

Summary of SI1162 Statistical Physics

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Abstract

This is a summary of SI1161 Statistical physics. It contains discussions of the relevant theory.

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1 Handy Mathematics

Combinations and Permutations Permutations are sequences of some kind. Combinations are permutations where order does not matter. From a collection of n elements, the number of possible permutations of k elements is

$$\Omega = \frac{n!}{(n-k)!}$$

and the number of possible combinations is

$$\Omega = \binom{n}{k}.$$

Stirling's Formula In the limit of large n , Stirling's formula gives

$$\ln n! \approx n \ln n - n.$$

Exact Differentials The differential of a quantity f on a phase space described by the vector \mathbf{r} is an exact differential if

$$df = \vec{\nabla} f \cdot \mathbf{r}.$$

The implication is that f is a function on phase space, which is not true for all quantities.

The Reciprocal and Reciprocity Theorems Consider a function $x(y, z)$, and suppose that this function can be inverted to a function $z(x, y)$. We can write the differentials of x and z to obtain

$$dx = \left(\frac{\partial x}{\partial z} \right)_y dz + \left(\frac{\partial x}{\partial y} \right)_z dy, \quad dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy.$$

Combining these yields

$$\begin{aligned} dx &= \left(\frac{\partial x}{\partial z} \right)_y \left(\left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \right) + \left(\frac{\partial x}{\partial y} \right)_z dy \\ &= \left(\left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y \right) dx + \left(\left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x + \left(\frac{\partial x}{\partial y} \right)_z \right) dy. \end{aligned}$$

This implies

$$\left(\frac{\partial x}{\partial z} \right)_y = \frac{1}{\left(\frac{\partial z}{\partial x} \right)_y}, \quad \left(\frac{\partial x}{\partial y} \right)_z = - \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial x}{\partial z} \right)_y,$$

which can be combined to yield

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1.$$

The Gamma Function The gamma function is defined as

$$\Gamma(z) = \int_0^{\infty} dx x^{z-1} e^{-x}.$$

It is convergent for $\text{Re}(z) > 0$. It has the following properties:

- $\Gamma(z+1) = z\Gamma(z)$.

The Riemann Zeta Function The Riemann Zeta function is defined as

$$\zeta(z) = \sum_{n=1}^{\infty} \frac{1}{n^z}.$$

It is convergent for $z > 1$.

The Polylogarithm Function The polylogarithm function is defined as

$$\text{Li}_n = \sum_{k=1}^{\infty} \frac{z^k}{k^n}$$

on the open unit disc in the complex plane, but can be analytically continued over the rest of the complex plane.

Solid Angle Consider a function in d dimensions such that $f(\mathbf{r}) = f(r)$. When integrating such functions, we would like to do it in a coordinate system which separates out direction from distance (an example of a fitting coordinate system is spherical coordinates for $d = 3$), such that the integral of f is simplified. In order to do that, however, it would seem that we have to identify the coordinate change from cartesian coordinates which allows us to separate the integral. However, for a function with directional symmetry, we can circumvent this problem by introducing the solid angle. Before doing that, we need to study the Jacobian of the coordinate change. As only one of the new coordinates contains the distance, the Jacobian must depend on r only according to a factor r^{d-1} . In other words, we have

$$J(r, \theta) = r^{d-1} g_d(\theta)$$

where θ is the set of new coordinates describing direction. We thus have

$$\int d^d \mathbf{r} f(r) = \int d^{d-1} \theta g(\theta) \int dr f(r) r^{d-1}.$$

This defines the solid angle as

$$\Omega_d = \int d^{d-1} \theta g(\theta).$$

What its value, then? In order to determine that, we need a reference integral which we can compute. A good example is a Gaussian in d dimensions. We have

$$\int d^d \mathbf{r} e^{-r^2} = \left(\int_{-\infty}^{\infty} dx e^{-x^2} \right)^d = \pi^{\frac{d}{2}}.$$

On the other hand, we have

$$\begin{aligned} \int d^d \mathbf{r} e^{-r^2} &= \omega_d \int_0^{\infty} dr r^{d-1} e^{-r^2} \\ &= \frac{1}{2} \omega_d \int_0^{\infty} du u^{\frac{d}{2}-1} e^{-u} \\ &= \frac{1}{2} \Gamma\left(\frac{d}{2} - 1\right) \omega_d, \end{aligned}$$

and thus

$$\Omega_d = \frac{2\pi^{\frac{d}{2}}}{\Gamma\left(\frac{d}{2} - 1\right)}.$$

2 Thermodynamics

Functions of State A quantity f is a function of state if its equilibrium value is a function of the equilibrium values of the variables describing the state.

Intensive and Extensive Variables Intensive variables do not depend on the size of the system, whereas extensive variables do. Examples of the former are pressure and temperature, and examples of the latter are volume and total energy.

Heat Heat is the flow of energy.

Internal Energy The internal energy U of a system is the sum of the energy of all the internal degrees of freedom of a system.

Quasistatic Processes A process is quasistatic if the system is in equilibrium at each point during the process. Reversible processes must be performed quasistatically.

Work The work performed on a system is a mechanical addition of energy. It is generally of the form

$$\mathrm{d}W = X \mathrm{d}x,$$

where X is an intensive generalized force and x an extensive generalized displacement. For gases, around which most of the following discussions will focus, we have $X = -p$ and $x = V$. Other examples would include elastic rods, with X as the rod tension and x as its extension, or liquid surfaces, with X as the surface tension and x as the surface area.

This might of course seemingly imply that work is indeed a function of state - after all, it seems to be an exact differential. The flaw in this argument lies in the work only looking like this when performed in a reversible manner.

The First Law Energy is conserved and heat and work are both forms of energy. In mathematical form:

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W.$$

This implies the convention that positive differentials correspond to energy supplied to the system.

The Second Law of Thermodynamics The second law comes in two different statements:

- **Clausius' statement:** No process is possible whose sole result is the transfer of heat from a colder to a hotter body.
- **Kelvin's statement:** No process is possible whose sole result is the complete conversion of heat into work.

Equivalence of Statements Consider two heat reservoirs. We want to show that the existence of a system that violates one statement implies the existence of a system that violates the other.

