann weight factors of independent motions multiply, so do their partition functions. Thus, the total single-particle partition function is  $Z_{\text{sp}} = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}}$ .
- 2) Polyatomic molecular rotations – semiclassical 3D treatment
  - a. Angular velocity  $\boldsymbol{\omega}$  and angular momentum  $\mathbf{L} = \mathbf{I} \cdot \boldsymbol{\omega}$  are vectors whose directions lie along the right-handed rotation axis. Moment of inertia  $\mathbf{I}$  is a symmetric rank-2 tensor. Kinetic rotational energy  $E = \frac{1}{2} \boldsymbol{\omega} \cdot \mathbf{I} \cdot \boldsymbol{\omega}$  is a scalar.
  - b. Assume the principle-axis coordinate system of the molecule, wherein  $\mathbf{I}$  is diagonal, and make the semiclassical substitution  $\mathbf{L} = \mathbf{J}\hbar$ , to obtain
 
$$E = \frac{1}{2} (I_x \omega_x^2 + I_y \omega_y^2 + I_z \omega_z^2) = \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z} \rightarrow \left( \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z} \right) \hbar^2.$$
  - c. Define convenience parameter  $\alpha = \frac{\theta}{T} = \frac{\hbar^2}{2Ik_B T}$  in terms of a characteristic rotational temperature  $\theta$  for each axis, which depends on the moment of inertia around that axis.
 
$$\frac{E}{k_B T} = \frac{\hbar^2}{2k_B T} \left( \frac{J_x^2}{I_x} + \frac{J_y^2}{I_y} + \frac{J_z^2}{I_z} \right) = \alpha_x J_x^2 + \alpha_y J_y^2 + \alpha_z J_z^2$$
  - d. The rotational partition function can be expressed as a sum over all possible rotational states, which reduces to an integral in the classical limit of very closely-spaced states.
 
$$\begin{aligned} Z_{\text{rot}} &= \sum e^{-E_s/k_B T} \rightarrow \int_0^\infty e^{-(\alpha_x J_x^2 + \alpha_y J_y^2 + \alpha_z J_z^2)} dJ_x dJ_y dJ_z \\ &= \left( \int_0^\infty e^{-\alpha_x J_x^2} dJ_x \right) \left( \int_0^\infty e^{-\alpha_y J_y^2} dJ_y \right) \left( \int_0^\infty e^{-\alpha_z J_z^2} dJ_z \right) = \left( \frac{\pi}{4} \right)^{3/2} \frac{1}{\alpha_x^{1/2}} \frac{1}{\alpha_y^{1/2}} \frac{1}{\alpha_z^{1/2}} \\ &\approx \frac{1}{\alpha_x^{1/2}} \frac{1}{\alpha_y^{1/2}} \frac{1}{\alpha_z^{1/2}} = \frac{T^{3/2}}{(\theta_{\text{rot}x} \theta_{\text{rot}y} \theta_{\text{rot}z})^{1/2}} = \left( \frac{T}{\theta_{\text{rot}}} \right)^{3/2} \rightarrow Z_{\text{rot}} = \left( \frac{T}{\theta_{\text{rot}}} \right)^{n_{\text{rot}}/2} \end{aligned}$$
  - e. Things to consider:
    - i.  $\theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B}$ , where  $\bar{I} = (I_x I_y I_z)^{1/3}$  is the geometric mean of  $I_x$ ,  $I_y$ , and  $I_z$ .
    - ii. The 3 in the exponent is actually number of rotation axes  $n_{\text{rot}}$  with non-zero moments of inertia. There are three cases of interest:  $n_{\text{rot}} = 3$  for a general polyatomic molecule,  $n_{\text{rot}} = 2$  for a linear molecule (no quantum energy for spinning around the linear axis), and  $n_{\text{rot}} = 0$  for a monatomic molecule.
    - iii. The high- $T$  limit is inherent to a semiclassical calculation; classical rotations are always accessible. In contrast, a quantum rotor can only begin to rotate when  $k_B T$  is comparable to the energy of the first rotational excited state.
    - iv. We didn't count orientational states, though doing so should add a prefactor of  $2\pi^2/\sigma_{\text{sym}}$ , where the number of rotational molecular symmetries ( $\sigma_{\text{sym}}$ ) avoids the overcounting of symmetry-equivalent orientations.  $2\pi^2$  is the area of a 3-sphere in 4-dimensions (the sum of all possible orientations). The factor is  $\sigma_{\text{sym}}$  important when comparing the entropies of different gasses.
    - v. We dropped the prefactor  $(\pi/4)^{3/2}$  as an unimportant semiclassical quirk.



3) Quantum linear rotor (simple case of a linear molecule which has only one value of  $I$ )

## a. Partition function

i.  $E_J = \frac{\hbar^2}{2I} J(J+1)$ , which is analogous to classical  $\frac{L^2}{2I} = \frac{1}{2} I \left(\frac{L}{I}\right)^2 = \frac{1}{2} I \omega^2$ .

ii. Define notational convenience parameter  $\alpha = \frac{\hbar^2}{2Ik_B T} = \frac{\theta_{rot}}{T}$ .

iii. Degeneracy at fixed energy:  $g_J = (2J+1)$  because  $m_J \in \{-J, \dots, +J\}$ . This is not the Lande  $g_J$  factor.

iv.  $Z_{rot} = \sum g_J e^{-E_J/k_B T} = \sum (2J+1) e^{-\alpha J(J+1)}$

 b. High temperature partition function (large range of accessible  $J$  states)

i.  $Z_{rot} \approx \sum 2J e^{-\alpha J^2} \rightarrow 2 \int_0^\infty J e^{-\alpha J^2} dJ = \frac{2}{2\alpha} = \frac{1}{\alpha} = \frac{T}{\theta_{rot}}$

ii. We have recovered the semi-classical linear molecule result of  $n_{rot} = 2$ .

## 4) Molecular vibrations (classical treatment)

a. For a molecule with  $n_{atoms}$  atoms, there will be  $n_{vib} = 3n_{atoms} - 6$  vibrational modes (eigenvectors), each of which may have a unique vibrational eigenfrequency. The exception is a linear molecule, which has  $n_{vib} = 3n_{atoms} - 5$  vibrational modes because it replaces one rotation with a vibration.

b. Symmetry considerations tell us that each normal mode of vibration will be independent of the others and will have its own partition function.

c. The energy of the  $i^{th}$  harmonic of the  $m^{th}$  vibrational mode is  $\epsilon_{m,i} = (1/2 + i)\Delta\epsilon_m$ , where  $\Delta\epsilon_m$  is the energy-level spacing of the mode.

d. For notational convenience, define  $\alpha_m = \frac{\Delta\epsilon_m}{k_B T} = \frac{\theta_m}{T}$ .

e. The partition function of the  $m^{th}$  mode is

$$Z_{vib(m)} = \sum_{i=0}^{\infty} e^{-\epsilon_{m,i}/k_B T} = \sum_{i=0}^{\infty} e^{-(1/2+i)\alpha_m} = \frac{1}{2} \operatorname{csch}\left(\frac{\alpha_m}{2}\right) = \frac{1}{2} \operatorname{csch}\left(\frac{1}{2} \frac{\theta_m}{T}\right).$$

At high temperatures (small  $\alpha = \frac{\theta_m}{T}$ ), this becomes  $Z_{vib(m)} \approx \frac{T}{\theta_m}$ .

f. The full single-particle vibrational partition function is  $Z_{vib} = \prod_{m=1}^{n_{vib}} Z_{vib(m)}$ , so that for multiple independent oscillator modes, we have  $Z_{vib} = \left(\frac{T}{\theta_1}\right) \left(\frac{T}{\theta_2}\right) \dots \left(\frac{T}{\theta_{n_{vib}}}\right)$ .

We then rewrite this as  $Z_{vib} = \left(\frac{T}{\theta_{vib}}\right)^{n_{vib}}$ , where  $k_B \theta_{vib} = \left(\prod_{m=1}^{n_{vib}} \Delta\epsilon_m\right)^{1/n_{vib}}$  is the geometric mean of the energy-level spacings over all vibrational modes.

## 5) Translational motion

a. We express the translational single-particle partition function in a notationally convenient form, which employs a temperature-like parameter  $\theta_{trans} = \frac{2\pi\hbar^2}{a^2 m k_B}$ . The result is

$$Z_{trans} = V n_Q = V \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} = V \left(\frac{T}{a^2 \theta_{trans}}\right)^{n_{trans}/2}, \text{ where } n_{trans} = 3 \text{ is the number of}$$

translational modes of a molecule in three dimensions. The parameter  $a$  is an arbitrary (i.e. meaningless) length scale that makes the units work out; its presence here is evidence that translational modes do NOT have a characteristic temperature because they are accessible at any temperature. We employ  $\theta_{trans}$  here only to achieve a matching form for  $Z_{trans}$ .

## 6) The complete ideal gas

- a. Define gas constant  $c = \frac{n_{\text{modes}}}{2} = \frac{1}{2}(n_{\text{trans}} + n_{\text{rot}} + 2n_{\text{vib}})$  is the total number of translational, rotational, and vibrational modes accessible to the molecule. As new modes become accessible with increasing temperature, its value increases.
- b.  $Z_{\text{sp}} = Z_{\text{trans}}Z_{\text{rot}}Z_{\text{vib}} = V \left( \frac{T}{a^2 \theta_{\text{trans}}} \right)^{n_{\text{trans}}/2} \left( \frac{T}{\theta_{\text{rot}}} \right)^{n_{\text{rot}}/2} \left( \frac{T}{\theta_{\text{vib}}} \right)^{2n_{\text{vib}}/2} = \frac{VT^c}{\text{const}}$
- c. We sometimes say that  $Z_{\text{tot}} = Z_{\text{trans}}Z_{\text{int}}$ , where  $Z_{\text{int}} = Z_{\text{rot}}Z_{\text{vib}}$  is the *internal* partition function associated with the internal degrees of freedom of the molecule.
- d. 
$$F = -k_B T \ln(Z_N) = -k_B T \{N \ln(Z_{\text{sp}}) - \ln(N!)\} \approx -Nk_B T \left\{ 1 + \ln \left( \frac{Z_{\text{sp}}}{N} \right) \right\}$$

$$= -Nk_B T \{1 + \ln(Z_{\text{trans}}Z_{\text{rot}}Z_{\text{vib}})\} = -Nk_B T \left\{ 1 + \ln \left( \frac{VT^c}{N} \right) - \ln(\text{const}) \right\}$$
- e. The value of the constant in the free energy can be determined using the temperature-like quantities above (various  $\theta$  values) if needed, or we can express it in terms of a reference state  $(V_0, T_0, N_0)$ , i.e. as  $\text{const} = V_0 T_0^c / N_0$ .
- f. 
$$F = -Nk_B T \left\{ 1 + \ln \left[ \left( \frac{V}{V_0} \right) \left( \frac{T}{T_0} \right)^c \left( \frac{N_0}{N} \right) \right] \right\} = -Nk_B T \left\{ 1 + \ln \left[ \frac{I}{I_0} \right] \right\}.$$

All ideal-gas magic is derived from this fundamental relation!
- g. Entropy  $S = Nk_B \left\{ (c+1) + \ln \left[ \left( \frac{V}{V_0} \right) \left( \frac{T}{T_0} \right)^c \left( \frac{N_0}{N} \right) \right] \right\} = Nk_B \{ (c+1) + c \ln[T] + \dots \}$  depends on  $c$ .
- h. We often only care about *changes* in free energy, entropy, or chemical potential, in which case the constant reference terms are eliminated in the difference calculation. Other thermodynamic properties of interest involve derivatives of the free energy, which also eliminate the constant. For example,  $U = Nk_B T^2 \frac{1}{Z_{\text{sp}}} \frac{\partial Z_{\text{sp}}}{\partial T} = cNk_B T$  and  $C_V = \left( \frac{\partial U}{\partial T} \right)_{N,V} = cNk_B$  do not contain the reference values. Observe that  $U$  and  $C_V$  are both linear in  $c$  so as to effectively *measure* the number of accessible modes!
- i. Observe that the free energy, entropy, internal energy, and heat capacity can each be described as a sum of contributions from each of the accessible modes. Thus, it is common to speak separately of the translational, rotational, or vibrational entropies, energies, and heat capacities.
- j. There are three cases of interest.
  - i. **General** (all modes):  $c = \frac{3+0+2 \cdot 0}{2} = \frac{3}{2}$  at low  $T$ ,  $c = \frac{3+3+2 \cdot 0}{2} = 3$  at room  $T$ , or  $c = \frac{3+3+2(3n_{\text{atoms}}-6)}{2} = 3n_{\text{atoms}} - 3$  at high  $T$ .
  - ii. **Linear** (2 rotations, one more vibration):  $c = \frac{3+0+2 \cdot 0}{2} = \frac{3}{2}$  at low  $T$ ,  $c = \frac{3+2+2 \cdot 0}{2} = \frac{5}{2}$  at room  $T$ , or  $c = \frac{3+2+2(3n_{\text{atoms}}-5)}{2} = 3n_{\text{atoms}} - \frac{5}{2}$  at high  $T$ .
  - iii. **Monatomic** (no rotations or vibrations):  $c = \frac{3+0+2 \cdot 0}{2} = \frac{3}{2}$  at all  $T$ .
- k. We previously determined that for a monatomic ideal gas,  $U = \frac{3}{2} Nk_B T = N \frac{1}{2} m v_{\text{rms}}^2$ , so that  $v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$ . For a polyatomic gas, we know that  $U = cNRT$ , suggesting a modification to the rms velocity. Because the other molecular degrees of freedom contained within  $c$  are internal rather than external, they play no role in the rms velocity. It is not necessary to modify this kinetic-theory expression for  $v_{\text{rms}}$ .

## 7) Optional details regarding rotational degeneracy

- a. The quantum-rotor derivation yielded  $n_{\text{rot}} = 2$ , corresponding to a linear molecule as expected. But where, exactly, was this decision made? The degeneracy factor  $g_J \propto J^{(n_{\text{rot}}-1)}$  encodes the  $n_{\text{rot}}$  dependence.
- b. Consider a 3D ( $n_{\text{rot}} = 3$ ) semi-classical rotor with the same moment of inertia on each axis:  $Z_{\text{rot}} = \int_0^\infty e^{-\alpha J^2} dJ_x dJ_y dJ_z = \frac{1}{8} \int_0^\infty e^{-\alpha J^2} (4\pi J^2) dJ = \int_0^\infty g(J) e^{-\alpha J^2} dJ$ .  
The degeneracy factor (i.e. the density of states) is  $g(J) = \pi J^2 / 2 \propto J^{(n_{\text{rot}}-1)}$ , which represents 1/8 of the surface of a sphere of radius  $J$ .
- c. For a linear ( $n_{\text{rot}} = 2$ ) semi-classical rotor,  $g(J) = \frac{2\pi J}{4} \propto J^{n_{\text{rot}}-1}$ , which is 1/4 of the circumference of a circle of radius  $J$ .
- d. For a circular planar ( $n_{\text{rot}} = 1$ ) semi-classical rotor, there is no degeneracy:  $g(J) \propto J^{n_{\text{rot}}-1} = 1$ .
- e. Useful integrals:  $\int x^{D-1} e^{-\alpha x^2} dx$  is  $\frac{\sqrt{\pi/4}}{\alpha^{1/2}}$  for  $D = 1$ ,  $\frac{1}{2\alpha}$  for  $D = 2$ ,  $\frac{1}{2} \frac{\sqrt{\pi/4}}{\alpha^{3/2}}$  for  $D = 3$ .

## Lecture 28: Exam Review

## Lecture 29: General treatment of ensembles, a grand-canonical ensemble treatment of the ideal gas

### 1) General ensemble associated with thermodynamic potential $\Phi$

- In general, the Boltzmann factor and partition function for the ensemble of states natural to thermodynamic potential  $\Phi$  has the form  $Z_\Phi = \sum_s e^{-(\Phi_s + TS)/k_B T}$ .
- Because the partition function is different for each thermodynamic potential, we'll indicate the type of potential  $\Phi$  as a subscript on  $Z$ , which we did not do previously.
- The associated microstate probabilities are  $P_s = \frac{1}{Z_\Phi} e^{-(\Phi_s + TS)/k_B T}$ .
- Substituting this probability into the Shannon entropy,  $S/k_B = -\sum_s P_s \ln(P_s)$ , yields the fundamental relation  $\langle \Phi \rangle = -k_B T \ln(Z_\Phi)$ .
- Take a moment to prove that this fundamental relation can also be presented as  $\frac{S}{k_B} = \ln[\sum_s e^{-(\Phi_s - \langle \Phi \rangle)/k_B T}]$ . This is a very general construct. See that a microstate with a low value of the thermodynamic potential (relative to the average value) carries the most information (i.e. contributes most to the entropy).

### 2) Microcanonical (isolated-system or fixed- $U$ ) ensemble

- Internal energy  $\Phi = U(S, V, N)$ . For an isolated system, every physically-accessible microstate has the same internal energy  $E_s = U$ , so that each state has the same Boltzmann factor. We could refer to the microstate energy as  $U_s$ , but have been calling it  $E_s$  all along, and so continue to do so.
- $Z_U = \sum_s e^{-(E_s + TS)/k_B T} = e^{-(U + TS)/k_B T} \sum_s 1 = \Omega e^{-(U + TS)/k_B T}$ , and each microstate has the same probability  $P_s = \frac{1}{Z_U} e^{-(U + TS)/k_B T} = \frac{1}{\Omega}$ .
- $U = -k_B T \ln(Z_U) = -k_B T \ln(\Omega e^{-(U + TS)/k_B T}) = -k_B T \ln(\Omega) + U + TS$ . Because  $U$  appears on both sides, we can rearrange this as  $S(U, V, N) = k_B \ln \Omega$ , which is the usual form of the FR of an isolated system. Though this might feel like a different approach to the microcanonical ensemble, it is actually the same approach.
- Alternatively,  $\frac{S}{k_B} = \ln[\sum_s e^{-(U_s - \langle U \rangle)/k_B T}] = \ln[\sum_s e^{-(U - U)/k_B T}] = \ln[\sum_s 1] = \ln(\Omega)$ .

### 3) Canonical (fixed- $T$ ) ensemble

- Helmholtz free energy  $\Phi = F(T, V, N) = U - TS$ . System is in contact with a temperature reservoir so that energy  $E_s$  varies from microstate to microstate and has mean values of  $\langle E \rangle$ , whereas  $T$  is constant.
- The "canonical" partition function is  $Z_F = \sum_s e^{-(F_s + TS)/k_B T} = \sum_s e^{-(E_s - TS + TS)/k_B T} = \sum_s e^{-E_s/k_B T}$ , and the microstate probability is  $P_s = \frac{1}{Z_F} e^{-E_s/k_B T}$ , as expected.
- The resulting fundamental relation is  $\langle F(T, V, N) \rangle = -k_B T \ln(Z_F)$ .
- For systems with independent particles (e.g. Einstein solid, paramagnet, or ideal gas), we can further add subscript  $N$  or "sp" to  $Z$  to indicate when we're using a multi-particle or single-particle partition function:  $Z_{FN} = Z_{Fsp}^N$  or  $Z_{Fsp}^N/N!$ . Unfortunately, not all systems are so convenient.