To prove that Clausius' statement implies Kelvin's, we introduce a Clausius violator which can transfer heat from a cold to a hot reservoir. Suppose that the violator transfers a heat Q_1 between the reservoirs and introduce a heat engine which produces work while transferring heat Q_h from the hot reservoir and leaving Q_1 in the cold reservoir. The combination of these two systems thus convert heat $Q_h - Q_1$ to work with no other results, violating Kelvin's statement.

To prove that Kelvin's statement implies Clausius', we introduce a Kelvin violator which can convert heat directly to work. Suppose that the violator converts a heat W into work, and let this work run a reverse heat engine between the reservoirs taking heat Q_1 from the cold reservoir and leaving heat Q_h in the cold reservoir. The combination of these two systems thus transfer heat Q_1 from the cold reservoir to the hot reservoir with no other results, violating Kelvin's statement.

Ideal Gases Consider a gas with negligible internal interactions. For such a gas experiments have revealed

$$pV = nRT.$$

Heat Capacity of a Gas For a gas we have

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV,$$

as U is a function of state. The subscript indicates which variables are constant when the derivatives are computed. The first law gives

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\left(\frac{\partial U}{\partial V}\right)_T + p\right) dV.$$

Heat capacities are defined as derivatives of Q with respect to temperature. We thus obtain

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V, \quad C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + p\right) \left(\frac{\partial V}{\partial T}\right)_p.$$

In particular, we have for an ideal gas (where there are no interactions, and the internal energy thus does not depend on the volume) that

$$C_p = C_V + p \frac{nR}{p} = C_V + nR.$$

Heat capacities may be derived similarly for other kinds of systems.

Molar Heat Capacities Molar heat capacities, denoted with a small c , are heat capacities per mole.

Adiabatic Index The adiabatic index is defined as

$$\gamma = \frac{C_p}{C_V}.$$

Processes on Ideal Gases Processes performed on ideal gases may be characterized as

- isobaric, where the pressure is constant.
- isochoric, where the volume is constant.
- isothermal, where the temperature is constant. For such processes, we also have that pV is constant.
- adiabatic, where the gas does not exchange heat with its surroundings. For such processes, we have

$$\begin{aligned} dQ &= dU - p dV = 0, \\ C_V dT &= \frac{nRT}{V} dV, \\ \frac{C_V}{T} dT &= \frac{nR}{V} dV = \frac{C_p - C_V}{V} dV, \\ \ln \frac{T}{T_0} &= (\gamma - 1) \ln \frac{V}{V_0}, \end{aligned}$$

meaning that $TV^{\gamma-1}$ is constant. This may of course be re-expressed in terms of other combinations of thermodynamic variables.

The Carnot Cycle Consider a machine performing work based on the energy transfer between two heat reservoirs. One way to extract the energy is by using a Carnot process, which uses an ideal gas. The cycle connects four different points in a pV diagram with two adiabatics and two isothermals.

More specifically, introduce the two heat reservoirs $T_h > T_l$ and the notation for each step according to figure 1.

During step a, the gas expands isothermally, and we have

$$\Delta U = 0, \quad Q = W = nRT_h \ln \frac{V_b}{V_a}.$$

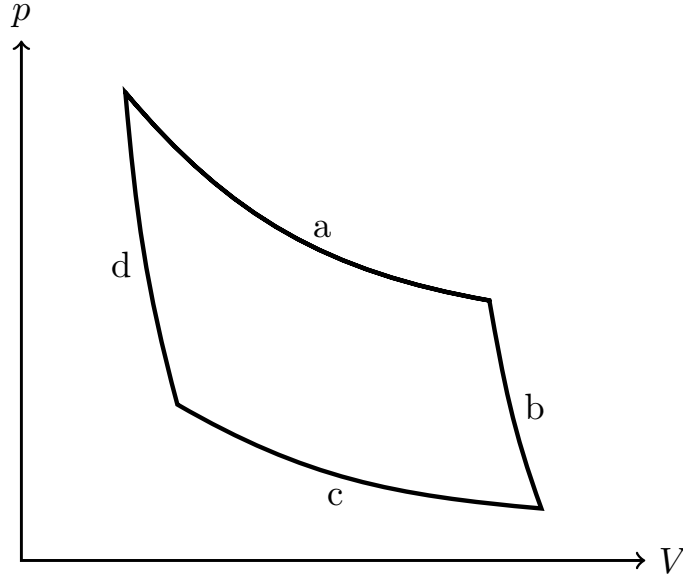


Figure 1: Schematic of a Carnot cycle.

During step b, the gas expands adiabatically, and we have

$$Q = 0, \quad W = \Delta U = C_V(T_l - T_h).$$

During step c, the gas compresses isothermally, and we have

$$\Delta U = 0, \quad Q = W = nRT_l \ln \frac{V_d}{V_c}.$$

During step d, the gas compresses adiabatically, and we have

$$Q = 0, \quad W = \Delta U = C_V(T_h - T_l).$$

We use the previously derived expressions for adiabatic processes to write

$$T_h V_a^{\gamma-1} = T_l V_d^{\gamma-1}, \quad T_h V_b^{\gamma-1} = T_l V_c^{\gamma-1}.$$

Thus we obtain for the isothermal compression that

$$Q = nRT_l \ln \left(\frac{\left(\frac{T_h}{T_l} \right)^{\frac{1}{\gamma-1}} V_a}{\left(\frac{T_h}{T_l} \right)^{\frac{1}{\gamma-1}} V_b} \right) = nRT_l \ln \left(\frac{V_a}{V_b} \right),$$

and thus $\frac{|Q|}{T}$ is constant for the two heat-exchanging steps.

Efficiency The efficiency of a machine has various definitions, but the general definition is the ratio between the energy you get out and the energy you put in.

Carnot's Theorem No heat engine working between two heat reservoirs is more efficient than a Carnot engine.