4) Grand-canonical (fixed- $T$  and fixed- $\mu$ ) ensemble

- a. Landau free energy  $\Phi = L(T, V, \mu) = U - TS - \mu N$ . System is in contact with both temperature and particle reservoirs, so that energy  $E_s$  and particle number  $N_s$  both vary by microstate and have respective mean values of  $\langle U \rangle$  and  $\langle N \rangle$ , whereas  $T$  and  $\mu$  are constant. Be aware that for macroscopic systems, where the relative fluctuations are small, we may not consistently display angle brackets on statistical variables.
- b. The “grand canonical” partition function is  $Z_L = \sum_s e^{-(L_s + TS)/k_B T} = \sum e^{-(E_s - TS - \mu N_s + TS)/k_B T} = \sum e^{-(E_s - \mu N_s)/k_B T}$ , and the microstate probability is  $P_s = \frac{1}{Z_L} e^{-(E_s - \mu N_s)/k_B T}$ .
- c. The resulting fundamental relation is  $\langle L(T, V, \mu) \rangle = -k_B T \ln(Z_L)$ .
- d. We’ll use this FR to calculate partial derivative  $\partial L / \partial \mu$ :
 
$$-\left(\frac{\partial L}{\partial \mu}\right)_{V,T} = k_B T \frac{1}{Z_L} \frac{\partial Z_L}{\partial \mu} = k_B T \frac{1}{Z_L} \sum \frac{\partial}{\partial \mu} e^{-(E_s - \mu N_s)/k_B T}$$

$$= k_B T \frac{1}{Z_L} \sum \left(\frac{N_s}{k_B T}\right) e^{-(E_s - \mu N_s)/k_B T} = \sum N_s \frac{1}{Z_L} e^{-(E_s - \mu N_s)/k_B T} = \sum N_s P_s = \langle N \rangle$$
- e. Because the differential form of  $L(T, V, \mu)$  is  $dL = -SdT - PdV - Nd\mu$ , it had to be true that  $\left(\frac{\partial L}{\partial \mu}\right)_{V,T} = -\langle N \rangle$ , regardless of the nature of the system.

## 5) Grand-canonical analysis of the ideal gas

- a. For a single particle, there is no distinction between microstates and energy levels. The probability of occupying the  $i^{th}$  energy level is proportional to Boltzmann factor  $P_s = \frac{1}{Z_L} e^{-(E_s - \mu N_s)/k_B T} \rightarrow P_i = \frac{\langle n_i \rangle}{\langle N \rangle} = \frac{1}{Z_{Lsp}} g_i e^{-(\epsilon_i - \mu)/k_B T} = \frac{1}{Z_{Lsp}} e^{\mu/k_B T} (g_i e^{-\epsilon_i/k_B T})$ .
- b. Here, we have defined a new quantity called the *fugacity*,  $z \equiv e^{\mu/k_B T}$ , which arises due to contact with a particle reservoir. And the single-particle Grand-canonical partition function is  $Z_{Lsp} = \sum_i g_i e^{-(\epsilon_i - \mu)/k_B T} = z (\sum_i g_i e^{-\epsilon_i/k_B T}) = z Z_{Fsp} = z n_Q V$ . See that we borrowed a previous result from past work on the canonical partition function associated with the Helmholtz potential.
- c. Because  $N$  is now a statistical variable, summing over all possible system states in the partition function requires summing over all possible values of  $N$ . This significantly impacts our calculation of the grand-canonical partition function, which achieves an especially simple form. With the series expansion of  $e^x$  in mind, we obtain  $Z_L = \sum Z_{LN} = \sum_N Z_{Lsp}^N / N! = e^{Z_{Lsp}} = e^{zn_Q V}$ .
- d. The Landau potential’s fundamental relation also has a very simple form.  $L(\mu, V, T) = -k_B T \ln(Z_L) = -k_B T Z_{Lsp} = -k_B T e^{\mu/k_B T} \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} V$
- e. The grand-canonical ensemble generates a few surprises. Here’s a big one involving the particle-number state equation.  $\langle N \rangle = -\left(\frac{\partial L}{\partial \mu}\right)_{V,T} = k_B T n_Q V \left(\frac{\partial z}{\partial \mu}\right) = z n_Q V = Z_{Lsp}$

This relationship was also evident from the form of  $Z_{Lsp}$  determine above, since

$$\sum \langle n_i \rangle = \sum \frac{\langle N \rangle}{Z_{Lsp}} z g_i e^{-\epsilon_i/k_B T} = \frac{\langle N \rangle}{Z_{Lsp}} z \sum g_i e^{-\epsilon_i/k_B T} = \frac{\langle N \rangle}{Z_{Lsp}} z n_Q V = \langle N \rangle.$$

- f. This relationship further allows us to derive the state equation  $L = -\langle N \rangle k_B T$ .
  - g. One can obtain the familiar Helmholtz FR from the Landau potential by a Legendre transform that swaps  $N$  for  $\mu$ . We'll skip a few steps by using above state equations.
    - i.  $L = U - TS - \mu \langle N \rangle = F - \mu \langle N \rangle$
    - ii.  $F = L + \mu \langle N \rangle = -\langle N \rangle k_B T + k_B T \ln(z) \langle N \rangle = -\langle N \rangle k_B T \{1 - \ln(z)\}$   
 $= -\langle N \rangle k_B T \left\{1 - \ln\left(\frac{\langle N \rangle}{n_Q V}\right)\right\} = -\langle N \rangle k_B T \left[1 + \ln\left(\frac{n_Q}{\langle n \rangle}\right)\right]$
    - iii. This is clearly the canonical-ensemble result, except that particle number and concentration are now statistical variables.
- 6) What is fugacity?
- a. Using the ideal-gas state equation,  $\frac{\mu}{kT} + \frac{s}{k} = c + 1$  and the Sackur-Tetrode equation,  $\frac{s}{k} = \ln\left(\frac{n_Q}{n}\right) + (c + 1)$ . we have previously shown that  $\frac{\mu}{kT} = -\ln\left(\frac{n_Q}{n}\right) = \ln\left(\frac{n}{n_Q}\right)$ .
  - b. See that the definition of ideal-gas fugacity ( $z = e^{\mu/k_B T}$ ) then implies that  $z = \frac{n}{n_Q}$ .  
 This may seem obvious in retrospect given that  $\langle N \rangle = z n_Q V$ .
  - c. We have at times referred to this concentration ratio as  $\frac{n}{n_Q} = \frac{I_0}{I} = \frac{P}{P_0} \left(\frac{T_0}{T}\right)^{c+1}$ , which is proportional to pressure at fixed temperature. Here,  $P_0$  and  $T_0$  refer to a reference state at the quantum concentration.
  - d. In the context of a real (non-ideal) gas, the fugacity coefficient  $\phi$  is defined in a slightly different way, which emphasizes the difference in chemical potential of a real gas versus ideal gas at the same (constant) temperature. Let  $P$  and  $P'$  be the respective pressures of an ideal gas and a real gas at temperature  $T$  and concentration  $n$ . The corresponding difference in chemical potential will be  $\frac{\Delta\mu}{kT} = \frac{\mu' - \mu}{kT} = \ln\left(\frac{P'}{P}\right) = \ln(\phi)$ , so that  $\phi = 1$  and  $\Delta\mu = 0$  for an ideal gas.

## Lecture 30: Quantum statistics

### 1) Particle interchange symmetry in quantum mechanics

- a. Two distinguishable particles:  $|0,0\rangle$ ,  $|1,1\rangle$ ,  $|0,1\rangle$ , and  $|1,0\rangle$  are distinct states.
- b. Two indistinguishable particles that are symmetric under particle interchange have states of the form  $\frac{|a\rangle|b\rangle+|b\rangle|a\rangle}{\sqrt{2}}$ . The 3 possible states are  $|0,0\rangle$ ,  $|1,1\rangle$  and  $\frac{|0\rangle|1\rangle+|1\rangle|0\rangle}{\sqrt{2}}$ . There are two ways for the particles to be in the same state, but only one way for them to be in different states. Particles whose multi-particle wave functions are symmetric under particle interchange are called “bosons”. Bosons can either be in different states or in the same state.
- c. Two indistinguishable particles that are antisymmetric under particle interchange have states of the form  $\frac{|a\rangle|b\rangle-|b\rangle|a\rangle}{\sqrt{2}} = -\frac{|b\rangle|a\rangle-|a\rangle|b\rangle}{\sqrt{2}}$ . Clearly, both  $|0\rangle|0\rangle - |0\rangle|0\rangle$  and  $|1\rangle|1\rangle - |1\rangle|1\rangle$  are identically zero. The only possible state is  $\frac{|0\rangle|1\rangle-|1\rangle|0\rangle}{\sqrt{2}}$ . In other words, there is exactly one way for the particles to be in different states, but no way for them to be in the same state. Particles whose multi-particle wave functions are antisymmetric under particle interchange are called “fermions”. No two fermions can occupy the same state.
- d. The spin-statistics theorem of relativistic quantum field theory tells us that bosons must have integer spins, and fermions must have half-integer spins.
- e. The elementary bosons include photons, W&Z bosons, and gluons (all with  $s = 1$ ), Higgs bosons (spin 0), and gravitons (spin 2), whereas the elementary fermions include all quarks and leptons (all with  $s = \frac{1}{2}$ ). Fermion-composite particles can be either bosons or fermions depending the number of fermions involved. A meson (consisting of two quarks) and a neutral He atom (one electron pair) have integer spins, and so are both bosons. A baryon (consisting of three quarks) and an  $\text{Fe}^{2+}$  ion (five unpaired outer-shell electrons) have half-integer spins, and so are fermions.

### 2) Quantum statistics

- a. We’ve been using the symbol  $n$  in two different ways:  $n_i \rightarrow n(\epsilon)$  is the number of particles per energy level, and  $n_{conc} = \frac{N}{V}$  is the number of particles per unit volume.
- b. While considering the quantum states of particles in a box, we previously assumed that  $n_i \ll g_i$  for an ideal gas, which allowed us to define a single-particle partition function and take a product over independent particles, resulting in  $n_{conc} \ll n_Q(T)$ . We’re now interested in high concentrations,  $n_i \geq g_i$  and  $n_{conc} \geq n_Q(T)$ , where the particles compete for scarce states and so are NOT independent.
- c. In this scenario, the average spacing between particles becomes smaller than their deBroglie wavelength, so their quantum wave functions overlap and interfere. We say the system becomes *degenerate*, or that it enters the *quantum statistics* regime. This use of the word “degenerate” indicates multiple particles sharing the same physical space, which is completely different our recent use of the same word to indicate multiple ( $g_i$ ) states per energy level or multiple ( $\Omega$ ) microstates per macrostate. Try not to be confused by different uses of this word in close proximity.
- d. In summary, the classical regime has  $n_i \ll g_i$  and  $n_{conc} \ll n_Q(T)$ , while the quantum or degenerate regime has  $n_i \geq g_i$  and  $n_{conc} \geq n_Q(T)$ .



## 3) Quantum statistics in the grand-canonical ensemble

- a. Due to temperature and particle reservoir contact, particle number, energy, and energy-level occupancy are all statistical averages rather than fixed quantities.
- b. In the quantum-statistics regime, we'll need a new approach to calculating the partition function. Here's the key: The quantized momentum states of a given energy level are always independent, even if the particles themselves are not. So, instead of considering the quantum (momentum) states accessible to a specific particle, we'll now consider the particle-occupancies accessible to a specific quantum state.
- c. We previously defined  $g_i$  and  $\langle n_i \rangle$  as the respective number of momentum states and average occupancy (average number of particles) in the  $i^{th}$  energy level. Go back and review the figure illustrating definition of  $g_i$  in the Lecture 26 notes. We now also define  $\langle f_i \rangle \equiv \langle n_i \rangle / g_i$  to be the single-state occupancy factor, which is the average number of particles per state within the  $i^{th}$  energy level.
- d. The average total number of particles in the system is  $\langle N \rangle = \sum_i \langle n_i \rangle = \sum_i g_i \langle f_i \rangle$ , and probability that a given particle is in the  $i^{th}$  energy level is  $P(\epsilon_i) = \langle n_i \rangle / \langle N \rangle$ .
- e. The probability that the occupancy of a given quantum state of the  $i^{th}$  energy level is exactly  $f_i$  turns out to be proportional to the grand-canonical Boltzmann factor  $e^{-(E_s - \mu N_s) / k_B T} \rightarrow e^{-(\epsilon_i f_i - \mu f_i) / k_B T} = e^{-f_i(\epsilon_i - \mu) / k_B T} = (e^{-(\epsilon_i - \mu) / k_B T})^{f_i}$ , where  $N_s \rightarrow f_i$  and  $E_s \rightarrow \epsilon_i f_i$  are the number of particles and energy of each quantum state.
- f. We now define the single-state partition function for a specific quantum state in the  $i^{th}$  energy level as  $Z_{ssi} = \sum_{f_i} e^{-f_i(\epsilon_i - \mu) / k_B T}$ , where the sum is over all allowed values of  $f_i$ . The allowed values will be different for fermions and bosons. The probability of observing single-state occupancy  $f_i$  is then  $P(f_i) = \frac{1}{Z_{ssi}} e^{-f_i(\epsilon_i - \mu) / k_B T}$ , and the average single-state occupancy is computed as  $\langle f_i \rangle = \sum_{f_i} f_i P(f_i)$ .
- g.  $Z_{ssi}$  is the same for each of the  $g_i$  quantum states of the  $i^{th}$  energy level, and the grand-canonical partition function for the entire system is the product of the partition functions of each of the  $g_i$  independent states in each of the independent energy levels:  $Z_L = \prod_i Z_{ssi}^{g_i}$ .
- h. The Landau potential turns out to have distinct contributions from each energy level:  $L = -k_B T \ln(Z_L) = -k_B T \ln(\prod_i Z_{ssi}^{g_i}) = \sum_i L_i$ , where  $L_i = -k_B T g_i \ln(Z_{ssi})$ .
- i. Let's use this expression to verify the expected particle-number state equation for a degenerate quantum system (without differentiating between bosons and fermions):
 
$$-\left(\frac{\partial L}{\partial \mu}\right)_{V,T} = -\sum_i \left(\frac{\partial L_i}{\partial \mu}\right)_{V,T} = k_B T \sum_i \frac{\partial}{\partial \mu} \ln(Z_{ssi}^{g_i}) = k_B T \sum_i \frac{g_i}{Z_{ssi}} \frac{\partial Z_{ssi}}{\partial \mu} =$$

$$k_B T \sum_i \frac{g_i}{Z_{ssi}} \frac{\partial}{\partial \mu} \left\{ \sum_{f_i} e^{-f_i(\epsilon_i - \mu) / k_B T} \right\} = k_B T \sum_i \frac{g_i}{Z_{ssi}} \left\{ \sum_{f_i} \left( \frac{f_i}{k_B T} \right) e^{-f_i(\epsilon_i - \mu) / k_B T} \right\} =$$

$$\sum_i g_i \left\{ \sum_{f_i} f_i \frac{e^{-f_i(\epsilon_i - \mu) / k_B T}}{Z_{ssi}} \right\} = \sum_i g_i \left\{ \sum_{f_i} f_i P_{f_i} \right\} = \sum_i g_i \langle f_i \rangle = \sum_i \langle n_i \rangle = \langle N \rangle \quad \text{It works!}$$
- j. The energy associated with the  $i^{th}$  level is  $\langle U_i \rangle = \langle n_i \rangle \epsilon_i = g_i \langle f_i \rangle \epsilon_i$ , so that the total system energy is  $\langle U \rangle = \sum_i \langle U_i \rangle = \sum_i g_i \langle f_i \rangle \epsilon_i$ . Think again about the figure from the Lecture 26 notes.

## 4) Degenerate fermion statistics

- When treating fermions, refer to the single-state occupancy function as the Fermi-Dirac distribution. Its discrete and continuous forms can be written as  $\langle f_i \rangle_{FD}$  and  $f_{FD}(\epsilon)$ . Because only  $f_i = 0$  and  $1$  are allowed, the partition function has two terms.
- $Z_{ssi(FD)} = \sum_{f_i} (e^{-(\epsilon_i - \mu)/k_B T})^{f_i} = \sum_{f_i=0}^1 x_i^{f_i} = 1 + x_i = 1 + e^{-(\epsilon_i - \mu)/k_B T}$
- Approach involving derivative of the Landau free energy:  

$$\langle f_i \rangle = \frac{\langle n_i \rangle}{g_i} = -\frac{1}{g_i} \frac{\partial L_i}{\partial \mu} = \frac{k_B T}{Z_{ssi(FD)}} \frac{\partial Z_{ssi(FD)}}{\partial \mu} = k_B T \frac{x_i/k_B T}{1+x_i} = \frac{1}{1/x_i + 1} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}$$
- Alternative approach that emphasizes probabilities:  

$$\langle f_i \rangle = \sum_{f_i} f_i P(f_i) = \frac{1}{Z_{ssi(FD)}} \sum_{f_i=0}^1 f_i x_i^{f_i} = \frac{0 x_i^0 + 1 x_i^1}{1+x_i} = \frac{1}{1/x_i + 1} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}$$
- The fundamental relation looks a bit complicated due to the infinite sum. It could be expressed more simply in terms of  $q$ -Pochhammer symbols, which is not worth it. ☺  

$$L = \sum_i L_i = -k_B T \sum_i g_i \ln(Z_{ssi(FD)}) = -k_B T \sum_i g_i \ln(1 + e^{-(\epsilon_i - \mu)/k_B T})$$

## 5) Degenerate boson statistics

- When treating bosons, refer to single-state occupancy function as the Bose-Einstein distribution. Its discrete and continuous forms can be written as  $\langle f_i \rangle_{BE}$  and  $f_{BE}(\epsilon)$ . All non-negative values of  $f_i$  from  $0$  to  $\infty$  are allowed for bosons.
- $Z_{ssi(BE)} = \sum_{f_i} e^{-f_i(\epsilon_i - \mu)/k_B T} = \sum_{f_i=0}^{\infty} x_i^{f_i} = \frac{1}{1-x_i} = \frac{1}{1-e^{-(\epsilon_i - \mu)/k_B T}}$  for  $\epsilon_i > \mu$
- Approach involving derivative of the Landau free energy:  

$$\langle f_i \rangle = \frac{\langle n_i \rangle}{g_i} = -\frac{1}{g_i} \frac{\partial L_i}{\partial \mu} = \frac{k_B T}{Z_{ssi(BE)}} \frac{\partial Z_{ssi(BE)}}{\partial \mu} = \frac{k_B T}{Z_{ssi(BE)}} \frac{\partial Z_{ssi(BE)}}{\partial x} \frac{\partial x_i}{\partial \mu} = \frac{1}{1/x_i - 1} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} - 1}$$
- Alternative approach that emphasizes probabilities:  

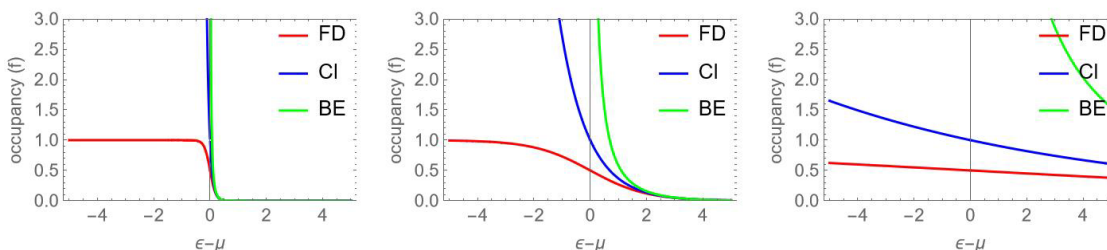
$$\langle f_i \rangle = \sum_{f_i} f_i P(f_i) = \frac{1}{Z_{1i}} \sum_{f_i=0}^{\infty} f_i x_i^{f_i} = (1-x_i) \frac{x_i}{(1-x_i)^2} = \frac{1}{1/x_i - 1} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} - 1}$$
- The fundamental relation still looks a bit complicated due to the infinite sum.  

$$L = \sum_i L_i = -k_B T \sum_i g_i \ln(Z_{ssi(BE)}) = k_B T \sum_i g_i \ln(e^{(\epsilon_i - \mu)/k_B T} - 1)$$

## 6) The quantum-classical transition

- Passing from  $\langle n_i \rangle < g_i$  to  $\langle n_i \rangle > g_i$  is called the quantum-classical transition.
- $\frac{\langle n_i \rangle}{g_i} = f(\epsilon_i) = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} \pm 1}$  where  $+/-$  signs apply to fermions/bosons, respectively.
- In the limit of low-concentration,  $\langle n_i \rangle \ll g_i$ , which requires that  $e^{(\epsilon_i - \mu)/k_B T} \gg 1$ , we have  $\langle f_i \rangle \rightarrow e^{-(\epsilon_i - \mu)/k_B T}$  and  $\langle n_i \rangle \rightarrow g_i e^{-(\epsilon_i - \mu)/k_B T} = z g_i e^{-\epsilon_i/k_B T}$ .
- We recover classical statistics, where  $Z_{LSP} = z \sum_i g_i e^{-\epsilon_i/k_B T} = \sum_i \langle n_i \rangle = \langle N \rangle$ . Recall the ideal gas case from a previous lecture, for example.

Compare Fermi-Dirac, Bose-Einstein, and classical single-state occupancy distributions as a function of  $\epsilon - \mu$  for three temperatures:  $k_B T = \{0.1, 1, 10\}$ . Observe that the  $0 \leq \langle f \rangle_{FD} \leq 1$ . Also notice that  $\langle f \rangle_{BE} \rightarrow \infty$  as  $\epsilon \rightarrow \mu_-$ . The classical result lies in between the two.



## Lecture 31: Degenerate Fermi gas

### 1) Introduction and review of related concepts

- a. We'll now explore the thermodynamics of a degenerate Fermi gas using the same quantized grid of momentum states previously employed for the ideal gas, which merely assumes quantum particles in a box. But we now assume the particles to be fermions and to be degenerate, meaning that their wave functions spatially overlap.
- b. Examples of Fermi gasses (some of which will appear in HW assignments) include:
  - i. Electrons in a normal metal
  - ii. Metallic hydrogen
  - iii. Inertial confinement fusion
  - iv. Dissociated electrons in a white-dwarf
  - v. Neutrons in a neutron star
  - vi. Quark-gluon plasma in high-energy particle collision or after the Big Bang.
- c. The FD single-state occupancy function is  $\langle f_i \rangle_{FD} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}$ , and the fundamental relation is  $L = -k_B T \sum_i g_i \ln(Z_{ssi(FD)}) = -k_B T \sum_i g_i \ln(1 + e^{-(\epsilon_i - \mu)/k_B T})$  for a quantum-degenerate ( $n_i \geq g_i$ ,  $n_{conc} \geq n_Q$ ) collection of fermions.
- d. We now aim to develop the density of states  $g_i$  and energy-level occupancy function  $\langle n_i \rangle_{FD} = \langle f_i \rangle_{FD} g_i$  for a Fermi gas, which are needed to analyze its thermodynamics. With an appropriate form for  $g_i$ , one can imagine a simple closed-form expression for the fundamental relation above. In practice, this is quite tricky and involves special mathematical functions that are beyond the scope of our class. Rather than a full thermodynamic treatment, most undergraduate textbooks focus more narrowly on the temperature dependence of the heat capacity, which can be understood just in terms of  $\langle n_i \rangle_{FD} = \langle f_i \rangle_{FD} g_i$ . We'll take the same approach.
- e. It is convenient to work in the limit where energy levels are closely spaced and energy is treated as a continuous variable:  $\epsilon_i \rightarrow \epsilon$ ,  $\langle f_i \rangle \rightarrow f(\epsilon)$ ,  $g_i \rightarrow g(\epsilon)d\epsilon$ , and  $\langle n_i \rangle \rightarrow n(\epsilon)$ . G&W use discrete notation in Ch. 6 and continuous notation in Ch. 7.

### 2) The *spin degeneracy* (or *internal degeneracy*) factor of a particle is indicated here by the symbol $g_s$ , where subscript "s" means "spin" rather than specifying a microstate. The spin degeneracy of a particle allows more states per energy level than would otherwise be present.

- a. All spinless particles have  $g_s = 2 \cdot 0 + 1 = 1$ .
- b. Massive particles with spin  $s > 0$  have  $g_s = 2s + 1$ .
  - i. Electrons (spin  $1/2$ ) have  $g_s = 2 \cdot \frac{1}{2} + 1 = 2$ .
  - ii.  $^{87}\text{Rb}$  nucleus (spin  $3/2$ ) have  $g_s = 2 \cdot \frac{3}{2} + 1 = 4$ .
- c. Light-speed particles with spin  $s > 0$  have  $g_s = 2$ .
  - i. Photons (spin 1):  $g_s = 2$  even though  $2 \cdot 1 + 1 = 3$ . These two degenerate states are referred to as distinct *transverse polarizations* of light. Quantum-field theory dictates that longitudinal modes are inaccessible to particles that travel at the speed of light in vacuum (any free massless particle).
- d. Phonons have a 3D vector polarization, which is analogous to having spin = 1. Though massless, these quasiparticles don't travel at the speed of light in vacuum, and therefore have both longitudinal and transverse modes. Their internal (not really "spin") degeneracy is then equal to  $g_s = 2 \cdot 1 + 1 = 3$ .

## 3) Density of momentum states (fermions or bosons, relativistic or non-relativistic)

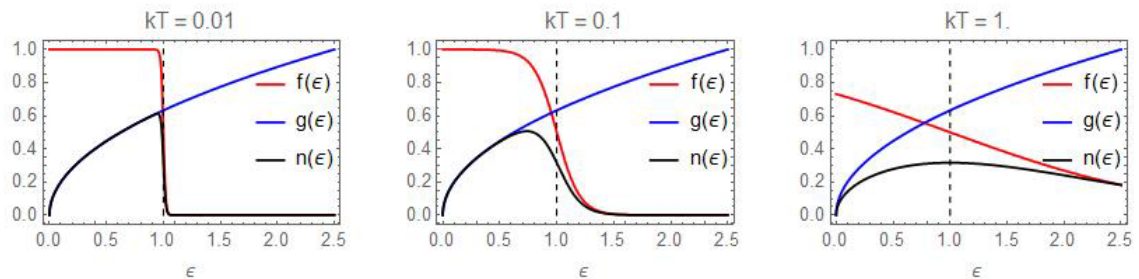
- i. For particles in a box of volume  $V = a^3$ , define a 3D momentum-state grid with spacing  $\Delta p = \frac{h}{2a} = \frac{\pi h}{a}$  in each direction, and count the number of states  $G(p)$  inside the positive octant of a sphere of radius equal to momentum  $p$ . The result is identical to earlier ideal-gas result, except that we now include the spin-degeneracy factor:  $G(p) = g_s \frac{1}{8} \frac{4\pi}{3} \left(\frac{p}{\Delta p}\right)^3 = g_s \frac{\pi}{6} \left(\frac{pa}{\hbar}\right)^3 = \frac{g_s V p^3}{6\pi^2 \hbar^3}$ .
- ii. The density of momentum states is  $g(p)dp = \frac{\partial G(p)}{\partial p} dp = \frac{g_s V p^2}{2\pi^2 \hbar^3} dp$ .

## b. Energy distribution (fermions or bosons)

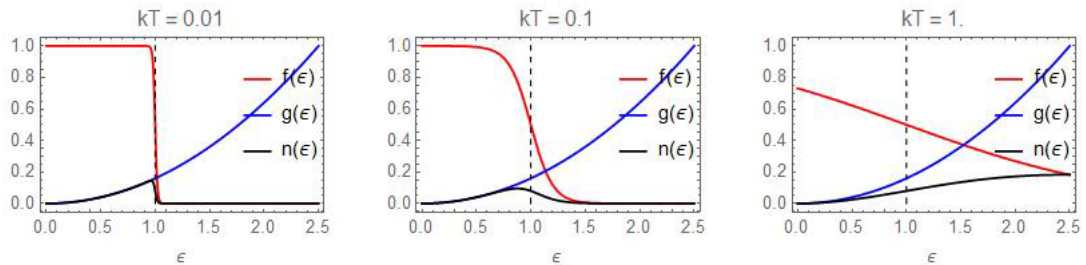
- i. Non-relativistic ( $\epsilon = \frac{p^2}{2m}$ ):  $g(\epsilon)d\epsilon = g(p(\epsilon)) \left(\frac{dp}{d\epsilon}\right) d\epsilon = \left(\frac{g_s m V (2m\epsilon)^{1/2}}{2\pi^2 \hbar^3}\right) d\epsilon$
- ii. Ultra-relativistic ( $\epsilon = pc$ ):  $g(\epsilon)d\epsilon = g(p(\epsilon)) \left(\frac{dp}{d\epsilon}\right) d\epsilon = \left(\frac{g_s V \epsilon^2}{2\pi^2 \hbar^3 c^3}\right) d\epsilon$
- c. Other distributions of interest include those for  $\omega = \frac{\epsilon}{\hbar}$ ,  $k = \frac{p}{\hbar}$ , and  $\lambda = \frac{h}{p}$ .

## 4) Energy-level occupancy

- a. Non-relativistic:  $n_{FD}(\epsilon) = f_{FD}(\epsilon)g(\epsilon) = \left(\frac{g_s m V (2m\epsilon)^{1/2}}{2\pi^2 \hbar^3}\right) \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$



- b. Ultra-relativistic:  $n_{FD}(\epsilon) = f_{FD}(\epsilon)g(\epsilon) = \left(\frac{g_s V \epsilon^2}{2\pi^2 \hbar^3 c^3}\right) \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$



- c. Interpret integrated areas:  $\int g(\epsilon)d\epsilon = \#$  of states and  $\int n_{FD}(\epsilon)d\epsilon = \#$  of particles.
- d. The plots shown here are little different that what is requested in the homework, both in terms of the temperatures and plot options.

## 5) Fermi energy (non-relativistic case)

- a. The chemical potential depends weakly on temperature. We define the *Fermi energy* to be the chemical potential at absolute zero temperature:  $\epsilon_F = \mu(T = 0)$ .
- b. At  $T = 0$ , observe that  $f_{FD}(\epsilon)$  is 1 for  $\epsilon \leq \epsilon_F$  and 0 for  $\epsilon > \epsilon_F$ . In other words, at absolute zero temperature, all states below the Fermi energy are fully occupied, whereas all states above the Fermi energy are unoccupied.
- c.  $\langle N \rangle = \int_0^\infty n_{FD}(\epsilon) d\epsilon = \int_0^{\epsilon_F} (1) g(\epsilon) d\epsilon = \int_0^{\epsilon_F} \frac{g_s m V (2m\epsilon)^{1/2}}{2\pi^2 \hbar^3} d\epsilon = \frac{2mV(2m)^{1/2}}{2\pi^2 \hbar^3} \left( \frac{2}{3} \epsilon_F^{3/2} \right)$ .
- d.  $n_{conc} = \frac{\langle N \rangle}{V} = \frac{1}{3\pi^2} \left( \frac{2m\epsilon_F}{\hbar^2} \right)^{3/2}$  and  $\epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n_{conc})^{2/3}$ . See that the Fermi energy depends on only particle concentration.
- e. The density of states in terms of the Fermi energy:  $g(\epsilon) d\epsilon = \langle N \rangle \frac{3}{2} \left( \frac{\epsilon}{\epsilon_F} \right)^{1/2} \frac{d\epsilon}{\epsilon_F}$
- f. Define a Fermi temperature  $T_F = \epsilon_F / k_B$ .
- g. Quantum statistics occur when  $n_{conc} = \frac{1}{3\pi^2} \left( \frac{2mk_B T_F}{\hbar^2} \right)^{3/2} \geq \left( \frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} = n_Q$  or  $T \leq T_F$ .
- h. Typical metals have electron densities of order  $n_{conc} = 10^{29} \text{ e/m}^3$ , Fermi energies of order  $\epsilon_F = 5 \text{ eV}$  and the Fermi temperatures of order  $T_F = 60,000 \text{ K}$ . The actual values may be higher or lower depending on the metal.

## 6) Heat capacity of a non-relativistic Fermi gas

- a. As temperature increases, the sharp corners on  $n_{FD}(\epsilon) = f_{FD}(\epsilon) g(\epsilon)$  become rounded as electrons get excited from energy levels below  $\epsilon_F$  to those above it. This increases the internal energy and is associated with an electronic heat capacity.
- b. Because didn't generate a fundamental relation in closed form, calculating the heat capacity requires a little cleverness.
- c.  $\frac{U(T=0)}{\langle N \rangle} = \langle \epsilon(T=0) \rangle = \frac{1}{\langle N \rangle} \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon = \frac{3}{2} \frac{1}{\epsilon_F^{3/2}} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon = \frac{3}{2} \frac{1}{\epsilon_F^{3/2}} \frac{2}{5} \epsilon_F^{5/2} = \frac{3}{5} \epsilon_F$
- d.  $U(T)/\langle N \rangle = \langle \epsilon \rangle = \epsilon_F + \langle \epsilon - \epsilon_F \rangle = \epsilon_F + \int_0^\infty (\epsilon - \epsilon_F) f(\epsilon) g(\epsilon) d\epsilon$ .
- e. Assume that  $\mu \approx \epsilon_F$  because it varies little with temperature (decreases very slowly).
- f.  $C_V = \frac{dU}{dT} = \int_0^\infty (\epsilon - \epsilon_F) g(\epsilon) \frac{df(\epsilon)}{dT} d\epsilon \approx g(\epsilon_F) \int_0^\infty (\epsilon - \epsilon_F) \frac{df(\epsilon)}{dT} d\epsilon$  because only  $f$  depends on  $T$  and because  $df(\epsilon)/dT$  is zero except in a narrow region around  $\epsilon_F$ .
- g.  $\frac{df(\epsilon)}{dT} = \frac{d}{dT} \frac{1}{e^{(\epsilon - \epsilon_F)/k_B T} + 1} = \frac{d}{dT} \left( \frac{1}{e^{\alpha} + 1} \right) = \frac{e^{\alpha}}{(e^{\alpha} + 1)^2} \frac{(\epsilon - \epsilon_F)}{k_B T^2} = \frac{\alpha e^{\alpha}}{T(e^{\alpha} + 1)^2}$
- h.  $C_V = \frac{dU}{dT} = g(\epsilon_F) \int_{-\epsilon_F/k_B T}^\infty (\alpha k_B T) \frac{\alpha e^{\alpha}}{T(e^{\alpha} + 1)^2} (k_B T d\alpha) \approx k_B^2 T g(\epsilon_F) \int_{-\infty}^\infty \frac{\alpha^2 e^{\alpha}}{(e^{\alpha} + 1)^2} dx = k_B^2 T \left( \frac{3}{2} \frac{\langle N \rangle}{\epsilon_F} \right) \left( \frac{\pi^2}{3} \right) = \frac{\pi^2}{2} \frac{N k_B^2 T}{\epsilon_F} = \frac{\pi^2}{2} \langle N \rangle k_B \left( \frac{T}{T_F} \right)$ , where we assumed that  $\epsilon_F / k_B T \rightarrow \infty$  because  $\epsilon_F \gg k_B T$  in the strongly degenerate domain.  
Heat capacity of a non-relativistic degenerate Fermi gas is  $C_V = \frac{\pi^2}{2} \langle N \rangle k_B \left( \frac{T}{T_F} \right)$ .
- i. For a metal, the electronic heat capacity is much smaller than the vibrational heat capacity. At room temperature, it's smaller by a factor of  $\frac{T}{T_F} \approx 0.01$ .
- j. Integrate to obtain the internal energy (as a series expansion), which increases quadratically with temperature:  $\frac{U(T)}{\langle N \rangle} \approx \frac{U(T=0)}{\langle N \rangle} + \int_0^T C_V dT = \frac{3}{5} \epsilon_F + \frac{\pi^2}{4} \frac{(k_B T)^2}{\epsilon_F}$ .

- k. Pressure can be computed as  $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\left(\frac{\partial U}{\partial V}\right)_{T,N} + T\left(\frac{\partial S}{\partial V}\right)_{T,N}$ . At very low temperatures,  $P \approx -\left(\frac{\partial U}{\partial V}\right)_{T,N} = -\frac{\partial U}{\partial \epsilon_F} \frac{\partial \epsilon_F}{\partial V} = -\frac{3}{5}\langle N \rangle \left(-\frac{2}{3} \frac{\epsilon_F}{V}\right) = \frac{2}{3} \frac{U}{V}$ , so that  $U = \frac{3}{2} PV$ . In other words, the electronic pressure of a degenerate Fermi gas has the same form as that of a non-degenerate monatomic ideal gas. This result turns out to be exact at all temperatures. The low-temperature approximation made here merely mitigates previous approximations in the energy derivation above. See Gould & Tobochnik page 333 for a more rigorous derivation of this state equation.