To prove this, suppose that you create an engine producing the same work W as a Carnot heat engine, but for an energy Q' as opposed to the energy Q needed to run the Carnot engine. Now let your new engine be used to power a reversed Carnot engine. As the process must be performed cyclically, the statement that this new engine is more efficient is expressed as

$$\frac{W}{Q'} > \frac{W}{Q} \implies Q > Q'.$$

During the process each engine gives off some heat Q_1 to the cold reservoir. The first law of thermodynamics implies

$$W = Q' - Q'_1 = Q - Q_1.$$

As $Q - Q' > 0$, so is $Q_1 - Q'_1$. Now, $Q - Q'$ is the net energy left in the hot reservoir during a cycle and $Q_1 - Q'_1$ is the energy extracted from the cold reservoir. The sole result of this process is thus to extract energy from a cold reservoir to a hot one, which violates the second law.

Corollary All reversible heat engines working between two temperatures have the same efficiency as a Carnot engine.

To show this, suppose a Carnot engine is working between two reservoirs and running another engine undoing that process. This other engine cannot be more efficient than the Carnot engine, meaning that it delivers a greater amount of energy to the hot reservoir than the Carnot engine took, violating the second law of thermodynamics. Thus the two engines must have the same efficiency.

Clausius' Theorem Consider some arbitrary cyclic process. We can describe this as a sequence of the system being connected to temperatures T_i , with heats dQ_i being supplied at every stage. The total work performed during the cycle is given by

$$W = \sum dQ_i.$$

Now suppose that the heat at each point is supplied by a Carnot engine operating between two reservoirs at temperature T and T_i . Using the constant ratio for Carnot cycles which was derived previously, we have

$$\frac{dQ_i}{T_i} = \frac{dQ_i + dW_i}{T}$$

where dW_i is the work done by the Carnot engine. This process cannot violate the second law of thermodynamics, hence

$$W + \sum dW_i \leq 0.$$

Hence

$$\sum dQ_i + \sum dQ_i \left(\frac{T}{T_i} - 1 \right) = T \sum \frac{dQ_i}{T_i} \leq 0.$$

The temperature T is constant and positive, and can thus be ignored. In the limit of considering the process in a continuous manner, this becomes

$$\int dQ \frac{1}{T} \leq 0.$$

This is Clausius' theorem, where equality necessarily holds for a reversible cycle.

Entropy As we have seen, the integral

$$\int dQ \frac{1}{T}$$

is path independent for a reversible process. We thus define the state function

$$dS = \frac{dQ}{T}$$

to be the entropy.

The Second Law and Entropy Consider two points connected by a reversible and an irreversible process such that the two form a cycle. Clausius' theorem yields

$$\int_A^B dQ \frac{1}{T} + \int_B^A dQ_{\text{rev}} \frac{1}{T} \leq 0 \implies \int_A^B dQ \frac{1}{T} \leq \int_A^B dQ_{\text{rev}} \frac{1}{T}.$$

This holds for two arbitrary points, meaning

$$dS \geq \frac{dQ}{T}.$$

Considering a thermally isolated system, we obtain

$$dS \geq 0.$$

This is a restatement of the second law of thermodynamics, and essentially an equilibrium condition for any isolated system.

The First Law and Entropy For a reversible process on a gas we obtain

$$dU = T dS - p dV,$$

or more generally

$$dU = T dS + X dx.$$

However, as all involved quantities are functions of state, this must hold even if the process in question is irreversible.

The Third Law The third law was initially concerned with the issue of determining absolute entropies. Three different statements of the third law were finally coined:

- **Nernst's statement:** Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.
- **Planck's statement:** The entropy of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero.
- **Simon's statement:** The contribution to the entropy of a system by each aspect of the system which is in internal thermodynamic equilibrium tends to zero when approaching absolute zero.

Simon's idea of aspects are based on a closer and closer inspections of a system. Considering a crystal for instance, it can be studied as a macroscopic entity or in terms of the individual atoms comprising it. These are, in turn, built up of nucleons, which are made up of quarks and so on (potentially). Each of these is termed an aspect.

Consequences of the Third Law Now we examine some of the consequences of the third law.

The first consequence is for heat capacities near absolute zero. We have

$$C = T \frac{\partial S}{\partial T} = \frac{\partial S}{\partial \ln T} \rightarrow 0.$$

One might suspect that the first equality implies it (and I don't know why it does not). But the second statement guarantees it somehow, as the third law implies that the entropy is bounded at low temperatures.

A second consequence is for thermal expansion. The third law implies

$$\left(\frac{\partial S}{\partial p} \right)_T \rightarrow 0$$

near absolute zero, which implies

$$\left(\frac{\partial V}{\partial T}\right)_p \rightarrow 0.$$

A third consequence is for ideal systems, such as the ideal gas and non-interacting spin systems. These cannot be ideal at low temperatures, a fact that might be guessed at based on tendencies in their entropies, but can also be justified by the fact that interactions between units in the system can be disregarded at high temperatures, where the ideal models are valid, but not at lower temperatures.

A final consequence is the fact that one cannot cool to $T = 0$ in a finite number of steps, a fact which is not easy to prove rigorously.

Natural Variables For Internal Energy Our restatement of the first law implies that U is most naturally written as a function of S and x (naturally it could be written in terms of other variables too, but you would have to change variables from S and x in order to do that. A switch from S to T would for instance be rewriting U as $U(S(T), x)$). The restatement also implies

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial x}\right)_S = X.$$

Chemical Potential In addition to the dependence of the internal energy on entropy and volume, there is a dependence on the number of particles of type i . This is contained in the chemical potential, defined as

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S, x, N_j}$$

where $j \neq i$. From now on, summation rules will be used for chemical potentials, i will signify all sets of possible values of i , and $j \neq i$ may always be assumed to be true unless otherwise specified.

Entropy We can re-express the differential of internal energy as a differential of entropy or use the reciprocal and reciprocity theorems to obtain

$$dS = \frac{1}{T} dU - \frac{X}{T} dx.$$

This implies that the entropy is a function of U , x and N_i , as well as

$$\left(\frac{\partial S}{\partial U}\right)_{x, N_i} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial x}\right)_{U, N_i} = -\frac{X}{T}, \quad \left(\frac{\partial S}{\partial N_i}\right)_{U, x, N_j} = -\frac{\mu_i}{T}.$$

Enthalpy The enthalpy is defined as

$$H = U + pV.$$

We have

$$dH = dU + p dV + V dp = T dS - p dV + \mu_i dN_i + p dV + V dp = T dS + V dp + \mu_i dN_i,$$

implying that H is a function of S , p and N_i , as well as

$$\left(\frac{\partial H}{\partial S}\right)_{p, N_i} = T, \quad \left(\frac{\partial H}{\partial p}\right)_{S, N_i} = V, \quad \left(\frac{\partial H}{\partial N_i}\right)_{S, V, N_j} = \mu_i.$$

Helmholtz Free Energy The Helmholtz free energy is defined as

$$F = U - TS.$$

We have

$$dF = dU - T dS - S dT = T dS - p dV + \mu_i dN_i - T dS - S dT = -p dV - S dT + \mu_i dN_i,$$

implying that F is a function of T , V and N_i , as well as

$$\left(\frac{\partial F}{\partial T}\right)_{V, N_i} = -S, \quad \left(\frac{\partial F}{\partial V}\right)_{T, N_i} = -p, \quad \left(\frac{\partial F}{\partial N_i}\right)_{T, V, N_j} = \mu_i.$$

Gibbs Free Energy The Gibbs free energy is defined as

$$G = H - TS.$$

We have

$$dG = dH - T dS - S dT = T dS + V dp + \mu_i dN_i - T dS - S dT = V dp - S dT + \mu_i dN_i,$$

implying that G is a function of T , p and N_i , as well as

$$\left(\frac{\partial G}{\partial T}\right)_p = -S, \left(\frac{\partial G}{\partial p}\right)_T = V, \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_j} = \mu_i.$$

The Grand Potential The grand potential is defined as

$$\Phi_G = F - \mu_i N_i.$$

We have

$$d\Phi_G = -p dV - S dT + \mu_i dN_i - \mu_i dN_i - N_i d\mu_i = -p dV - S dT - N_i d\mu_i,$$

implying that Φ_G is a function of V , T and μ_i , as well as

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu}, p = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}, N_i = -\left(\frac{\partial \Phi_G}{\partial \mu_i}\right)_{T,V,N_j}.$$

Reinterpretation of the Chemical Potential and Grand Potential Consider a system of only one kind of particles which is scaled by a factor λ . The entropy, expressed as a function of U , V and N is extensive, yielding that it, too, is scaled by a factor λ . Let a subscript λ denote quantities for a scaled system. We thus have

$$S_\lambda = \lambda S.$$

Differentiating with respect to λ

$$S = \left(\frac{\partial S_\lambda}{\partial U_\lambda}\right)_{V_\lambda,N_\lambda} \frac{\partial U_\lambda}{\partial \lambda} + \left(\frac{\partial S_\lambda}{\partial V_\lambda}\right)_{U_\lambda,N_\lambda} \frac{\partial V_\lambda}{\partial \lambda} + \left(\frac{\partial S_\lambda}{\partial N_\lambda}\right)_{U_\lambda,V_\lambda} \frac{\partial N_\lambda}{\partial \lambda}.$$

Setting $\lambda = 1$ or arguing that temperature is intensive yields that this is equal to

$$S = \frac{U}{T} + \frac{p}{T} - \frac{\mu}{T}.$$

We can rewrite this as

$$U - TS + pV = G = \mu N,$$

and thus that μ is the Gibbs free energy per particle. For a system of multiple kinds of particles we instead obtain

$$G = \mu_i N_i,$$

and we now interpret μ_i as the Gibbs free energy per particle of type i .

This also implies

$$\Phi_G = -pV.$$

Availability and Equilibrium The availability is a more general quantity which can be defined appropriately for systems with given constraints. Its differential will give both the maximal amount of work that can be performed by a system and a general equilibrium condition for the system.

As an example, consider a system in contact with surroundings at temperature T_0 and pressure p_0 (which may be chosen independently of the constraints on the system as both pressure and temperature are extensive and we assume the surroundings to be much larger than the system). If heat dQ is supplied to the system during some process, the entropy change satisfies $T_0 dS \geq dQ$, where S is the entropy of the system. The first law implies

$$dQ = dU - dW - (-p_0 dV),$$

where we have separated the work into a term arising due to the change in volume and a term describing other sources. Combining this yields

$$\begin{aligned} T_0 dS &\geq dU - dW - (-p_0 dV), \\ dW &\geq dU - T_0 dS + p_0 dV. \end{aligned}$$

Defining the availability for this case as

$$A = U + p_0 V - T_0 S$$

implies

$$dW \geq dA,$$

where equality is obtained for a reversible processes. Thus changes in the availability are equal to the maximal amount of useful work that can be extracted from a system.

If the system is mechanically isolated from the surroundings, such that only volume-changing work can be performed, we have

$$dA \leq 0.$$

Looking more closely at the differential of the availability, we obtain

$$dA = dU + p_0 dV - T_0 dS = d(U + p_0 V - T_0 S) = dG.$$

Hence the equilibrium condition is that Gibbs free energy is minimized.

In a similar fashion we find that for thermally isolated systems at fixed volume, the appropriate availability is $A = -T_0 S$, and hence for such systems the entropy is maximized. For a system at fixed temperature and volume the appropriate availability is $A = U - T_0 S = F$, and hence for such systems the Helmholtz free energy is minimized.

Equilibrium Between Systems For systems in contact, equilibrium is determined by minimizing the total availability.

As an example, consider two systems at fixed volume in thermal contact. For such a system the equilibrium condition is that the entropy is maximized. We obtain

$$dS = dS_1 + dS_2 = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2 \geq 0.$$

Energy conservation implies that the two internal energy changes must balance each other, yielding

$$\left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 \geq 0,$$

and hence the systems reach equilibrium when they reach the same temperature.

Maxwell Relations Using the symmetry of partial derivatives for a state function, one can obtain relations between derivatives of other state functions.

As an example, the derivatives of F are $-S$ and $-p$, computed with respect to T and V . This implies

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V.$$

Chemical Potential Without Particle Conservation For certain systems, there are no conservation laws for the number of particles. In such cases, if the chemical potential is fixed, the system will evolve in such a way as to minimize the availability with respect to the number of particles, which corresponds to $\mu = 0$. If there is a conservation law present, one must instead construct a constraint on the chemical potentials.