- 7) For a closed system, fermion number is conserved:  $N = \int_0^\infty n_{FD}(\epsilon) d\epsilon = \int_0^\infty \frac{g(\epsilon)}{e^{(\epsilon-\mu)/k_B T} + 1} d\epsilon$ . As temperature increases,  $N$  should clearly increase slightly at fixed  $\mu$ . Thus, for a closed system,  $\mu(T)$  must actually decrease slightly with temperature in order to keep  $N$  fixed. The first few terms in the series expansion of  $\mu(T)$ , which are derived using a Sommerfeld expansion, are as follows:

$$\mu = \epsilon_F \left\{ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{\epsilon_F} \right)^2 - \frac{\pi^4}{80} \left( \frac{k_B T}{\epsilon_F} \right)^4 + \dots \right\}$$



## Lecture 32: Black-body radiation and the photon gas

### 1) Fundamental relation for the photon gas.

- a. Black-body radiation can be understood as a photon gas, where the word “gas” implies that a collection of free (not necessarily independent) particles whose states can be defined in terms of a uniform momentum space. As ultrarelativistic massless spin-1 bosons, photons have an internal degeneracy factor of  $g_s = 2$  and energy levels governed by the dispersion relation  $\epsilon = pc$ . The cosmic microwave background of the universe is often modelled as a photon gas.
- b. The density of states are defined in the same way for both boson and fermion gases, as shown in the previous lecture. For a photon gas, we have the following:
  - i. Momentum density of states:  $g(p) = \frac{g_s V p^2}{2\pi^2 \hbar^3} = \frac{V p^2}{\pi^2 \hbar^3}$
  - ii. Relativistic energy density of states  $g(\epsilon) = \frac{g_s V \epsilon^2}{2\pi^2 (\hbar c)^3} = \frac{V \epsilon^2}{\pi^2 (\hbar c)^3}$
- c. An equilibrium photon gas always requires the use of quantum statistics. There are always low-energy ( $\epsilon < k_B T$ ) quantum-degenerate states with  $\langle n \rangle_{BE} / g = \langle f \rangle_{BE} > 1$ , despite the long tail of non-degenerate high-energy states with  $\langle f \rangle_{BE} < 1$ .
- d. The boundaries of a cavity inside a black body should be viewed as photon permeable. In equilibrium, the walls, which have finite temperature, emit photons into the cavity, and also absorb photons from the cavity, so that walls and the cavity have the same temperature and the same chemical potential. Because there are no photons present there,  $\mu = 0$  within the walls themselves. This implies that the chemical potential is zero in the cavity as well.
- e. Since  $\mu = 0$ , the grand-canonical Boltzmann simplifies to the form  $e^{-f_i \epsilon_i / k_B T}$ , the Bose-Einstein single-state partition function simplifies to  $Z_{ssi(BE)} = \frac{1}{1 - e^{-\epsilon_i / k_B T}}$ , and the average single-state occupancy simplifies to  $\langle f_i \rangle_{BE} = \frac{1}{e^{\epsilon_i / k_B T} - 1}$ .
- f. The Landau free energy,  $L = -k_B T \sum_i g_i \ln(Z_{ssi})$ , simplifies to
 
$$L = -k_B T \sum_i g_i \ln\left(\frac{1}{1 - e^{-\epsilon_i / k_B T}}\right) \rightarrow k_B T \int g(\epsilon) \ln(1 - e^{-\epsilon / k_B T}) d\epsilon =$$

$$\frac{(k_B T)^4 V}{\pi^2 (\hbar c)^3} \left\{ \int_0^\infty \epsilon^2 \ln(1 - e^{-\epsilon / k_B T}) d\epsilon \right\} = \frac{(k_B T)^4 V}{\pi^2 (\hbar c)^3} \left\{ \int_0^\infty \alpha^2 \ln(1 - e^{-\alpha}) d\alpha \right\}.$$
 Here, the zero value of the chemical potential has provided us with an integral that has a very convenient closed-form result. The quantity in curly brackets evaluates to  $-\pi^4/45$ .
- g.  $L(T, V) = -\frac{1}{3} \left\{ \frac{\pi^2 k_B^4}{15 (\hbar c)^3} \right\} V T^4 = -\frac{1}{3} b V T^4$ , where  $b = \frac{\pi^2 k_B^4}{15 (\hbar c)^3}$ . This is an FR!
- h. Observe that  $\mu$ , being identically zero, does not appear explicitly in the FR. In this sense, a photon gas is simpler than an ideal gas. The equilibrium state can be defined with only two variables.
- i. Pressure state equation:  $P = -\left(\frac{\partial L}{\partial V}\right)_T = -\left(\frac{\partial}{\partial V} \left[-\frac{1}{3} b V T^4\right]\right)_T = \frac{1}{3} b T^4$
- j.  $F(T, V) = L(T, V) - \mu N = L(T, V) = -\frac{1}{3} b V T^4$ . Because  $\mu = 0$ , the Helmholtz and Landau free energies prove to be identical.

k. Perform a Legendre transformation to obtain an FR for the internal energy.

i.  $S(T, V) = \left(-\frac{\partial F}{\partial T}\right)_V = \frac{4}{3} bVT^3$

ii.  $T(S, V) = \left(\frac{3}{4} \frac{S}{bV}\right)^{1/3}$

iii.  $U(S, V) = F + TS = \left(-\frac{1}{3} + \frac{4}{3}\right) bVT^4 = bVT^4 = bV \left(\frac{3}{4} \frac{S}{bV}\right)^{4/3} = \left(\frac{3^4}{4^4} \frac{S^4}{bV}\right)^{1/3}$

iv.  $S(U, V) = \frac{4}{3} (bVU^3)^{1/4}$ . We previously introduced this entropic FR without explanation in thermodynamics.

## 2) Counting photons

a. Neither chemical potential  $\mu$ , which is zero, nor photon number  $N$ , which is conjugate to  $\mu$ , appear in the photon gas FR. Though  $N$  is a useful state variable, we can't calculate it as a derivative of the FR. We'll find another way.

b. Useful integral:  $\int_0^\infty \frac{x^m dx}{e^x - 1} = m! \zeta(m+1)$ , where  $\zeta(m)$  is the Riemann zeta function.

$$\zeta(2) = \frac{\pi^2}{6} \approx 1.645, \quad \zeta(3) \approx 1.202, \quad \zeta(4) = \frac{\pi^4}{90} \approx 1.082, \quad \zeta(m) \rightarrow 1 \text{ as } m \rightarrow \infty$$

c.  $\langle N \rangle = \int n_{BE}(\epsilon) d\epsilon = \int g(\epsilon) f_{BE}(\epsilon) d\epsilon = \frac{2 \zeta(3)}{\pi^2} \frac{V (k_B T)^3}{(\hbar c)^3} = aVT^3$ , where  $a = \frac{2 \zeta(3)}{\pi^2} \frac{k_B^3}{(\hbar c)^3}$ .

d.  $\langle U \rangle = \int \epsilon n_{BE}(\epsilon) d\epsilon = \int \epsilon g(\epsilon) f_{BE}(\epsilon) d\epsilon = \frac{\pi^2 V (k_B T)^4}{15 (\hbar c)^3} = bVT^4$  (knew this already)

e. In equilibrium at 300 K

i.  $\hbar c \approx 1975 \text{ eV} \cdot \text{\AA}$  and  $k_B T = 25.9 \text{ meV}$

ii.  $n_{conc} = \frac{\langle N \rangle}{V} = 5.47 \times 10^{14} / \text{m}^3$  and  $u = \frac{\langle U \rangle}{V} = 2.26 \times 10^{-6} \text{ J/m}^3$

## 3) Summary of common thermodynamic state equations for a photon gas.

a.  $S = \frac{4}{3} (bVU^3)^{1/4} = \frac{4}{3} bVT^3$ ,  $N = aVT^3$ ,  $U = bVT^4 = 3PV$ ,  $P = \frac{1}{3} bT^4$

b. A variety of other three-variable state equations can also be derived.

## 4) Stefan-Boltzmann power law

a. For a gas, the mass flux density (units of mass/area/second) incident on a surface with inward normal vector  $\hat{n}$  is  $J = \langle \rho \mathbf{v} \cdot \hat{n} \rangle = \rho \langle v \cos(\theta) \rangle$ , where  $\rho$  is mass density,  $\mathbf{v}$  is fluid-particle velocity, and  $\cos(\theta)$  is the angle between the velocity of a given particle and the surface normal. Because gas particles move in every direction at every point in space with a distribution of velocity magnitudes, an average over velocity magnitudes and directions is needed.

b. In a photon gas, we care about energy density (energy per unit volume  $U/V$ ) rather than mass density, and also energy flux density or radiation intensity  $J$ , which is the amount of energy per unit area per unit time striking a surface. Because the relevant velocity is the speed of light, which is a constant, we have  $J = \frac{U}{V} c \langle \cos(\theta) \rangle$ .

Averaging over the half sphere of velocity directions that impinge on a planar surface yields  $\langle \cos(\theta) \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi/2} \cos(\theta) \sin(\theta) d\theta d\phi = 1/4$ .

c. So  $J = \frac{c}{4} \frac{U}{V} = \frac{c}{4} bT^4 = \frac{c}{4} \frac{\pi^2}{15} \frac{(k_B T)^4}{(\hbar c)^3}$ . We often write Stefan's law (a.k.a. the Stefan-Boltzmann law) as  $J = \sigma T^4$ , where  $\sigma = \frac{\pi^2}{60} \frac{k_B^4}{c^2 \hbar^3} = 5.67 \times 10^{-8} \text{ J/s/m}^2/\text{K}^4$ .



## 5) The black-body spectrum

- a. Spectral occupancy, or photons per frequency (
- $\nu$
- ) interval:

$$dN = n_{BE}(\epsilon)d\epsilon = n_{BE}(\epsilon(\nu))\frac{\partial \epsilon}{\partial \nu}d\nu \propto \frac{(h\nu)^2 d(h\nu)}{e^{h\nu/k_B T} - 1} \propto \frac{\alpha^2 d\alpha}{e^\alpha - 1} \text{ where } \alpha = \frac{\epsilon}{k_B T} = \frac{h\nu}{k_B T}.$$

This photon probability distribution over frequency peaks at  $\alpha_{peak} = 1.5936$ ; so photon concentration is greatest at  $\nu_{peak} = 1.5936 \left(\frac{k_B T}{h}\right)$ .

- b. Black-body frequency spectrum, or photon energy per frequency interval:

$$dU = \epsilon n_{BE}(\epsilon)d\epsilon = h\nu n_{BE}(\nu) h d\nu \propto \frac{(h\nu)^3 d(h\nu)}{e^{h\nu/k_B T} - 1} \propto \frac{\alpha^3 d\alpha}{e^\alpha - 1}. \text{ This is Planck's law!}$$

This function peaks at  $\alpha_{peak} = 2.8214$ ; so the concentration of photon energy is greatest at  $\nu_{peak} = 2.8214 \left(\frac{k_B T}{h}\right)$ .

- c. Spectral occupancy, or photons per wavelength (
- $\lambda$
- ) interval:

$$dN = n_{BE}(\epsilon)d\epsilon = n_{BE}(\epsilon(\lambda))\frac{\partial \epsilon}{\partial \lambda}d\lambda \propto \frac{\gamma^{-2}}{e^{1/\gamma} - 1} \left(\frac{d\gamma}{\gamma^2}\right) \propto \frac{\gamma^{-4} d\gamma}{e^{1/\gamma} - 1}, \text{ where } \gamma = \frac{k_B T}{\epsilon} = \frac{k_B T \lambda}{hc}.$$

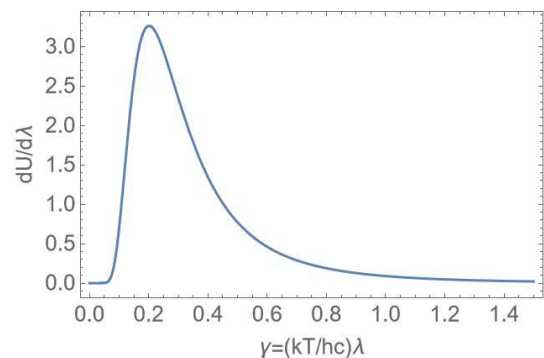
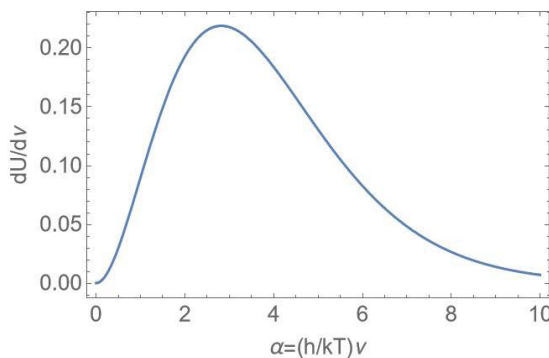
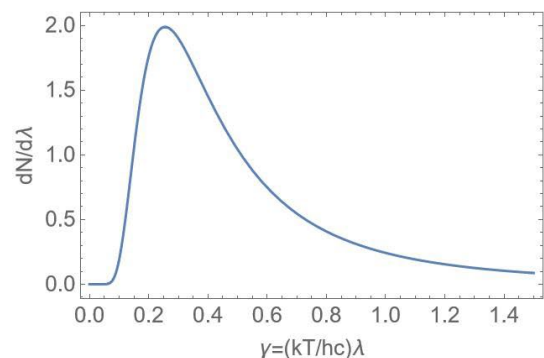
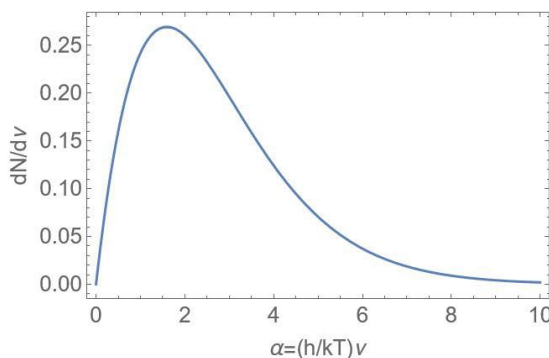
This photon probability distribution over wavelength peaks at  $\gamma_{peak} = 0.25506$ .

- d. Black-body wavelength spectrum, or photon energy per wavelength interval:

$$dU = \epsilon(\lambda) n_{BE}(\epsilon(\lambda)) \frac{\partial \epsilon}{\partial \lambda} d\lambda \propto \frac{\gamma^{-3}}{e^{1/\gamma} - 1} \left(\frac{d\gamma}{\gamma^2}\right) \propto \frac{\gamma^{-5} d\gamma}{e^{1/\gamma} - 1}. \text{ This is Planck's law!}$$

It peaks at  $\gamma_{peak} = 0.20141$ , so that  $\lambda_{peak} = 0.20141 \left(\frac{hc}{k_B T}\right) = \frac{(2.898 \times 10^{-3} \text{ m}\cdot\text{K})}{T}$ .

- e. The plots below show the probability distributions and the spectral densities (black-body spectra) for both frequency (proportional to energy) and wavelength (inversely proportional to energy). Unlike the plots requested in the homework, the horizontal-axis variables here depend on temperature, so that each plot applies simultaneously to all temperatures. The homework requires a sequence of fixed-temperature plots.



## Lecture 33: Phonons in solids

### 1) Quasiparticles

- a. The discussion of real/virtual photons in G&W chapter 8 is incorrect in the sense that their use of the word *virtual* contradicts common usage. Electromagnetic radiation consists of real rather than virtual photons. The fact that a particle isn't conserved doesn't mean it isn't real. Any boson or fermion particle can exist either in real (free) form or as a virtual vacuum fluctuation. Virtual *gauge bosons* (photon, gluon, W/Z) are of particular interest because they enact the fundamental forces of nature. This has nothing to do with the present content; it is mentioned here only to resolve confusion.
- b. A *quasiparticle* is a quantized excitation of a many-body system of interacting particles which itself behaves much like a fundamental particle; it exhibits the usual wave/particle properties of energy, frequency, momentum, wavelength, and position in time and space. Examples include phonons, magnons, plasmons, semiconductor electrons/holes, polarons, fractional quantum Hall effect quasiparticles (charge+flux), Cooper pairs, magnetic monopoles (in Dy spin ice), Dirac fermions (in graphene) and Majorana fermions (surface excitations in InSb superconducting nanowires).

### 2) Phonons in crystals

- a. A phonon is a quantized vibration of the atomic structure of a material. Even an amorphous solid or a liquid can have phonon excitations. But phonons are most often considered in the context of crystalline solids, where they are referred to as quantized *lattice* vibrations. In its vibrational ground state, the crystal is essentially a box in which phonons can move about freely like particles in a gas.
- b. Phonons are spinless ( $s = 0$ ), and therefore have no spin degeneracy, but still have internal degeneracy based on vibrational polarization. For a solid in three dimensions, the internal degeneracy factor of phonons is  $g_s = 3$ , corresponding to two transverse and one longitudinal polarizations. A liquid, on the other hand, can only support the longitudinal polarization, so that  $g_s = 1$ .
- c. A solid with  $N_a$  atoms will have  $3N_a$  vibrational modes (states), which are conceptually identical to the normal modes of vibration of a molecule or of a finite collection of balls and springs. Of course, the number of modes is much higher for a macroscopic solid for which  $N_a$  approaches Avogadro's number. A single vibrational mode (state) of momentum  $p$  and energy  $\epsilon$  is a standing wave involving the interactions amongst many atoms. While the atoms are NOT independent of one another, each vibrational mode (state) is effectively an independent oscillator which can store multiple energy quanta (phonons).
- d. The single-mode (single-state) occupancy factor  $f(\epsilon)$  counts the number of phonons per mode. Because they are bosons, there is no limit to the number of phonons we can distribute over a finite number of modes. The classical amplitude of a mode is proportional to the number of phonons it holds.
- e. As was the case for photons, phonon particle number is not conserved, so that  $\mu = 0$ . The single-state partition function and single-state occupancy function of a continuous energy variable are again simplified to the forms  $Z_{ss}(\epsilon) = 1 - e^{-\epsilon/k_B T}$  and  $f(\epsilon) = \frac{1}{e^{\epsilon/k_B T} - 1}$ . As before, the grand canonical partition function is the product of single-state partition functions over all states and all energy levels.

## 3) Density of states

- Each phonon momentum state has a dispersion relation of the form  $v = \epsilon/p = \omega/k$ , which looks relativistic; phonons are massless but travel only at the speed of sound in the material rather than at the speed of light. We treat the speed of sound as a constant (independent of  $\omega$ ) here, though this is at best a very rough approximation.
- The density of momentum states is just as derived previously for other gases:  

$$g(p)dp = \frac{g_s V p^2}{2\pi^2 \hbar^3} dp, \text{ with } g_s = 3.$$
- The density of energy states is  $g(\epsilon)d\epsilon = g(p(\epsilon)) \left( \frac{dp}{d\epsilon} \right) d\epsilon = \left( \frac{3V \epsilon^2}{2\pi^2 \hbar^3 v^3} \right) d\epsilon$ .
- For whatever reason, we most commonly discuss the phonon density of states in terms of angular frequency:  $g(\omega)d\omega = g(\epsilon(\omega)) \left( \frac{d\epsilon}{d\omega} \right) d\omega = \frac{3V \omega^2}{2\pi^2 v^3} d\omega$ .