Gaseous Chemical Reactions

Latent Heat Consider a phase transition. During such a transition the temperature is constant, and in order for the transition to occur a certain amount of heat must be supplied. This is called the latent heat and is given by

$$L = T_c \Delta S.$$

Trouton's Rule For an interaction-free fluid, the multiplicity is proportional to the volume, yielding that the molar multiplicity ratio is

$$\frac{\Omega_{\text{vapour}}}{\Omega_{\text{liquid}}} = \left(\frac{V_{\text{vapour}}}{V_{\text{liquid}}} \right)^{N_A} = \left(\frac{\rho_{\text{liquid}}}{\rho_{\text{vapour}}} \right)^{N_A} \approx 10^{3N_A},$$

as liquids are approximately 1000 times as dense as vapours. The molar latent heat of fusion is thus

$$\frac{L}{n} = 7RT_c.$$

The Clausius-Clapeyron Equation Consider two phases, denoted 1 and 2, in equilibrium. We are interested in computing the coexistence curve between the two phases, i.e. the curve of all points such that the two phases are in equilibrium. The experimentally relevant constraints are typically constant pressure and temperature, so we want to study the coexistence curve in the $p - T$ diagram and find the coexistence curve when these two variables are fixed.

At any point of coexistence we have

$$dG = \mu_1 dN_1 + \mu_2 dN_2 = 0.$$

Conservation of particle number implies that

$$\mu_1 = \mu_2.$$

Now, supposing we were to move along the coexistence curve in the $p - T$ plane, the fact that the chemical potential is the Gibbs free energy per particle we have

$$-s_1 dT + v_1 dp = -s_2 dT + v_2 dp$$

where s and v are entropies and volumes per particle. Solving this yields

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{l}{T(v_2 - v_1)},$$

where l is the latent heat per particle. We finally obtain

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)},$$

which is the Clausius-Clapeyron equation. Yes, this derivation handles the differences between particles poorly.

3 Basic Concepts in Statistical Physics

Avogadro's Number Statistical physics discusses systems of many particles. A relevant measure of the number of particles to be studied is $N_A = 6.022 \times 10^{23}$.

Molar Mass The molar mass of a substance is defined as $M = mN_A$, where m is the mass of a single atom or molecule.

Atomic Units When discussing atoms and molecules, we use relative units. These units are relative to the atomic mass unit a.u. = 1.66×10^{-27} kg, defined as $\frac{1}{12}$ the mass of ^{12}C . This happens to be close to the mass of a hydrogen atom.

The Thermodynamic Limit The thermodynamic limit is the limit of the statistical consideration of a system when the number of particle is large. In this limit, quantities such as temperature, pressure and density can be defined as we know them and macroscopic equilibria can be achieved.

Microstates A microstate of a system is any complete description of all particles in a system, for instance a specification of all positions and velocities of the particles in a gas.

Macrostates A macrostate of a system is a description of the macroscopic properties of a system.

Multiplicity The multiplicity of a macrostate is the number of microstates that yield the same macrostate.

The Fundamental Postulate The fundamental postulate of statistical mechanics is that all microstates available to a system are observed with equal probability.

Equilibrium and Multiplicity Combining the fundamental postulate with our knowledge of thermodynamics, it is clear that a system in thermal equilibrium is in the macrostate corresponding to maximal multiplicity.

The Boltzmann Constant and Microscopic Temperature Consider two isolated systems in contact. The total energy and multiplicity is given by

$$E = E_1 + E_2, \quad \Omega = \Omega_1(E_1)\Omega_2(E_2).$$

At equilibrium, the total multiplicity is maximal. Differentiating with respect to E_1 gives

$$\begin{aligned} \frac{\partial \Omega}{\partial E_1} &= \Omega_2 \frac{d\Omega_1}{dE_1} + \Omega_1 \frac{d\Omega_2}{dE_2} \frac{dE_2}{dE_1} = \Omega_2 \frac{d\Omega_1}{dE_1} - \Omega_1 \frac{d\Omega_2}{dE_2}, \\ \frac{1}{\Omega_1} \frac{d\Omega_1}{dE_1} &= \frac{1}{\Omega_2} \frac{d\Omega_2}{dE_2}, \end{aligned}$$

which we can rewrite as

$$\frac{d \ln \Omega_1}{dE_1} = \frac{d \ln \Omega_2}{dE_2}.$$

We define either side to be equal to $\frac{1}{k_B T}$.

The Boltzmann Factor Consider a thermal bath in contact with a small system. The energy of the small system is ε , hence the bath has energy $E - \varepsilon$. Assuming that the multiplicity of the small system is independent of its energy, we Taylor expand the total multiplicity to obtain

$$\ln \Omega(E - \varepsilon) \approx \ln \Omega(E) - \varepsilon \frac{d \ln \Omega}{dE} = \ln \Omega(E) - \frac{\varepsilon}{k_B T},$$

with solution

$$\Omega(E - \varepsilon) = \Omega(E) e^{-\frac{\varepsilon}{k_B T}}.$$

This exponential factor is called the Boltzmann factor.

A consequence of this is that the probability of finding the small system in the macrostate with energy ε is, according to the fundamental hypothesis, proportional to $e^{-\frac{\varepsilon}{k_B T}}$.

The Statistical Basis For Entropy We have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V.$$

Combining this with our definition of temperature from a microscopic perspective, we obtain

$$S = k_B \ln \Omega.$$

Another, slightly more ad hoc way of arguing this, is to consider the entropy as a function of the multiplicity. Supposing that we have a system comprised of two non-correlated parts, the extensivity of the entropy yields

$$S = S_1 + S_2.$$

Now, the total multiplicity is $\Omega = \Omega_1 \Omega_2$, so requiring the entropy to be extensive takes the form

$$S(\Omega_1 \Omega_2) = S(\Omega_1) + S(\Omega_2).$$

A simple choice of entropy function is thus to choose one among the elementary functions. The function which does this is the natural logarithm. At this point we may introduce the Boltzmann constant as the constant of proportionality required to give S a dimension, and thus start our statistical definitions with our new entropy formula. The statistical definition of entropy will follow from that.

The Gibbs Factor Consider a system of N particles with internal energy U exchanging energy and particles with a smaller system with energy ε and n particles. The entropy of the reservoir is

$$S \approx S_0 - \varepsilon \left(\frac{\partial S}{\partial U} \right)_{N,V} - n \left(\frac{\partial S}{\partial N} \right)_{U,V} = S_0 - \frac{1}{T} (\varepsilon - \mu n).$$

Writing this in terms of the multiplicity we have

$$\ln \Omega(E - \varepsilon, N - n) = \ln \Omega(E, N) - \frac{\varepsilon - \mu n}{k_B T},$$

$$\Omega(E - \varepsilon, N - n) = \Omega(E, N) e^{-\frac{\varepsilon - \mu n}{k_B T}},$$

implying

$$P(\varepsilon, n) \propto e^{-\beta(\varepsilon - \mu n)}.$$

Entropy and Probability Consider a system with N available microstates, all equally likely and indistinguishable by experiment. These are divided into groups called to macrostates, distinguishable by experiment, with n_i microstates in each macrostate. We have

$$\sum n_i = N,$$

and the probability of finding the system in a particular macrostate is thus

$$P_i = \frac{n_i}{N}.$$

The total entropy is $S_{\text{tot}} = k_B \ln N$, but cannot be measured as the microstates are indistinguishable. Nevertheless, as entropy is extensive, the total entropy is a sum of the freedom to explore the microstates for a given macrostate and the freedom to explore the different macrostates, i.e.

$$S_{\text{tot}} = S + S_{\text{micro}}.$$

The entropy due to exploring microstates is an expectation value over the different macrostates of the entropy, given by

$$S_{\text{micro}} = \sum P_i S_i = k_B \sum P_i \ln n_i.$$

This yields

$$\begin{aligned} S &= S_{\text{tot}} - S_{\text{micro}} \\ &= k_B \ln N - k_B \sum P_i \ln n_i \\ &= k_B \sum P_i (\ln N - \ln n_i) \\ &= -k_B \sum P_i \ln P_i. \end{aligned}$$

4 Ensembles

Definition For a given system, an ensemble is a collection of all possible states of the system such that a certain set of quantities are preserved.

The Microcanonical Ensemble The microcanonical ensemble has N_i , V and E preserved.

The Canonical Ensemble The canonical ensemble has N_i , V and T preserved.

The Grand Canonical Ensemble The grand canonical ensemble has μ_i , V and T preserved.

5 Gases - Kinetics and Thermodynamics

The Maxwell-Boltzmann Velocity Distribution Consider a system of n (approximately) non-interacting particles. Assuming the separations to be much larger than the particle size and neglecting rotational and vibrational degrees of freedom, each particle has total energy $E = \frac{1}{2}mv^2$. We can now treat each particle as a small system in contact with a heat reservoir (namely the other particles). The results concerning the Boltzmann factor thus hold for this molecule. A single velocity component is thus described by the probability distribution

$$g(v_i) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{mv_i^2}{2k_B T}}.$$

This is of course true for all particles in the gas, meaning that the fraction of molecules with v_i in the range v_i to $v_i + dv_i$ is equal to $g(v_i) dv_i$.

It can be shown that

$$\langle v_i \rangle = 0, \quad \langle |v_i| \rangle = \sqrt{\frac{2k_B T}{m}}, \quad \langle v_i^2 \rangle = \frac{k_B T}{m}.$$

The Maxwell-Boltzmann Speed Distribution Consider instead the distribution of the particle speed. The distribution satisfying that the fraction of particles with speed in the range v to $v + dv$ is

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{v^2}{2k_B T}},$$

where the quadratic factor arises due to the integration volume.

It can be shown that

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}, \quad \langle v^2 \rangle = \frac{3k_B T}{m}$$

and that f has a maximum for

$$v = \sqrt{\frac{2k_B T}{m}}.$$

Directions and the Speed Distribution Because the velocity distribution is isotropic, the fraction of molecules whose trajectories lie in some solid angle range $d\Omega$ is given by $\frac{d\Omega}{4\pi}$. In three dimensions we can choose some direction and define an azimuthal angle θ relative to that direction, yielding that a fraction

$$\frac{1}{2} n f(v) \sin \theta dv d\theta$$

are travelling close to the angle θ to the chosen direction with a speed close to v per unit volume (n is the amount of particles per volume).

The Ideal Gas Law from Statistics Consider a wall with area A with a gas on one side. In a time interval dt the molecules travelling at angle θ to the wall normal sweep out a volume $A \cos \theta v dt$. This means that the number of molecules hitting the wall during dt is given by

$$A \cos \theta v dt \cdot \frac{1}{2} n f(v) \sin \theta dv d\theta.$$

Per unit area this number becomes

$$\cos \theta v dt \cdot \frac{1}{2} n f(v) \sin \theta dv d\theta.$$

Each particle imparts a momentum $2mv \cos \theta$ to the wall. The total momentum imparted to the wall per unit area by particles travelling at a specified speed and direction is thus

$$2mv \cos \theta \cdot \cos \theta v dt \cdot \frac{1}{2} n f(v) \sin \theta dv d\theta,$$

meaning that the impulse per area, i.e. the pressure, from these particles is

$$dp = 2mv \cos \theta \cdot \cos \theta v \cdot \frac{1}{2} n f(v) \sin \theta dv d\theta.$$

Integrating this, the total pressure is

$$p = \frac{1}{3} nm \langle v^2 \rangle = nk_B T.$$

Using the fact that $n = \frac{N}{V}$ we finally obtain the ideal gas law

$$pV = Nk_B T.$$

Dalton's Law For a mixture of ideal gases, the total pressure is a sum of the partial pressures of each gas. This is essentially due to the fact that the number of particles can be added.

Gas Flux and Effusion We define the particle flux of a gas as the number of molecules striking a unit area per time. We can integrate a previously obtained expression (the number of particles striking the wall?) to obtain

$$\Phi = \frac{p}{\sqrt{2\pi m k_B T}}.$$

The velocity distribution of molecules effusing out of a container is modified by a factor v . This can be noted from the form of the expression for the number of particles striking a unit area.