## 4) Debye energy, frequency, and temperature

- The biggest difference in treating phonons vs photons, is that phonons have a minimum wavelength equal to twice the interatomic spacing in the material, leading to a maximum phonon energy and a maximum phonon frequency. We call them the Debye energy ( $\epsilon_D = \hbar \omega_D$ ) and Debye frequency ( $\omega_D = 2\pi v/\lambda_{min}$ ), respectively. We also define a Debye temperature ( $\theta_D = \hbar \omega_D/k_B$ ).
- Debye's key innovation was to assume that integrating the density of states  $g(\omega)$  from 0 to the  $\omega_D$  yields the total number ( $3N_a$ ) of accessible phonon modes (states).  

$$3N_a = \int_0^{\omega_D} g(\omega) d\omega = \frac{3V}{2\pi^2 v^3} \int_0^{\omega_D} \omega^2 d\omega = \frac{3V}{2\pi^2 v^3} \frac{\omega_D^3}{3} \rightarrow \omega_D = \left( 6\pi^2 \frac{N_a}{V} \right)^{1/3} v.$$
- Define unitless variable  $x = \frac{\hbar \omega}{k_B T}$ , so that  $x_D = \frac{\hbar \omega_D}{k_B T} = \frac{\theta_D}{T} = \left( 6\pi^2 \frac{N_a}{V} \right)^{1/3} \frac{\hbar v}{k_B T}$ .

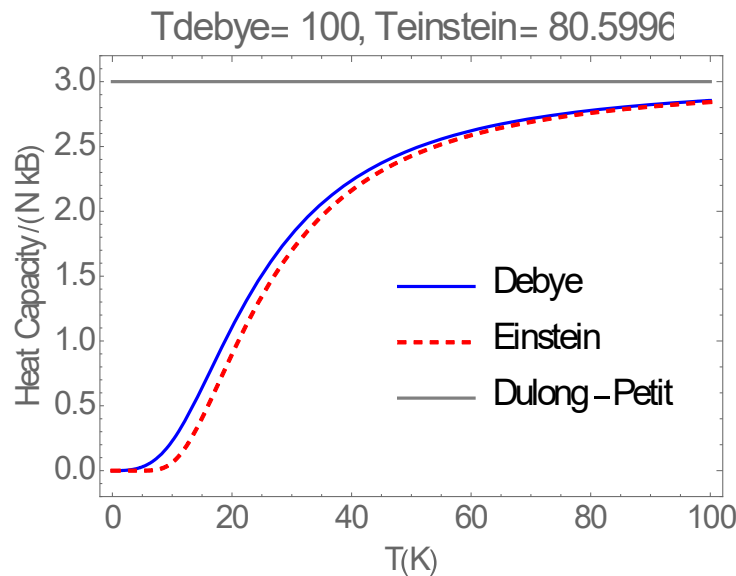
## 5) Phonon count, internal energy, and heat capacity of a Debye solid

- To obtain the number of phonons and the total internal vibrational energy, we only integrate up to the Debye frequency rather than to infinity.
- Define special function:  $I_m(x_D) \equiv \int_0^{x_D} \frac{x^m}{e^x - 1} dx \rightarrow m! \zeta(m+1)$  as  $x_D \rightarrow \infty$
- $\langle N \rangle = \int_0^{\omega_D} g(\omega) f(\omega) d\omega = \int_0^{\omega_D} \frac{3V \omega^2}{2\pi^2 v^3} \frac{d\omega}{e^{\hbar \omega/k_B T} - 1} = \frac{3V}{2\pi^2} \frac{(k_B T)^3}{(\hbar v)^3} \left\{ \int_0^{x_D} \frac{x^2 dx}{e^x - 1} \right\}$   

$$= \frac{3(N_a 6\pi^2)}{2\pi^2} \left\{ \frac{V}{N_a 6\pi^2} \frac{(k_B T)^3}{(\hbar v)^3} \right\} I_2(x_D) = \left( \frac{9N_a}{x_D^3} \right) I_2(x_D) = 9N_a \left( \frac{T}{\theta_D} \right)^3 I_2(x_D)$$
- $\langle U \rangle = \int_0^{\omega_D} \epsilon(\omega) g(\omega) f(\omega) d\omega = \int_0^{\omega_D} \frac{3V \omega^2}{2\pi^2 v^3} \frac{(\hbar \omega) d\omega}{e^{\hbar \omega/k_B T} - 1} = \frac{3V}{2\pi^2} \frac{(k_B T)^4}{(\hbar v)^3} \left\{ \int_0^{x_D} \frac{x^3 dx}{e^x - 1} \right\}$   

$$= \frac{3(N_a 6\pi^2)}{2\pi^2} k_B T \left\{ \frac{V}{N_a 6\pi^2} \frac{(k_B T)^3}{(\hbar v)^3} \right\} I_3(x_D) = \left( \frac{9N_a k_B T}{x_D^3} \right) I_3(x_D) = 9N_a k_B \left( \frac{T}{\theta_D} \right)^4 I_3(x_D)$$
- $C_V = \frac{\partial U}{\partial T} = 9N_a k_B \left( \frac{T^3}{\theta_D^3} \right) \left\{ \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2} \right\}$ . Derive this using integration variable  $\omega$ .
- Consider low temperatures, where  $x_D \rightarrow \infty$ .
  - $\langle N \rangle = (2\zeta(3)) \frac{9N_a}{x_D^3} = 21.646 N_a \left( \frac{T}{\theta_D} \right)^3$
  - $\langle U \rangle = \left( \frac{\pi^4}{15} \right) \frac{9N_a k_B T}{x_D^3} = \frac{3\pi^4}{5} \frac{N_a k_B T^4}{\theta_D^3}$
  - $C_V = \frac{12\pi^4}{5} N_a k_B \left( \frac{T}{\theta_D} \right)^3$

- g. Consider **high temperatures**, where  $e^x - 1 \rightarrow x$ .
- $\int_0^{x_D} \frac{x^2 dx}{e^x - 1} \rightarrow \int_0^{x_D} x dx = \frac{1}{2} x_D^2$  and  $\int_0^{x_D} \frac{x^3 dx}{e^x - 1} \rightarrow \int_0^{x_D} x^2 dx = \frac{1}{3} x_D^3$  and  $\int_0^{x_D} \frac{x^4 dx}{(e^x - 1)^2} \rightarrow \int_0^{x_D} x^2 dx = \frac{1}{3} x_D^3$
  - $\langle N \rangle = \frac{9N_a}{2x_D} = \frac{9}{2} N_a \left( \frac{T}{\theta_D} \right)$
  - $\langle U \rangle = 3N_a k_B T$
  - $C_V = 3N_a k_B$  as expected for a solid.
- h. For a typical metal **near room temperature** (an intermediate value):
- $9I_2(x_D)/x_D^3$  and  $9I_3(x_D)/x_D^3$  are of both of order 1, so that  $\langle N \rangle \approx N_a$  and  $\langle U \rangle \approx N_a k_B T$  to within an order of magnitude.
  - A cubic meter of copper has about 350 MJ of thermal energy. That amount of energy, in another form, could run a 100 W light bulb for well over a month!
- i. Compare sound velocities and densities for different materials using the link below (“Sound velocities in various solids”) to predict their Debye-temperature and low-temperature heat capacities. Aluminum and gold provide a nice comparison. Verify predictions using the online Mathematica demonstration called “Debye heat capacity”, which compares heat capacity curves.  
<https://www.rfcafe.com/references/general/velocity-sound-media.htm>
- j. See [https://en.wikipedia.org/wiki/Debye\\_model](https://en.wikipedia.org/wiki/Debye_model) for more details.
- 6) For a magnetic metal, consider the vibrational, electronic and magnetic degrees of freedom simultaneously in the total heat capacity. At low-temperatures vibrations scale like  $T^3$  while the electron gas contribution scales like  $T$ . The magnetic degrees of freedom, on the other hand, die off exponentially, and can be neglected relative to the other terms. The electronic term should dominate at low  $T$ , and the vibrational term should dominate at high  $T$ .
- $C_{\text{electronic}} = \frac{\pi^2}{2} \langle N_e \rangle k_B \left( \frac{T}{T_F} \right) = \frac{12\pi^4}{5} N_a k_B \left( \frac{T}{\theta_D} \right)^3 = C_{\text{phonon}}$  marks the crossover.
  - $T_{\text{crossover}} = \left( \frac{5}{24\pi^2} \frac{\langle N_e \rangle \theta_D^3}{N_a T_F} \right)^{1/2}$
- 7) Compare the vibrational heat capacities of the Debye and Einstein models:
- The vibrational heat capacity of an Einstein solid is  $C_V = 3N_a k_B \left( \frac{\theta_E}{2T} \right)^2 \text{csch}^2 \left( \frac{\theta_E}{2T} \right)$ , where  $\theta_E = \frac{\Delta\epsilon}{k_B} = \frac{\hbar\omega_E}{k_B}$ , and  $\Delta\epsilon$  and  $\omega_E$  are the respective energy spacing and fundamental frequency of the single-atom harmonic oscillators of the model. It is straightforward to show that  $\omega_E = \pi v \left( \frac{N_a}{V} \right)^{1/3} = \omega_D \left( \frac{\pi}{6} \right)^{1/3}$ .
  - High temperature limit: Einstein and Debye models agree nicely that  $C_V \rightarrow 3N_a k_B$ .
  - Low temperature limit: Einstein model predicts  $C_V \rightarrow 3N_a k_B \left( \frac{\theta_E}{T} \right)^2 e^{-\theta_E/T}$ , which is very different from the  $C_V = \frac{12\pi^4}{5} N_a k_B \left( \frac{T}{\theta_D} \right)^3$  decay predicted for the Debye model!
  - The Einstein solid contains independent oscillators that can be excited to arbitrarily high-energy levels. The Debye solid possesses collective vibrations in which all atoms are involved simultaneously, and so is much more accurate. Both improve on the Dulong-Petit model, which has a temperature-independent heat capacity.



- 8) Phonon band structure in crystals (for enlightenment – not tested)
- Crystals, which are defined by translational symmetry, have very interesting phonons.
  - Recall that  $p = \hbar k$ , so that momentum and wavevector can be used interchangeably to define the state space.
  - If there are  $N_{cell}$  repeating units in the crystal, where each repeating unit has  $N_{unit}$  atoms, there will be  $3N_{unit}$  different phonon branches, each containing  $N_a$  modes that follow a well-defined dispersion curve. Three of these branches will have linear dispersion near  $k = 0$  (the acoustic phonon branches) while all others will have finite values at  $k = 0$  (the optic modes). We only concern ourselves with acoustic phonons in the analysis above (one atom per repeating unit).
  - Each branch has a different  $k$ -dependent velocity in general.
  - The density of states has a singularity whenever the dispersion curve has a horizontal tangent ( $d\omega/dk = 0$ ).
  - Each segment of the band-structure diagram is a trace along a high-symmetry direction in 3D  $k$  space. The  $\Gamma$  point is the origin – acoustic modes go to zero there.
  - Even when you have a really complicated band-structure diagram, the heat capacity curve will look pretty much the same.
  - In an isotropic material, the phonon velocity is determined as  $\rho v^2 = C$ , where  $C$  is the bulk modulus (stiffness) of the material.
  - In an anisotropic solid, define the elastic dynamical matrix,  $D = \frac{1}{\rho} C_{i,j} k_i k_j$ , which is a symmetric matrix with three real eigenvalues and eigenvectors corresponding to three different acoustic branches. The eigenvalues are the  $\omega^2 = k^2 v^2$  values, and the three eigenvectors are the corresponding polarization directions. Quoted sound velocities are often directional averages of the real direction-dependent velocities.
  - Search online for “phonon band structure images” to find good visuals.
- 9) One can develop  $L(T, V)$  as an FR for the phonon gas in terms of special functions.

## Lecture 34: Bose-Einstein condensation

### 1) BEC introduction

- a. In a macroscopic system with a large number of states, any given state will normally hold only a small fraction of the total population. However, bosons do have the property that more than one particle can occupy the same quantum-mechanical state.
- b. Bose and Einstein predicted that when a collection of bosons is cooled below the quantum-classical transition temperatures, a macroscopic fraction of the particles will condense into the ground state. We refer to such a state as a Bose-Einstein condensate (BEC). Phase transitions in matter typically arise due to inter-particle interactions. The condensation of a BEC, however, is a quantum statistical phenomenon, and occurs even in the absence of inter-particle interactions.
- c. Being a quantum-degenerate gas, the wave-functions of the ground-state atoms of a BEC overlap, causing them to become mutually coherent on a macroscopic scale. This macroscopic quantum coherence gives a BEC remarkable properties. Beyond solids, liquids, gasses and plasmas, BECs are an entirely different phase of matter. See this BEC animation: <https://www.youtube.com/watch?v=shdLjlkRaS8>
- d. Though more exotic situations might exist, we will only concern ourselves with BECs based on a gas of non-relativistic baryonic particles, which implies the following:
  - i. The dispersion relation is  $\epsilon = p^2/2m$ .
  - ii. The momentum density of states is  $g(p) = \frac{g_s V p^2}{2\pi^2 \hbar^3}$ .
  - iii. The energy density of states is  $g(\epsilon) = \frac{g_s m V (2m\epsilon)^{1/2}}{2\pi^2 \hbar^3}$ .
  - iv. The spin-degeneracy factor for a spin- $S$  particle is  $g_s = 2S + 1$ .
  - v. Particle number is conserved, so that  $\mu \neq 0$ , which is essential for BEC. Photons and phonons do not form BECs for this reason.

### 2) Chemical potential and concentration

- a. The Bose-Einstein single-state occupancy is  $f_{BE}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} - 1}$ . We must require that  $\epsilon > \mu$  in order to avoid unphysical negative occupancies.
- b. We'll use the symbol  $\epsilon_G$  to refer to the energy of the lowest-energy state (i.e. the ground state) of the system. In a BEC,  $f_{BE}(\epsilon_G) \rightarrow N$  and  $f_{BE}(\epsilon > \epsilon_G) \rightarrow 0$ .
- c. Can we explain BEC in terms of the behavior of  $f_{BE}(\epsilon_G)$  as  $T \rightarrow 0$  for a temperature-independent value of  $\epsilon_G - \mu > 0$ ? How does  $f_{BE}(\epsilon_G)$  behave in that limit? Clearly, this doesn't work.
- d. At high temperature, where  $n_{conc} \ll n_Q = \left(\frac{mk_B T}{2\pi \hbar^2}\right)^{3/2}$ , the system can be described as an ideal gas with chemical potential  $\mu - \epsilon_G = -k_B T \ln\left(\frac{n_Q(T)}{n_{conc}}\right) < 0$ , so that  $\mu < \epsilon_G$ . Note that we used  $\epsilon_G$  rather than 0 as the reference energy. As the quantum concentration  $n_Q(T)$  drop below the particle concentration  $n_{conc}$  with decreasing temperature, this same relation would make  $\mu > \epsilon_G$ , which is not permitted as it would create an unphysical negative value of  $f_{BE}$ . To achieve BEC, where  $f_{BE} \rightarrow N$  (very large), we must somehow achieve  $\mu \rightarrow \epsilon_G$  rather than  $\mu > \epsilon_G$  as  $T \rightarrow 0$  in the quantum-degeneracy regime. How can this be accomplished when the total atom number and volume, and hence the particle concentration  $n_{conc}$ , are constant? The resolution of this paradox is for  $n_{conc}$  to drop as well. Is this possible?



- e. Let  $N_G$  be the number of particles in the ground state, and  $N_{ex}$  be the number of particles in excited states. Consider that in the past, when converting a sum over energy states into an integral over a continuous density of states, we started integrating at  $\epsilon = 0$  rather than at the state with the lowest quantized energy. Taking more care, we now instead write  $g_{BE}(\epsilon) \propto (\epsilon - \epsilon_G)^{1/2}$ , which implies that  $g(\epsilon_G) = 0$  and  $n_{BE}(\epsilon_G) = 0$ . In other words, the integral  $\int n_{BE}(\epsilon) d\epsilon$  only counts the atoms in excited states; it doesn't count the atoms in the ground state! Thus, we express the excited-state particle concentration as  $n_{ex} = N_{ex}/N = \int n_{BE}(\epsilon) d\epsilon$ , and use this in place of  $n_{conc}$  in comparisons to  $n_Q(T)$ .
- f. Though the total number of atoms,  $N = N_G + N_{ex}$ , must be conserved, atoms are allowed to disappear from the excited states when they transition into the ground state! The total concentration is the sum of ground-state and excited-state concentrations:  $n_{tot} = n_G + n_{ex}$ , where  $n_{tot} = N/V$ ,  $n_G = N_G/V$ , and  $n_{ex} = N_{ex}/V$ , and where  $N$  is conserved and  $V$  is held constant.
- g. Define  $a = \frac{g_s m^{3/2}}{\sqrt{2\pi^2 \hbar^3}}$  for notational convenience, and employ the fact that  $\mu \approx \epsilon_G$  in the quantum-degenerate regime to obtain the concentration of excited state atoms:
- $$\begin{aligned} n_{ex}(T) &= \frac{N_{ex}(T)}{V} = \frac{1}{V} \int_{\epsilon_G}^{\infty} n_{BE}(\epsilon) d\epsilon = a \int_{\epsilon_G}^{\infty} \frac{\sqrt{\epsilon - \epsilon_G} d\epsilon}{e^{(\epsilon - \mu)/k_B T} - 1} \approx a \int_{\epsilon_G}^{\infty} \frac{\sqrt{\epsilon - \epsilon_G} d(\epsilon - \epsilon_G)}{e^{(\epsilon - \epsilon_G)/k_B T} - 1} \\ &= a \int_0^{\infty} \frac{\sqrt{\epsilon'} d\epsilon'}{e^{\epsilon'/k_B T} - 1} = a (k_B T)^{3/2} \left\{ \int_0^{\infty} \frac{x^{1/2} dx}{e^x - 1} \right\} = \frac{g_s m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} (k_B T)^{3/2} \left\{ \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right) \right\} \\ &= \zeta\left(\frac{3}{2}\right) g_s \left(\frac{mk_B T}{2\pi \hbar^2}\right)^{3/2} \rightarrow n_{ex}(T) = 2.612 g_s n_Q(T). \end{aligned}$$
- This is in contrast to a constant value of  $n_{ex} = n_{conc}$  in the high-temperature (non-degenerate) regime.
- h. As temperature drops, the  $2.612 g_s n_Q(T)$  threshold eventually decreases below the fixed value of  $n_{conc}$ , and we enter the quantum-degenerate regime, where the Bose-Einstein condensate begins to form. We call the transition temperature  $T_{BE}$ , and write  $n_{ex}(T_{BE}) = 2.612 g_s n_Q(T_{BE}) = n_{conc}$ . Thus, the transition temperature is  $T_{BE} = \left(\frac{2\pi \hbar^2}{mk_B}\right) \left(\frac{n_{conc}}{2.612 g_s}\right)^{2/3}$ .
- i. We can also see that  $\frac{n_{ex}(T)}{n_{conc}} = \frac{n_{ex}(T)}{n_{ex}(T_{BE})} = \frac{n_Q(T)}{n_Q(T_{BE})} = \left(\frac{T}{T_{BE}}\right)^{3/2}$ . This is just what we need maintain a negative value of  $\mu - \epsilon_G$  in  $f_{BE}$ .
- j. Below  $T_{BE}$ , the fraction of particles in the ground state is an order parameter that tracks the progress of the phase transition:  $\frac{n_G(T)}{n_{conc}} = 1 - \frac{n_{ex}(T)}{n_{conc}} = 1 - \left(\frac{T}{T_{BE}}\right)^{3/2}$ . See that the BEC formation is complete at  $T = 0$ .
- k. The fact that ground state occupancy  $f_{BE}(\epsilon_G) \rightarrow N$  as  $T \rightarrow 0$  implies the following temperature dependence of the chemical potential:  $\mu = \epsilon_G - \frac{k_B T}{N}$ . Why? Because the difference  $\epsilon_G - \mu$  is very small:  $\frac{1}{e^{(\epsilon_G - \mu)/k_B T} - 1} \approx \frac{1}{1 + \frac{\epsilon_G - \mu}{k_B T} - 1} = \frac{k_B T}{\epsilon_G - \mu} = N$ . Thus, chemical potential does approach the ground-state energy from below in the quantum degeneracy regime, as we anticipated it must.