Collision Time Consider a gas, where we (for now) treat all particles but one as stationary. This particle has velocity v and collision cross-section σ (to be discussed later, but it is essentially the area of the particle with which other particles can collide). In a time dt the particle sweeps out an area $\sigma v dt$, meaning that a collision occurs within dt is $n\sigma v dt$. We define $P(t)$ to be the probability of the particle not colliding up to time t . According to our reasoning, we must have $P(t + dt) = P(t)(1 - n\sigma v dt)$. Comparing this to a Taylor expansion of P , we obtain

$$P(t) + \frac{dP}{dt} dt = P(t)(1 - n\sigma v dt).$$

This has the solution

$$P(t) = e^{-n\sigma v t},$$

assuming our consideration started at $t = 0$. The probability of not colliding up to t and colliding during the next dt is

$$P'(t) = n\sigma v e^{-n\sigma v t},$$

which is normalized. Using this, we compute the collision time

$$\tau = \frac{1}{n\sigma v}.$$

Collision Cross-Section Consider two spherical particles of radius a_1 and a_2 interacting with a hard-sphere potential. Imagining a particle of type 1 moving in the vicinity of type 2 particles, the movement of the type 1 particle sweeps out a tube of radius $a_1 + a_2$ such that if type 2 particles enter the tube, a collision occurs. The area of this tube is the collision cross-section, and is in this case given by

$$\sigma = \pi(a_1 + a_2)^2.$$

Mean Free Path The mean free path is the mean distance a particle can move without colliding. It should be proportional to the collision time and some velocity, but which velocity? It turns out that to include the effects of all particles moving, we must use the relative velocity between the considered particle and the other particles. We have

$$v_r^2 = v_1^2 + v_2^2 - 2\mathbf{v}_1 \cdot \mathbf{v}_2.$$

The expected value of the cross-term is 0 due to symmetry, and hence

$$\langle v_r^2 \rangle = 2 \langle v^2 \rangle.$$

We approximate $\langle v_r \rangle$ and $\langle v \rangle$ to be their RMS counterparts. Hence the mean free path is

$$\lambda = \langle v_r \rangle \tau = \frac{\sqrt{\langle v_r^2 \rangle}}{n\sigma v} = \frac{\sqrt{2} \langle v \rangle}{n\sigma v} = \frac{1}{\sqrt{2}n\sigma} = \frac{k_B T}{\sqrt{2}p\sigma}.$$

The Wave Equation for Sound Waves Fluid mechanics give that the flow of a non-viscous gas is described by Euler's equation

$$\partial_t \mathbf{u} + (u \cdot \vec{\nabla}) \mathbf{u} = -\frac{1}{\rho} \vec{\nabla} p,$$

as well as the continuity equation

$$\partial_t \rho + \vec{\nabla} \cdot \rho \mathbf{u} = 0.$$

We simplify Euler's equations for small amplitudes by ignoring second-order terms in Euler's equations to obtain

$$\partial_t \mathbf{u} = -\frac{1}{\rho} \vec{\nabla} p.$$

We also expand the continuity equation to

$$\partial_t \rho + \rho \vec{\nabla} \cdot \mathbf{u} + \mathbf{u} \cdot \vec{\nabla} \rho = 0.$$

Dividing by ρ and introducing $s = \ln \frac{\rho}{\rho_0}$ yields

$$\partial_t s + \vec{\nabla} \cdot \mathbf{u} + \mathbf{u} \cdot \vec{\nabla} s = 0.$$

Once again ignoring second-order terms we obtain

$$\partial_t s + \vec{\nabla} \cdot \mathbf{u} = 0.$$

In order to proceed, we introduce the bulk modulus

$$B = -V \frac{\partial p}{\partial V}.$$

Using the fact that the density is inversely proportional to the volume, we obtain

$$B = \rho \frac{\partial p}{\partial \rho}.$$

This allows us to write

$$\partial_t \mathbf{u} = -\frac{1}{\rho} \frac{\partial p}{\partial \rho} \vec{\nabla} \rho = -\frac{B}{\rho^2} \vec{\nabla} \rho = -\frac{B}{\rho} \vec{\nabla} s.$$

We have thus far obtained

$$\partial_t s + \vec{\nabla} \cdot \mathbf{u} = 0, \quad \partial_t \mathbf{u} = -\frac{B}{\rho} \vec{\nabla} s.$$

Computing the time derivative of the first equation and the gradient of the second yields

$$\partial_t^2 s - \frac{B}{\rho} \nabla^2 s = 0,$$

which is a wave equation for the sound waves.

The Nature of Sound Waves As we have seen, sound waves are variations in the density of air caused by compressions and rarefactions. However, I have not specified how the air is compressed and rarefacted, and that makes a difference. We will now try to get an understanding of which it might be.

Sound waves propagate at a length scale of

$$\lambda = \frac{2\pi c}{\omega}$$

where c is the speed of sound. Temperature propagates at a length scale of

$$\delta = \sqrt{\frac{2D}{\omega}}$$

where D is the thermal diffusivity. It seems reasonable that if the sound waves propagate at smaller length scales than the temperature does, i.e. $\delta > \lambda$, the compressions should be isothermal, whereas otherwise they are adiabatic. It turns out that the latter is true most often, so sound waves are typically adiabatic compressions and rarefactions of air. In fact, the wavelengths at which the opposite is true is smaller than the mean free path in air, making it obvious that the adiabatic case is most relevant.

The Mach Number and Shock Waves Consider a sound source moving at speed v . The Mach number is defined as

$$M = \frac{v}{c}.$$

We see that for Mach numbers greater than 1, the source moves faster than the waves. This corresponds to a shift from the wave being led by circular wavefronts to being led by a cone, as new wavefronts are generated ahead of the previous ones and interferes constructively with the previous. This causes the formation of a shock wave, i.e. a very intense wavefront.

Conservation Laws for Shock Waves We will now try to formulate conservation laws for shock waves. We will do this by considering the gas as split into two regimes by the front of the shock wave, where the gas that has not yet met the shock wave is termed 1 and the other gas is termed 2. Studying the gas in the rest frame of the shock front, we have that the gas in each region is flowing with a velocity v_1 and v_2 respectively. We must have $v_1 = v$, where v is the speed of the source.