## 3) BEC thermodynamics

- a. 
$$U = \int_0^\infty \epsilon g(\epsilon) f_{BE}(\epsilon) d\epsilon = \frac{g_s V m^{3/2}}{\sqrt{2} \pi^2 \hbar^3} \int_{\epsilon_G}^\infty \frac{\epsilon'^{3/2}}{e^{\epsilon'/k_B T} - 1} d\epsilon' = \frac{g_s V m^{3/2} (k_B T)^{5/2}}{\sqrt{2} \pi^2 \hbar^3} \left\{ \int_0^\infty \frac{x^{3/2}}{e^x - 1} dx \right\}$$
  

$$= \frac{2}{\sqrt{\pi}} g_s n_Q V k_B T \left\{ \frac{3\sqrt{\pi}}{4} \zeta\left(\frac{5}{2}\right) \right\} = 2.0122 g_s n_Q V k_B T = U = 0.7703 N_{ex} k_B T \propto VT^{5/2}$$
- b. Heat capacity:  $C_V = \frac{\partial U}{\partial T} = \frac{5}{2} \frac{U}{T} = \frac{15}{4} \zeta\left(\frac{5}{2}\right) k_B g_s n_Q V = C_V = 1.9257 N_{ex} k_B \propto VT^{3/2}$ .
- c. Gould and Tobochnik show that condensate pressure is  $P = \frac{3}{2} \frac{U}{V}$ , which is quite remarkable. Thus,  $P \propto T^{5/2}$  independent of both  $N$  and  $V$  – quite unlike an ideal gas. The pressure arises from atoms in the excited states, which are dropping away into the ground state as temperature decreases.
- d. It is very interesting that only atoms in the excited states contribute to pressure, internal energy, and heat capacity!

## 4) History

- a. Albert Einstein and Satyendra Bose (1924-5) originally predicted the formation of ground-state boson condensates. The community largely ignored them saying that interactions were certain to prevent a macroscopic condensate.
- b.  $^4\text{He}$  observed to be a superfluid at 2.17 K in 1938. It has quantized vortices. Noone made the connection to BECs initially.
- c. In the 1960s, Fritz London studied superconductivity in electronic solids, which involved phenomena reminiscent of the Bose-Einstein theory, leading him to wonder if electrons are bosons. Of course they are not. But electrons turn out to form quasi-particle pairs (called Cooper pairs), which are bosons, and flow without electrical resistance.
- d.  $^3\text{He}$  becomes a superfluid at 2.5 mK due to bosonic Cooper-pair formation. Discovered in 1970s, this state contributed to the 1996 and 2003 Nobel prizes. In  $^4\text{He}$ , the inter-particle interactions are so strong that BEC theory must be substantially modified to be applicable; it is viewed as an impure BEC system.
- e. Eric Cornell and Carl Weimann achieved atomic BEC (June 5, 1995) with a gas of 2000 laser-cooled  $^{87}\text{Rb}$  atoms at 170 nK. Wolfgang Ketterle's group succeeded with over  $10^6$   $^{23}\text{Na}$  atoms in Sept 1995. They shared the 2001 Nobel prize.
- f. Mesons in the interiors of neutron stars, and those produced in certain high-energy collisions, are believed to form BECs.
- g. Photons in a white-wall microcavity form a type of BEC (Nov 2010). This is not really an equilibrium state, though it is still quite impressive.
- h. BEC condensates have been used for all sorts of interesting experiments since that time: superfluidity, slow light (ultra-high index of refraction), matter-wave interferometry, atom lasers, precision measurements, experimental access to weird quantum phenomena.



## Lecture 35: Interacting particles, mean-field theory, and the Van der Waals gas

### 1) Pairwise interactions

- For an ideal gas, the single-particle energy,  $E_a = p_a^2/2m$ , neglects interactions.
- If we add a pairwise interaction potential energy ( $\phi_{ab}$ ), the total energy becomes  $E = \sum_a \frac{p_a^2}{2m} + \frac{1}{2} \sum_{a \neq b} \phi_{ab}$ . We avoid infinite self energies by skipping the  $a = b$  terms in the sum; the factor of  $1/2$  avoids the double-counting of pairs.
- The potential might depend on the vector separation:  $\phi(\mathbf{r}_{ab} = \mathbf{r}_b - \mathbf{r}_a)$ , or merely on the magnitude of the separation:  $\phi(r_{ab} = |\mathbf{r}_b - \mathbf{r}_a|)$ , or be specific to each neighbor. Examples include springs:  $\phi_{ab} = \frac{1}{2} k r_{ab}^2$ , electrostatic charges:  $\phi_{ab} = k \frac{Q_a Q_b}{r_{ab}}$ , magnetic dipoles:  $\phi_{ab} = k \frac{3(\boldsymbol{\mu}_a \cdot \hat{\mathbf{r}}_{ab})(\boldsymbol{\mu}_b \cdot \hat{\mathbf{r}}_{ab}) - (\boldsymbol{\mu}_a \cdot \boldsymbol{\mu}_b)}{r_{ab}^3}$ . An especially simple way to allow scalar variables to interact is the *scalar contact* term,  $\phi_{ab} = -J \sigma_a \sigma_b$ , where the one-dimensional spin value  $\sigma_a$  at each site is equal to  $\pm 1$ .

### 2) Mean-field treatment of a non-ideal (Van der Waals) gas

- The partition function for a system of interacting particles can't be strictly separated into a product of independent single-particle partitions functions because the particles are not independent. Let's just assume that the total interaction of one atom with all other atoms is the same no matter which atom we pick. This is *mean field theory* (MFT), which accounts for interactions while still allowing us to use an approximate single-particle partition function; it's accuracy varies from problem to problem.

$$b. \quad Z_N = \frac{1}{N!} \sum e^{-E_s/k_B T} = \frac{1}{N!} \sum_{\{r, p\}} e^{-[\sum_a p_a^2/2m + (1/2) \sum_a \sum_{b \neq a} \phi(|r_b - r_a|)]/k_B T}$$

The sum  $\{r, p\}$  is over all possible combinations of multi-atom positions and momenta (the actual values of each of the variables  $\mathbf{r}_a$  and  $\mathbf{p}_a$ ).

Convert the exponential of a sum over atom index  $a$  into a product of exponentials,

$$Z_N = \frac{1}{N!} \sum_{\{p, r\}} \prod_a e^{-[p_a^2/2m]/k_B T} e^{-[(1/2) \sum_{b \neq a} \phi(|r_b - r_a|)]/k_B T}$$

- Invoke MFT to make the average interaction potential identical for each atom  $a$ , so that it doesn't matter where the atom is located. That way, we can imagine that  $\mathbf{r}_a$  is at the origin and call it  $\mathbf{r}_0$ . Define distance variable  $r' = |\mathbf{r}_b - \mathbf{r}_a| \rightarrow |\mathbf{r}_b - \mathbf{r}_0|$  for all  $b \neq 0$ . Define van der Waals parameters  $a$  and  $b$ , distinct from the atom indices  $a$  and  $b$ . Convert the sum over  $b \neq 0$  into an integral over the volume not occupied by the atom at  $\mathbf{r}_0$ , where  $r'$  is the integration variable.

$$a \equiv -\frac{1}{2} \sum_{b \neq 0} \phi(|\mathbf{r}_b - \mathbf{r}_0|) \frac{V}{N} = -\frac{1}{2} \int_{r_{\min}}^{\infty} \int \phi(r') dr'^3 = -\frac{1}{2} \int_{r_{\min}}^{\infty} \phi(r') 4\pi r'^2 dr'$$

Here, we let  $V/N \rightarrow dr'^3$ , which can be recast as  $4\pi r'^2 dr'$  after integrating out the angular degrees of freedom in the interaction potential due to spherical symmetry.

The excluded volume is  $b = \frac{4}{3} \pi r_{\min}^3$ , where  $r_{\min}$  is the closest possible half distance

for two neighboring atoms. The Lennard-Jones potential function,  $\phi(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$ ,

yields an especially simple result for  $a$ , though we won't specify  $\phi(r)$  here.

- d. The use of MFT allows us greatly simplify the partition function.

$$Z_N = \frac{1}{N!} \sum_{\{p,r\}} \prod_a (e^{-[p_a^2/2m]/k_B T} e^{a(N/V)/k_B T})$$

When summing/integrating over all possible positions  $\{r\}$ , however, we'll need to remember to exclude the volume  $b$  around each of the  $N$  atoms.

- e. Recalling the cereal-box analogy, convert the sum over multi-particle microstate products into a product of single-particle sums, and define single-particle partition function  $Z_{sp}$ .

$$\begin{aligned} Z_N &= \frac{1}{N!} \prod_a (\sum_{p_0 r_0} e^{-[p_0^2/2m]/k_B T} e^{a(N/V)/k_B T}) \\ &= \frac{1}{N!} (\sum_{p_0 r_0} e^{-[p_0^2/2m]/k_B T} e^{a(N/V)/k_B T})^N = \frac{1}{N!} Z_{sp}^N \end{aligned}$$

- f. As for the ideal gas case, convert the sums over  $p_0$  and  $r_0$  into integrals and separate the six-dimensional integral into momentum and position parts. Also, recall that the position integral needs to exclude the volume  $b$  around each of  $N$  atoms.

$$\begin{aligned} Z_{sp} &= \sum_{p_0, r_0} e^{-[p_0^2/2m]/k_B T} e^{a(N/V)/k_B T} = e^{a(N/V)/k_B T} \int e^{-[p_0^2/2m]/k_B T} \frac{dr_0 dp_0^3}{(\pi\hbar)^3} \\ &= e^{a(N/V)/k_B T} \left\{ \int e^{-p_0^2/2mk_B T} \frac{dp_0^3}{(\pi\hbar)^3} \right\} \left\{ \int_{\text{exclude } Nb} dr_0^3 \right\} \end{aligned}$$

In the first ideal-gas lecture, we found  $\int e^{-p_0^2/2mk_B T} \frac{dp_0^3}{(\pi\hbar)^3}$  to be the quantum concentration  $n_Q$ , so that  $Z_{sp} = n_Q(V - Nb)e^{a(N/V)/k_B T}$

- g. Fundamental relation for a Van der Waals gas:

i.  $Z_{sp} = n_Q(V - Nb)e^{a(N/V)/k_B T}$

ii.  $Z_N = \frac{(Z_{sp})^N}{N!}$

iii.  $F(N, V, T) = -k_B T \ln(Z_N)$

iv.  $P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = k_B T \frac{\partial \ln(Z_{sp}^N/N!)}{\partial V} = \frac{Nk_B T}{Z_{sp}} \frac{\partial Z_{sp}}{\partial V} = \frac{Nk_B T}{V - Nb} - a\left(\frac{N}{V}\right)^2$   
 $\rightarrow \left(P + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_B T$  Important VDW state equation.

## Lecture 36: Ising model

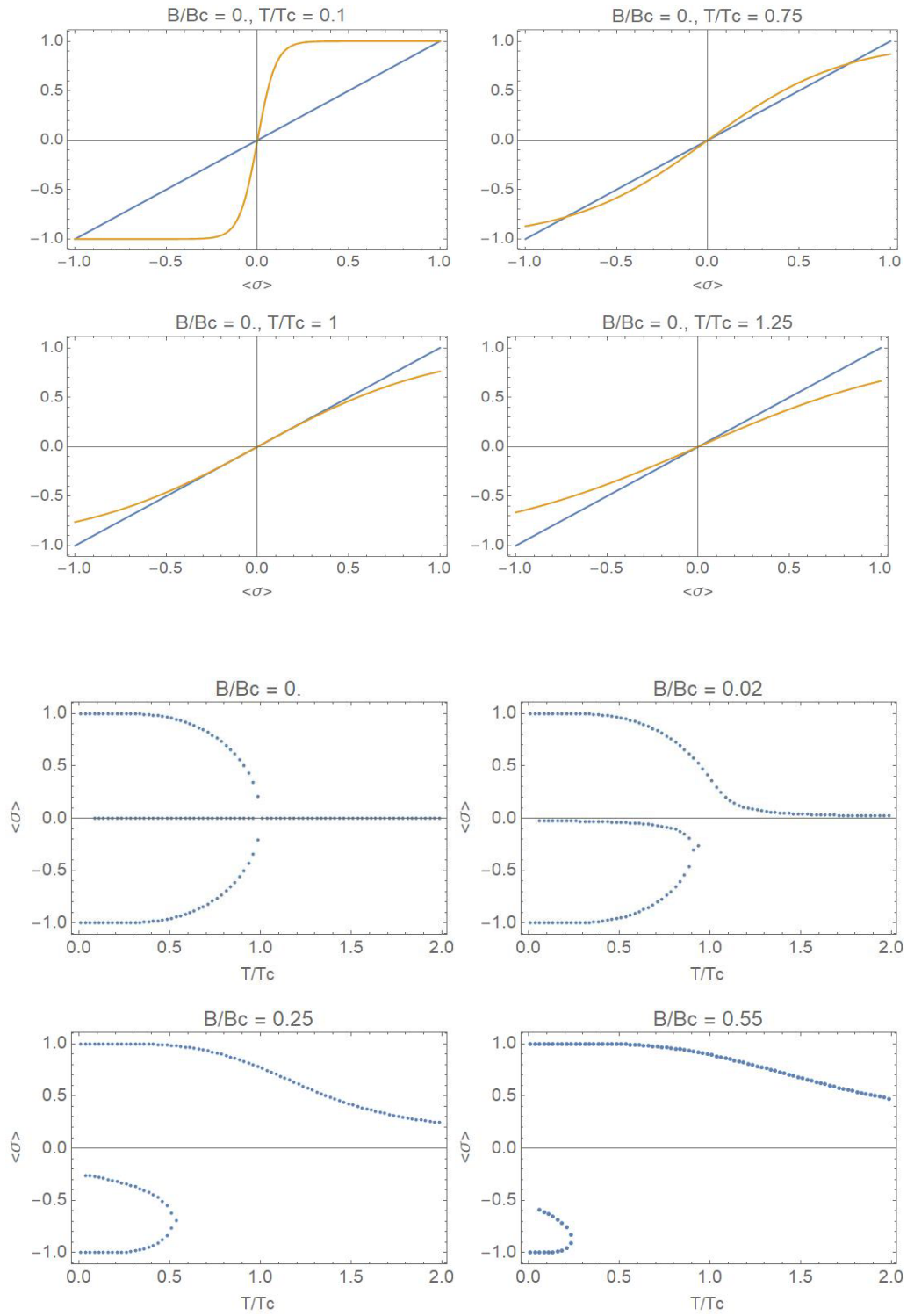
### 1) Ising model

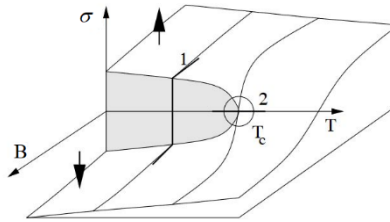
- a. Each particle is a two-state system described by a signed scalar variable ( $\sigma = \pm 1$ ). We usually think of  $\sigma$  as magnetic spin, though it can represent any two-state variable. An Ising model includes no translational/rotational freedom. It only has energy associated with the scalar variable  $\sigma$ .
- b. Distinguishable particles on a square or hexagonal lattice.
- c. Simple scalar-contact interactions:  $E = \frac{1}{2} \sum_{a \neq b} \phi_{ab} = -\frac{1}{2} \sum_{a \neq b} J_{ab} \sigma_a \sigma_b$ .
- d. Let  $J_{ab} = J$  for nearest neighbors and 0 otherwise, so that  $E = -J \sum_{\langle a, b \rangle} \sigma_a \sigma_b$ . Where the angle brackets around indices  $\langle a, b \rangle$  imply that the sum runs only over unique nearest neighbor pairs (also implying  $a \neq b$ ) without double counting. If you're worried about where the  $\frac{1}{2}$  went, refer to the article at [https://en.wikipedia.org/wiki/Mean-field\\_theory](https://en.wikipedia.org/wiki/Mean-field_theory).
- e. The interaction with an external magnetic field  $B$  involves energy  $-(\mu\sigma)B$  where  $\mu$  is the magnitude of the magnetic moment per particle.
- f. Total Ising-model microstate energy:  $E = -J \sum_{\langle a, b \rangle} \sigma_a \sigma_b - \mu B \sum_a \sigma_a$ .
- g. If  $J > 0$ , energy is minimized when neighboring spins have the same value. Such an interaction favors a ferromagnetic configuration (same spin on every site). If  $J < 0$ , energy is minimized when neighboring spins have the opposite value. Such an interaction favors an antiferromagnetic configuration wherein the spin variable alternates between  $\sigma = \pm 1$  in a checkerboard pattern for a square lattice. For a triangular network of spins, an anti-ferromagnetic interaction leads to magnetic *frustration*. Magnetic frustration lies at the heart of a wealth of exciting physics.

### 2) Mean-field treatment of the Ising model

- a.  $q$  is the number of nearest neighbors (depends on lattice shape and dimension). For a 2D square lattice,  $q = 4$ .
- b.  $\langle \sigma \rangle = \frac{1}{N} \sum_a \sigma_a$  is the time or configuration-averaged spin of the system
- c. Key insight -- mean field theory boils down to setting the average nearest-neighbor spin equal to  $\langle \sigma \rangle$  for every site. In essence, this says that there are no fluctuations -- the spin neighborhood of every site is representative of the mean. Of course, this is not true. But it is a very useful approximation that allows us to pretend that we have independent particles again.
- d. Single-site energy:  $E_a \approx -J \sum_{\langle \text{neighbors of } a \rangle} \langle \sigma \rangle \sigma_a - \mu \sigma_a B = -J q \langle \sigma \rangle \sigma_a - \mu \sigma_a B = -\mu \sigma_a \left( \frac{Jq}{\mu} \langle \sigma \rangle + B \right) = -\mu \sigma_a B_{\text{eff}}$ , where interactions with neighboring spins are folded into effective field:  $B_{\text{eff}} = \frac{Jq}{\mu} \langle \sigma \rangle + B$ .
- e. The partition function, summed over two possible states ( $\sigma = \pm 1$ ), is computed as  $Z_{sp} = \sum_{\sigma} e^{-E_{\sigma}/k_B T} = e^{\sigma_+ \mu B_{\text{eff}}/k_B T} + e^{\sigma_- \mu B_{\text{eff}}/k_B T} = e^{+\mu B_{\text{eff}}/k_B T} + e^{-\mu B_{\text{eff}}/k_B T} = e^{\alpha} + e^{-\alpha} = 2 \cosh(\alpha)$ , where  $\alpha = \mu B_{\text{eff}}/k_B T$ .
- f.  $Z_{\text{ising}} = Z_{sp}^N$ . Particles are distinguished by their position on the lattice.

- g. The magnetic Helmholtz free energy is:  $F(N, T, B) = -k_B T \ln(Z_{ising}) = -Nk_B T \ln(Z_{sp}) = -Nk_B T \ln(2 \cosh(\mu B_{eff}/k_B T))$ . This FR is identical to that of a classical two-state paramagnetic, except that  $B_{eff}$  depends on the average spin.
- h. The probabilities of these single-particle states are  $P_{\pm} = \frac{e^{\pm\alpha}}{Z_{sp}}$ . Use them to calculate  $\langle\sigma\rangle = \sigma_+ P_+ + \sigma_- P_- = \frac{(+1)e^{+\alpha}}{Z_{sp}} + \frac{(-1)e^{-\alpha}}{Z_{sp}} = \frac{(e^{\alpha} - e^{-\alpha})}{(e^{\alpha} + e^{-\alpha})} = \tanh(\alpha) = \tanh\left(\frac{\mu B_{eff}}{k_B T}\right) = \tanh\left(\frac{\mu B}{k_B T} + \frac{Jq\langle\sigma\rangle}{k_B T}\right)$ , which can be written as  $\langle\sigma\rangle = \tanh\left[\frac{T_c}{T}\left(\frac{B}{B_c} + \langle\sigma\rangle\right)\right]$ , where we defined critical mean-field temperature and comparable field:  $k_B T_c = Jq = \mu B_c$ .
- i. This is very different from a paramagnet. There exist non-trivial solutions for  $\langle\sigma\rangle$  even when  $B = 0$ , though they only arise below the critical temperature. The appearance of a spontaneous non-zero value of  $\langle\sigma\rangle$  marks a phase transition, for which  $\langle\sigma\rangle$  is the order parameter.
- j. Because  $\langle\sigma\rangle$  appears on both sides of the equation, and cannot be conveniently isolated, we must use numerical methods to obtain its value. Insert numerical values for  $\frac{T_c}{T}$  and  $\frac{B}{B_c}$ , and solve for  $\langle\sigma\rangle$  numerically, or simply plot the curves  $y = \langle\sigma\rangle$  and  $y = \tanh\left[\frac{T_c}{T}\frac{B}{B_c} + \frac{T_c}{T}\langle\sigma\rangle\right]$  on same graph to find their intersection.
- One stable solution at  $\langle\sigma\rangle = 0$ . This happens when  $B = 0$  and  $T \geq T_c$ .
  - Two stable solutions at  $\pm\langle\sigma\rangle \neq 0$  and one unstable solution at  $\langle\sigma\rangle = 0$ . This happens neither  $|B|$  nor  $T$  are too large. For example  $0 < |B| < B_c$  at  $T = 0$  and  $0 < T < T_c$  at  $|B| = 0$  meet this condition. To meet this condition in general, a larger  $|B|$  value requires a smaller  $T$  value, and vice versa.
  - One stable solution at  $\langle\sigma\rangle \neq 0$ . This happens when either  $B$  or  $T$  are sufficiently large. For example  $|B| > B_c$  at  $T = 0$  and  $T > T_c$  at  $|B| = 0$  meet this condition. To meet this condition in general, a larger  $|B|$  value relaxes the minimum  $T$  value, and vice versa.
  - One stable solution at  $\langle\sigma\rangle \neq 0$  and one unstable solution at an energy inflection point. This occurs at the transition between cases ii and iii.

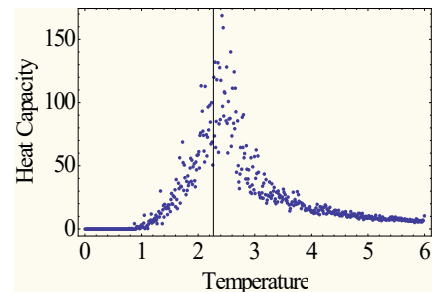
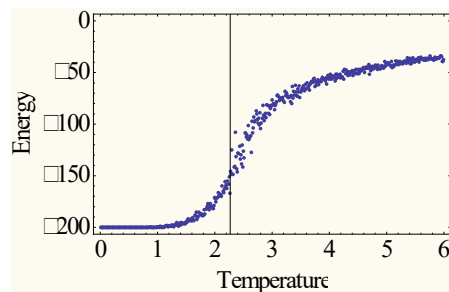
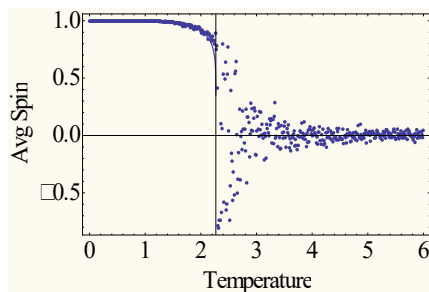
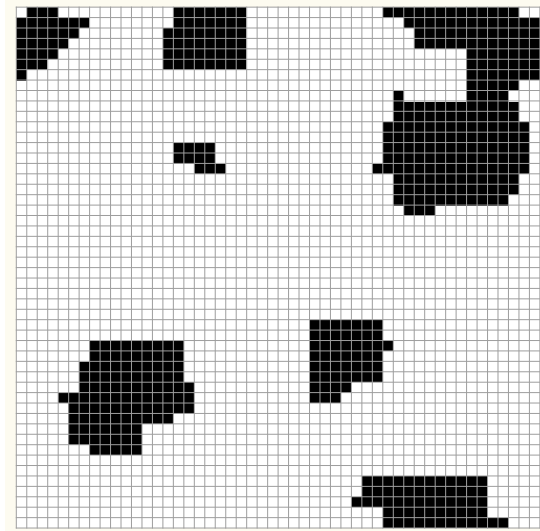




<https://www.tcm.phy.cam.ac.uk/~bds10/phase/introduction.pdf>

- 3) Exact solution to the zero-field 1D Ising model (spin chain)
  - a. The one-dimensional Ising problem (a chain of spins with nearest-neighbor interactions) was solved by Ernst Ising in 1924 (Ph.D work).
  - b. For  $T < T_c$  and  $B = 0$ , recall that MFT predicts the spontaneous appearance of a non-trivial value for  $\langle \sigma \rangle$ .
  - c. Ising found that there can be no spontaneous non-trivial  $\langle \sigma \rangle$  at any temperature. The magnetization is always zero when  $B = 0$ . His result disagrees with our mean-field analysis above! MFT analysis fails to capture the right physics in one dimension!!!
- 4) Exact solution to the zero-field 2D Ising model on a square lattice.
  - a. Solved by Lars Onsager in 1949. His derivation was a mathematical *tour de force* that still impresses readers today. Predicted a non-zero macroscopic spin at  $B = 0$ .
  - b. The order parameter has the form  $\langle \sigma \rangle = \left\{ 1 - \left[ \sinh \left( (1 + \sqrt{2}) \frac{T_c}{T} \right) \right]^{-4} \right\}^{1/8}$ , where the critical temperature is given by  $\sinh \left( \frac{2J}{k_B T_c} \right) = 1$  or  $k_B T_c = \frac{2J}{\ln(1+\sqrt{2})} \approx 2.269 J$ . This is  $4/2.269 = 1.763$  times smaller than the MFT prediction for  $k_B T_c$ .
  - c. As the dimensionality of an Ising lattice grows larger (2D, 3D, 4D, ...), the mean-field approach becomes increasingly accurate. This accuracy is important because no one has been able to cook up a closed-form solution for  $\langle \sigma \rangle$  in higher dimensions.
- 5) Critical fluctuations
  - a. As the system passes through the phase transition, spin fluctuations become very large. The *correlation length* can be roughly described as the average size of a domain of equal spins. The correlation length diverges with a power law dependence as  $T \rightarrow T_c$  from above. In other words,  $\xi \propto (T - T_c)^{-\nu} \rightarrow \infty$ .
  - b. As the correlation length grows, the total energy decreases. Below the transition, as a single dominant spin domain emerges, the energy continues to decrease and eventually reaches its limiting value at  $T = 0$ .
  - c. The heat capacity is measured as  $C_V \equiv \frac{\partial U}{\partial T} = \frac{1}{k_B T^2} \langle (E - \langle E \rangle)^2 \rangle$ , which effectively measures the squared magnitude of the fluctuations, and therefore also diverges at  $T_c$ .
  - d. Within the scope of our course materials, we could do a LOT more with critical fluctuations for a 2D Ising model. But in the interest of time, we'll focus on building some simulations.

- 6) 2D Ising model simulation with  $J = +1$  evolves to a uniform spin state below  $T_C$ .
- The larger the simulation, the more random steps at modest temperatures below  $T_C$  are required to achieve a uniform spin. More steps above the transition won't help. More steps too close to  $T = 0$  won't help. Here, we see a simulation on a  $100 \times 100$  grid with well defined spin domains; it didn't run long enough to become uniform.
  - The total spin fluctuates dramatically just above the phase transition. Large spin-up and spin-down domains form but fluctuate in and out of existence quickly; the system is unable to make up its mind between the two choices. The existence of these large domains substantially decreases the energy, which is low everywhere within a domain where each spin is aligned with its neighbors.
  - The heat capacity, which is calculated as the slope of the  $U(T)$  curve is large in the vicinity of the phase transition. Heat capacity varies quadratically with the size of the energy fluctuations, which are large near the transition.
  - When  $T$  dips below  $T_C$ , whichever spin (up or down) happens to be in the majority at that moment typically gets locked in as the eventual winner. As  $T$  continues to drop, the majority spin quickly gains ground until it dominates the entire landscape. If the simulation runs long enough as the system cools, the final state will be uniform.



## Lecture 37: Exam Review



## Lecture 38: Statistical mechanics equation summary

**Classical paramagnet:** a set of  $N$  distinguishable 3D classical magnetic moments of magnitude  $\mu$ , each of which can have an arbitrary direction with respect to the external field ( $B$ ).

Define  $\xi = \frac{\mu B}{k_B T}$ . We did this in an ensemble defined by reservoir and  $B$ -field contact.

Component partition function:  $Z_{sp} = \int e^{-\mu \cdot B / kT} d\theta d\phi = 4\pi \frac{\sinh(\xi)}{\xi}$

Total partition function:  $Z_N = (Z_{sp})^N$

Free-energy FR:  $F = -k_B T \ln(Z_N)$

Entropy: we didn't calculate this

Magnetic moment:  $M = -\left(\frac{\partial F}{\partial B}\right)_{N,T} = N\mu \left\{ \coth(\xi) - \frac{1}{\xi} \right\}$ .

Internal energy:  $U = k_B T^2 \left( \frac{\partial \ln Z_N}{\partial T} \right) = -N\mu B \left\{ \coth(\xi) - \frac{1}{\xi} \right\}$

Heat capacity:  $C = \left( \frac{\partial U}{\partial T} \right)_{V,N} = Nk_B \{ 1 - \xi^2 \operatorname{csch}^2(\xi) \}$

**General quantum paramagnet:** a set of  $N$  distinguishable 3D quantum spins with total spin quantum number  $J$ , each of which can have an arbitrary direction with respect to the external field ( $B$ ). Define  $\xi = \frac{g_J \mu_B B}{2k_B T}$ , where  $g_J$  is the Lande g-factor (not degeneracy!).

In a magnetic field, the different  $m_J$  states are non-degenerate anyway.

Component partition function:  $Z_{sp} = \sum e^{-\epsilon_i / k_B T} = \sum_{-J}^{+J} e^{-2m_J \xi} = \frac{\sinh[(2J+1)\xi]}{\sinh(\xi)}$

Total partition function:  $Z_N = (Z_{sp})^N$

Free-energy FR:  $F = -k_B T \ln(Z_N)$

Entropy: we didn't calculate this, but easily could have

Magnetic moment:  $M = -\left(\frac{\partial F}{\partial B}\right)_{N,T} = \frac{1}{2} N g_J \mu_B \{ (2J+1) \coth((2J+1)\xi) - \coth(\xi) \}$

Internal energy:  $U = k_B T^2 \left( \frac{\partial \ln Z_N}{\partial T} \right) = -MB$  (see  $M$  above).

Heat capacity: We didn't calculate this, but easily could have.

**Two-state ( $J = 1/2$ ) quantum paramagnet:** ( $g_J = 2$ ): Define  $\xi = \frac{\mu_B B}{k_B T}$ .

Component partition function:  $Z_{sp} = \sum e^{-\epsilon_i / k_B T} = 2 \cosh(\xi)$

Total partition function:  $Z_N = (Z_{sp})^N$

Free-energy FR:  $F = -k_B T \ln(Z_N)$

Entropy:  $S = -Nk_B \xi \tanh(\xi) + Nk_B \ln(2 \cosh(\xi))$

Magnetic moment:  $M = -\left(\frac{\partial F}{\partial B}\right)_{N,T} = N\mu_B \tanh(\xi)$

Internal energy:  $U = k_B T^2 \left( \frac{\partial \ln Z_N}{\partial T} \right) = -MB = -N\mu_B B \tanh(\xi)$

Heat capacity:  $C = \left( \frac{\partial U}{\partial T} \right)_{V,N} = Nk_B \xi^2 \operatorname{sech}^2(\xi)$

**Ising model magnet:** A collection of distinguishable scalar spins ( $\sigma_a = \pm 1, \mu_a = \mu \sigma_a$ ) with nearest-neighbor contact interactions and also interactions with an external field.

Interaction energy:  $E = -J \sum_{\langle a,b \rangle} \sigma_a \sigma_b - \sum_a (\mu \sigma_a) B$

Mean-field single-particle energy:  $E_a \approx -\frac{1}{2} J \sum_{\langle b \rangle} \langle \sigma \rangle \sigma_a - \mu B \sigma_a = -\mu \sigma_a \left( \frac{Jn}{2\mu} \langle \sigma \rangle + B \right)$

Effective field:  $B_{eff} = \frac{Jn}{2\mu} \langle \sigma \rangle + B$ .

Critical mean-field temperature and field:  $k_B T_c = \frac{nJ}{2} = \mu B_c$

Partition function:  $Z_{sp} = \sum_{\pm} e^{-E_{\pm}/k_B T} = e^{\mu B_{eff}/k_B T} + e^{-\mu B_{eff}/k_B T}$ .

Mean spin:  $\langle \sigma \rangle = \frac{(+1) e^{\mu B_{eff}/k_B T}}{Z_{sp}} + \frac{(-1) e^{-\mu B_{eff}/k_B T}}{Z_{sp}} = \tanh \left( \frac{\mu B}{k_B T} + \frac{Jn \langle \sigma \rangle}{2k_B T} \right) = \tanh \left[ \frac{T_c}{T} \left( \frac{B}{B_c} + \langle \sigma \rangle \right) \right]$

### Gas densities of states:

1) Momentum distribution: nonrelativistic and relativistic fermions and bosons alike

a. Define a momentum state grid with  $\Delta p = \frac{h}{2a} = \frac{\pi \hbar}{a}$

b.  $G(p) = g_s \frac{1}{8} \frac{4\pi}{3} \left( \frac{p}{\Delta p} \right)^3 = \frac{g_s}{6\pi^2} \left( \frac{pa}{\hbar} \right)^3 = \frac{g_s V p^3}{6\pi^2 \hbar^3}$

c.  $g(p) dp = \frac{\partial G(p)}{\partial p} dp = \frac{g_s V p^2}{2\pi^2 \hbar^3} dp$

2) Energy distribution

a. Non-relativistic ( $\epsilon = \frac{p^2}{2m}$ ):  $g(\epsilon) d\epsilon = g(p(\epsilon)) \left( \frac{dp}{d\epsilon} \right) d\epsilon = \left( \frac{g_s m V (2m\epsilon)^{1/2}}{2\pi^2 \hbar^3} \right) d\epsilon$

b. Ultra-relativistic ( $\epsilon = pc$ ):  $g(\epsilon) d\epsilon = g(p(\epsilon)) \left( \frac{dp}{d\epsilon} \right) d\epsilon = \left( \frac{g_s V \epsilon^2}{2\pi^2 (\hbar c)^3} \right) d\epsilon$

3) Transforms to other common variables ( $p = \hbar k$  and  $E = \hbar \omega = 2\pi \hbar c / \lambda$ )

**Canonical treatment of the monatomic ideal gas:** A dilute collection of  $N$  indistinguishable monatomic particles with independent translational degrees of freedom. Define  $n_Q =$

$$\left( \frac{mk_B T}{2\pi \hbar^2} \right)^{3/2}.$$

Component partition function:  $Z_{sp} = \int e^{-p^2/2(m k_B T)} \frac{dx^3 dp^3}{(2\pi \hbar)^3} = V \left( \frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} = V n_Q$

Canonical partition function:  $Z_N = \frac{(Z_{sp})^N}{N!}$

Helmholtz FR:  $F(T, V, N) = -k_B T \ln(Z_N) \approx -N k_B T \left\{ 1 + \ln \left( \frac{n_Q}{n_{conc}} \right) \right\}$

Entropy:  $S(T, V, N) = - \left( \frac{\partial F}{\partial T} \right)_{V, N} = N k_B \left\{ \frac{5}{2} + \ln \left( \frac{n_Q}{n_{conc}} \right) \right\}$

Internal energy:  $U = k_B T^2 \left( \frac{\partial \ln Z_N}{\partial T} \right) = \frac{3}{2} N k_B T$

Heat capacity:  $C_V = \left( \frac{\partial U}{\partial T} \right)_{V, N} = \frac{3}{2} N k_B$

**Canonical treatment of the polyatomic ideal gas:** A dilute collection of  $N$  indistinguishable polyatomic molecules ( $n_{poly}$  atoms per molecule) with independent translational degrees of freedom in the high- $T$  limit.

Define  $n_Q = \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}$ ,  $\theta_{rot} = \frac{\hbar^2}{2I_x k_B}$ ,  $\theta_{vib(m)} = \frac{\epsilon_m}{k_B} = \frac{h\nu_m}{k_B}$ .

Translational partition function:  $Z_{trans} = V n_Q \propto VT^{3/2}$

Rotational partition function:  $Z_{rot} = \int_0^\infty e^{-(\alpha_x J_x^2 + \alpha_y J_y^2 + \alpha_z J_z^2)} dJ_x dJ_y dJ_z = \left(\frac{T}{\theta_{rot}}\right)^{n_{rot}/2}$

Vibrational partition function:  $Z_{vib(m)} = \frac{1}{2} \text{csch}\left(\frac{1}{2} \frac{\theta_m}{T}\right) \rightarrow \frac{T}{\theta_m}$  and  $Z_{vib} = \prod \left(\frac{T}{\theta_{vib(m)}}\right) = \left(\frac{T}{\theta_{vib}}\right)^{n_{vib}}$

where  $n_{vib} = 3n_{poly} - 6$  at sufficiently high temperatures to activate all modes.

Complete ideal-gas partition function:  $Z_{sp} = Z_{trans} Z_{rot} Z_{vib} = Z_{trans} Z_{int} \propto VT^{(n_{modes}/2)}$

where  $n_{modes} = n_{trans} + n_{rot} + 2n_{vib} = 3 + 3 + 2(3n_{poly} - 6)$ ,

unless the temperature is too low to activate some of the modes.

Linear molecules: Convert one rotational mode into a vibrational mode.

Total partition function (indistinguishable particles):  $Z_N = \frac{(Z_{sp})^N}{N!}$

Helmholtz FR:  $F = -k_B T \ln(Z_N) = -Nk_B T \left\{1 + \ln\left(\frac{n_Q}{n_{conc}} Z_{int}\right)\right\}$

Internal energy:  $U = k_B T^2 \left(\frac{\partial \ln Z_N}{\partial T}\right) = \frac{n_{modes}}{2} Nk_B T = cNk_B T$

Pressure:  $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = Nk_B T/V$ .

Entropy:  $S = \frac{U-F}{T} = Nk_B \{(c+1) + \ln(Z_{sp}/N)\} = Nk_B \{(c+1) + \ln\left(\frac{n_Q}{n_{conc}} Z_{int}\right)\}$

Heat capacity:  $C_V = \frac{n_{modes}}{2} Nk_B = cNk_B$

**Grand-canonical treatment of the monatomic ideal gas:** A dilute collection of  $N$  indistinguishable monatomic non-relativistic gas particles.

Define quantum concentration  $n_Q \equiv \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}$  and fugacity  $z \equiv e^{\mu/k_B T}$

Single-particle partition function:  $Z_{sp} = \int g(\epsilon) e^{-(\epsilon-\mu)/k_B T} d\epsilon = z \int g(\epsilon) e^{-\epsilon/k_B T} d\epsilon = z n_Q V$

Grand partition function:  $Z_L = \sum Z_N z^N = \sum_N \frac{(Z_{sp})^N}{N!} = e^{Z_{sp}}$

Landau FR:  $L = -k_B T \ln(Z_L) = -k_B T Z_{sp}$

Differential Landau FR:  $dL = d(U - TS - \mu N) = -SdT - PdV - Nd\mu$

Particle number:  $N = -\left(\frac{\partial L}{\partial \mu}\right)_{V,T} = k_B T \left(\frac{\partial Z_{sp}}{\partial \mu}\right)_{V,T} = Z_{sp}$

A Legendre transform to  $U(S, V, N)$  will recover all of the familiar ideal-gas results.

**Degenerate Fermi gas:** A dense collection of  $N$  fermions. Only  $f_i = 0$  and  $1$  are allowed.

Define  $x = e^{-(\epsilon_i - \mu)/k_B T}$  for convenience.

Single-state partition function:  $Z_{ssi} = \sum_{f_i=0}^1 e^{-f_i(\epsilon_i - \mu)/k_B T} = 1 + x = 1 + e^{-(\epsilon_i - \mu)/k_B T}$

Occupancy factor:  $\langle f_i \rangle = \frac{\langle n_i \rangle}{g_i} = \frac{\sum_{f_i} f_i p_{f_i}}{Z_{ssi}} = \frac{1}{Z_{ssi}} \sum_{f_i} f_i x^{f_i} = \frac{0+x}{1+x} = \frac{1}{1/x+1} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}$

Total partition function:  $Z_L = \prod_i Z_{ssi}^{g_i} = \prod_i \left( \sum_{f_i} e^{-f_i(\epsilon_i - \mu)/k_B T} \right)^{g_i}$  (no nice closed-form solution)

Landau FR:  $L = -k_B T \ln(Z_L) = -k_B T \sum_i g_i \ln(Z_{ssi})$  (no nice closed-form solution)

Particle number:  $\langle N \rangle = -(\partial L / \partial \mu)_{T,V}$

See electrons in a metal below.

**Degenerate Bose gas:** A dense collection of  $N$  bosons. All non-negative integer  $f_i$  allowed.

Require that for  $\epsilon_i > \mu$ . Define  $x = e^{-(\epsilon_i - \mu)/k_B T}$  for convenience.

Single-state partition function:  $Z_{ssi} = \sum_{f_i} e^{-f_i(\epsilon_i - \mu)/k_B T} = \sum_{f_i=0}^{\infty} x^{f_i} = \frac{1}{1-x} = \frac{1}{1 - e^{-(\epsilon_i - \mu)/k_B T}}$

Occupancy factor:  $\langle f_i \rangle = \frac{\langle n_i \rangle}{g_i} = \frac{\sum_{f_i} f_i p_{f_i}}{Z_{ssi}} = \frac{1}{Z_{ssi}} \sum_{f_i=0}^{\infty} f_i x^{f_i} = \frac{1}{1/x - 1} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} - 1}$

Total partition function:  $Z_L = \prod_i Z_{ssi}^{g_i} = \prod_i \left( \sum_{f_i} e^{-f_i(\epsilon_i - \mu)/k_B T} \right)^{g_i}$  (no nice closed-form solution)

Landau FR:  $L = -k_B T \ln(Z_L) = -k_B T \sum_i g_i \ln(Z_{ssi})$  (no nice closed-form solution)

Particle number:  $\langle N \rangle = -(\partial L / \partial \mu)_{T,V}$

See photon gas, photon gas, and Bose-Einstein condensate below.

**Boltzmann gas (e.g. an ideal gas):** Hot dilute limit where  $\langle n_i \rangle \ll g_i$ .

Occupancy factor:  $f(\epsilon_i) = \frac{\langle n_i \rangle}{g_i} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} \pm 1} \rightarrow e^{-\epsilon_i/k_B T}$

**Electrons in a metal:** A dense collection of  $N$  electrons.

Fermi energy and temperature:  $k_B T_F = \epsilon_F = \frac{\hbar^2}{2m} \left( 3\pi^2 \frac{N}{V} \right)^{2/3}$

Non relativistic density of states in a metal:  $g(\epsilon) = \frac{3}{2} \frac{N}{\epsilon_F} \left( \frac{\epsilon}{\epsilon_F} \right)^{1/2}$ . Assume  $\mu \approx \epsilon_F$ .

Internal energy:  $\frac{U(T=0)}{\langle N \rangle} = \langle \epsilon(T=0) \rangle = \frac{1}{\langle N \rangle} \int_0^{\infty} \epsilon g(\epsilon) d\epsilon = \frac{3}{2} \frac{1}{\epsilon_F^{3/2}} \int_0^{\infty} \epsilon^{3/2} d\epsilon = \frac{3}{5} \epsilon_F$

Pressure:  $P(T=0) = - \left( \frac{\partial U}{\partial V} \right)_{S,N} = - \frac{\partial U}{\partial \epsilon_F} \frac{\partial \epsilon_F}{\partial V} = - \frac{3}{5} \langle N \rangle \left( - \frac{2}{3} \frac{\epsilon_F}{V} \right) = \frac{2}{3} \frac{U}{V}$

Internal energy:  $\frac{U(T)}{\langle N \rangle} = \epsilon_F + \int_0^{\infty} (\epsilon - \epsilon_F) f(\epsilon) g(\epsilon) d\epsilon \approx \frac{3}{5} \epsilon_F + \frac{\pi^2}{4} \frac{(k_B T)^2}{\epsilon_F}$

Heat capacity:  $C_V = \frac{dU}{dT} = \int_0^{\infty} (\epsilon - \epsilon_F) g(\epsilon) \frac{df(\epsilon)}{dT} d\epsilon \approx \frac{\pi^2}{2} \langle N \rangle k_B \left( \frac{T}{T_F} \right)$

**Photon gas:** A black-body cavity of volume  $V$  and temperature  $T$ . Relativistic density of states with  $g_s = 2$ . Photon particle number is not conserved, so that  $\mu = 0$ . Define  $x = \frac{\epsilon}{k_B T} = \frac{1}{y}$ .

Particle spectrum:  $dN = g(\epsilon)f(\epsilon)d\epsilon = \frac{2V}{2\pi^2(\hbar c)^3} \frac{\epsilon^2 d\epsilon}{e^{\epsilon/k_B T} - 1} \propto \frac{1}{2\zeta(3)} \frac{x^2 dx}{e^x - 1}$ .

Energy spectrum:  $dU = \epsilon n(\epsilon)d\epsilon = \frac{V(k_B T)^4}{\pi^2(\hbar c)^3} \frac{\epsilon^3 d\epsilon}{e^{\epsilon/k_B T} - 1} \propto \frac{x^3 dx}{e^x - 1}$ .

Wavelength spectrum:  $dU = \epsilon(\lambda)n(\epsilon(\lambda))\frac{\partial \epsilon}{\partial \lambda} d\lambda = \frac{V(k_B T)^4}{\pi^2(\hbar c)^3} \frac{y^{-3}}{e^{1/y} - 1} \left(\frac{dy}{y^2}\right) \propto \frac{y^{-5} dy}{e^{1/y} - 1}$

Energy peak at  $x_{peak} = 2.8214$ . Wavelength peak at  $y_{peak} = 0.20141$ .

Wein's Law:  $\lambda_{peak} T = 0.20141 \left(\frac{2\pi\hbar c}{k_B}\right) = 2.898 \text{ m} \cdot \text{mK}$ .

Particle number:  $\langle N \rangle = \int n(\epsilon)d\epsilon = \left(\frac{2\zeta(3)}{\pi^2}\right) \frac{V(k_B T)^3}{(\hbar c)^3} = aVT^3$

Internal energy:  $\langle U \rangle = \langle N\epsilon \rangle = \int \epsilon n(\epsilon)d\epsilon = \frac{\pi^2}{15} \frac{V(k_B T)^4}{(\hbar c)^3} = bVT^4$

Stefan-Boltzmann law:  $J = \frac{c}{4} \frac{\langle U \rangle}{V} = \left(\frac{\pi^2}{60} \frac{k_B^4}{c^2 \hbar^3}\right) T^4 = \sigma T^4 = (5.67 \times 10^{-8} \text{ J/s/m}^2/\text{K}^4) T^4$

Pressure:  $P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = -\frac{b}{a^{1/3}} \left(-\frac{1}{3}\right) \frac{N^{4/3}}{V^{4/3}} = \frac{1}{3} \frac{U}{V} \rightarrow U = 3PV$ .

Fundamental relation:  $U = \frac{b}{a^{1/3}} \frac{N^{4/3}}{V^{1/3}} = bV \left(\frac{3}{4} \frac{S}{bV}\right)^{4/3} \rightarrow S = \frac{4}{3} (bVU^3)^{1/4}$

Heat capacity: We didn't derive this, though it wouldn't be difficult.

**Bose-Einstein condensate:** A dense collection of  $N$  bosons, usually with fixed particle number, such that a macroscopic fraction of the particles drop into the ground state when  $T < T_{BE}$ .

Excited number:  $N_{ex} = \int_0^\infty g(\epsilon)f(\epsilon)d\epsilon = \frac{g_s m V (2m)^{1/2}}{2\pi^2 \hbar^3} \int_0^\infty \frac{\sqrt{\epsilon} d\epsilon}{e^{\epsilon/k_B T} - 1} = 2.612 g_s n_Q V$

The transition temperature:  $T_{BE} = \left(\frac{2\pi\hbar^2}{mk_B}\right) \left(\frac{n}{2.612 g_s}\right)^{2/3}$

Fraction in ground state:  $\frac{N_G}{N} = 1 - \frac{N_{ex}}{N}$

Internal energy:  $U = \int_0^\infty \epsilon g(\epsilon)f(\epsilon)d\epsilon = \frac{g_s m V (2m)^{1/2}}{2\pi^2 \hbar^3} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\epsilon/k_B T} - 1} = 0.7703 N_{ex} k_B T \propto VT^{5/2}$

Heat capacity ( $T < T_{BE}$ ):  $C_V = \frac{\partial U}{\partial T} = \frac{5}{2} \frac{U}{T} = \frac{15}{4} \zeta\left(\frac{5}{2}\right) k_B g_s n_Q V = 1.9257 N_{ex} k_B \propto VT^{3/2}$

Pressure  $P = \left(\frac{\partial U}{\partial V}\right)_{T,N} \propto T^{5/2}$

**Einstein solid:** a set of  $N$  distinguishable  $D$ -dimensional harmonic oscillators, each of which can hold an arbitrary number of quanta of energy  $\epsilon$ , such that the number of quanta is  $Q$  and the total energy is  $U = \left(\frac{D}{2}N + Q\right)\epsilon$ . Define:  $\theta_E = \frac{\epsilon}{k_B}$ .

Component partition function:  $Z_{sp} = \sum_0^\infty e^{-(1/2+i)\epsilon/k_B T} = z^{1/2} \sum_0^\infty z^i = \frac{z^{1/2}}{1-z} = \frac{1}{2} \text{csch}\left(\frac{\epsilon}{2k_B T}\right)$

Total partition function  $Z_N = Z_{sp}^N$

Microstates per macrostate:  $\Omega_m = \left(\frac{N!}{\prod n_i!}\right)_m$  where  $\sum n_i = N$  and  $\sum_{i=0}^{t-1} n_i * i = Q$

Euler equation:  $U = TS + \mu N$

Entropic FR:  $\frac{S}{k_B} = \ln\left[\left(Q + \frac{DN}{2} - 1\right)\right] = N\left\{\left(\frac{U}{N\epsilon} + \frac{D}{2}\right) \ln\left(\frac{U}{N\epsilon} + \frac{D}{2}\right) - \left(\frac{U}{N\epsilon} - \frac{D}{2}\right) \ln\left(\frac{U}{N\epsilon} - \frac{D}{2}\right)\right\}$

Internal energy:  $U = \frac{D}{2}N\epsilon \coth\left(\frac{\epsilon}{2k_B T}\right)$ , which was obtained by inverting  $S(U, V, N)$ .

Heat capacity:  $C = \left(\frac{\partial U}{\partial T}\right)_{V,N} = DNk_B \left(\frac{\epsilon}{2k_B T}\right)^2 \text{csch}^2\left(\frac{\epsilon}{2k_B T}\right) = 3Nk_B \left(\frac{\theta_E}{2T}\right)^2 \text{csch}^2\left(\frac{\theta_E}{2T}\right)$ .

Volume and pressure are not usually relevant to this model.

**Phonon gas (Debye solid):** A solid with  $N_a$  and  $3N_a$  quantized vibrational excitation modes (i.e. phonon modes with velocity  $v = \epsilon/p = \omega/k$  and polarization degeneracy of  $g_s = 3$ . Each mode is an independent oscillator that can hold multiple energy quanta. Because phonons are bosons, there is no limit to the number of phonons per mode. Phonon particle number is not conserved, so that  $\mu = 0$ . Define unitless variable  $x = \frac{\hbar\omega}{k_B T}$ .

Single-energy component partition function:  $Z_{ss}(\epsilon) = 1 - e^{-\epsilon/k_B T}$

Occupancy factor:  $f(\epsilon) = \frac{1}{e^{\epsilon/k_B T} - 1}$ .

Density of states:  $g(\epsilon)d\epsilon = \frac{3V\epsilon^2 d\epsilon}{2\pi^2(\hbar v)^3} = g(\omega)d\omega = \frac{3V\omega^2 d\omega}{2\pi^2 v^3}$

Debye frequency:  $\int_0^{\omega_D} g(\omega)d\omega = \frac{3V}{2\pi^2 v^3} \int_0^{\omega_D} \omega^2 d\omega = 3N_a \rightarrow \omega_D = v \left(6\pi^2 \frac{N_a}{V}\right)^{1/3}$ .

Debye temperature:  $\theta_D = \hbar\omega_D/k_B$ , and unitless cutoff:  $x_D^3 = \left(\frac{\hbar\omega_D}{k_B T}\right)^3 = \left(\frac{\theta_D}{T}\right)^3$ .

Particle number:  $\langle N \rangle = \int_0^{\omega_D} g(\omega)f(\omega)d\omega = 9N_a \left(\frac{T}{\theta_D}\right)^3 \left\{ \int_0^{x_D} \frac{x^2 dx}{e^x - 1} \right\}$

Internal energy:  $\langle U \rangle = \int_0^{\omega_D} \epsilon(\omega)g(\omega)f(\omega)d\omega = 9N_a k_B \left(\frac{T^4}{\theta_D^3}\right) \left\{ \int_0^{x_D} \frac{x^3 dx}{e^x - 1} \right\}$

Heat capacity:  $C_V = \frac{\partial U}{\partial T} = 9N_a k_B \left(\frac{T^3}{\theta_D^3}\right) \left\{ \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2} \right\}$ .

Limiting forms:  $C_V = \frac{12\pi^4}{5} N_a k_B \left(\frac{T}{\theta_D}\right)^3$  as  $T \rightarrow 0$  and  $C_V = \frac{\partial U}{\partial T} = 3N_a k_B$  as  $T \rightarrow \infty$ .