Mass conservation implies

$$\rho_1 v = \rho_2 v_2.$$

Newton's second law implies

$$p_1 + \rho_1 v^2 = p_2 + \rho_2 v_2^2.$$

Energy conservation implies

$$p_1 v + \left(\rho_1 \tilde{u}_1 + \frac{1}{2} \rho_1 v^2 \right) v = p_2 v_2 + \left(\rho_2 \tilde{u}_2 + \frac{1}{2} \rho_2 v_2^2 \right) v_2$$

where \tilde{u} is the energy per unit mass.

The Rankine-Hugoniot Conditions For an ideal gas we have

$$\tilde{u} = \frac{p}{(\gamma - 1)\rho}.$$

This yields

$$\gamma \rho_1 \tilde{u}_1 v + \frac{1}{2} \rho_1 v^3 = \gamma \rho_2 \tilde{u}_2 v_2 + \frac{1}{2} \rho_2 v_2^3.$$

Combining this with the mass conservation and the expression for the internal energy yields

$$\frac{\gamma}{\gamma - 1} \frac{p_1}{\rho_1} + \frac{1}{2} v^2 = \frac{\gamma}{\gamma - 1} \frac{p_2}{\rho_2} + \frac{1}{2} v_2^2.$$

The computations are long, so for now I will just state the final result

$$\frac{p_2}{p_1} = \frac{2\gamma M^2 - (\gamma - 1)}{\gamma + 1}, \quad \frac{\rho_2}{\rho_1} = \frac{v_1}{v_2} = \frac{(\gamma + 1)M^2}{2 + (\gamma - 1)M^2}.$$

6 Statistical Physics

Probability and Observables The purpose of statistical mechanics is to treat systems in a statistical manner. We will describe systems in terms of probability distributions in phase space and compute observables as expectation values from this probability. A first step to note is that, in terms of classical mechanics, these observables must be computed as time averages. However, the fundamental postulate allows us to replace this by ensemble averages. We thus obtain the formula

$$\langle A \rangle = \sum A_i P_i$$

where the summation is performed over all of phase space.

6.1 The Microcanonical Ensemble

6.2 The Canonical Ensemble

The Partition Function The partition function is defined as

$$Z = \sum e^{-\beta E_i},$$

where the E_i are possible values of the energy (or, rather, the Hamiltonian) and we now formally introduce $\beta = \frac{1}{k_B T}$. The summation is performed over all of phase space.

Probability Combining our knowledge we obtain

$$P_i = \frac{1}{Z} e^{-\beta E_i}.$$

Properties of the Partition Function Suppose that the Hamiltonian is redefined by adding a constant. We then obtain

$$Z' = \sum e^{-\beta(E_i + E_0)} = e^{-\beta E_0} Z.$$

The value of any observable is thus

$$\langle A' \rangle = \sum A'_i P'_i = \sum A'_i \frac{e^{-\beta(E_i + E_0)}}{e^{-\beta E_0} Z} = \frac{1}{Z} \sum A'_i e^{-\beta E_i}.$$

We see that the only way for the expectation value to change is if A_i itself depends on the energy (as is the case if A is the internal energy, for instance). Otherwise, we have

$$\langle A' \rangle = \langle A \rangle.$$

Suppose that the Hamiltonian is separable, i.e. can be written as a sum over Hamiltonians H_j describing the j th degree of freedom. We thus obtain

$$Z = \sum e^{-\sum \beta H_j} = \sum_{\text{dof } 1} \dots \sum_{\text{dof } N} e^{-\sum \beta H_j} = \prod_j \sum_{\text{dof } j} e^{-\beta H_j} = \prod_j Z_j$$

where each partition function describes a given degree of freedom. This also has the consequence that observables which only depend on a subset of the degrees of freedom may be computed without considering the other degrees of freedom.

Distinguishability For distinguishable particles (distinguished by, for instance, spatial separation) of the same kind we have

$$Z_N = Z_1^N.$$

However, for indistinguishable particles, an issue arises due to overcounting of states where two or more particles have different energies. This overcounting is by a factor of $n!$, where n is the number of particles occupying different states, as switching the n particles around does not yield a new state. However, if states where two

or more particles have the same energy can be ignored, we can solve the overcounting problem by accounting for the degeneracy of the remaining states according to

$$Z_N = \frac{Z_1^N}{N!}.$$

But hold on! In classical mechanics, the equations of motions themselves imply that all particles are distinguishable. After all, any set of positions and momenta are directly connected to a single particle. How can the issue of distinguishability be relevant? The answer is that in the beginning, this factor was added ad hoc in order to guarantee that the entropy would be extensive. At its heart, however, the idea of indistinguishable particles is quantum mechanical. This could be taken as an early sign of the strong connection between statistical physics and quantum mechanics.

Internal Energy In a statistical context, we define the internal energy as $U = \langle E \rangle$. We have

$$\begin{aligned} U &= \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} \\ &= \frac{-\frac{dZ}{d\beta}}{Z} \\ &= -\frac{\partial \ln Z}{\partial \beta}. \end{aligned}$$

Alternatively, in terms of temperature,

$$U = -\frac{\partial \ln Z}{\partial \beta} \frac{\partial T}{\partial \beta} = \frac{1}{k_B \beta^2} \frac{\partial \ln Z}{\partial T} = k_B T^2 \frac{\partial \ln Z}{\partial T}.$$

Entropy We have

$$\ln P_i = -\beta E_i - \ln Z.$$

The definition of entropy from probability thus implies

$$S = -k_B \sum P_i \ln P_i = k_B \sum P_i (\beta E_i + \ln Z) = k_B \ln Z + \frac{U}{T}.$$

Helmholtz Free Energy We have

$$F = U - TS = U - \frac{1}{k_B \beta} S = U - U - \frac{1}{\beta} \ln Z = -\frac{1}{\beta} \ln Z,$$

or

$$Z = e^{-\beta F}.$$

Heat Capacity The heat capacity is given by

$$C = \frac{\partial U}{\partial T} = 2k_B T \frac{\partial \ln Z}{\partial T} + k_B T^2 \frac{\partial^2 \ln Z}{\partial T^2}.$$

Alternatively, we may write

$$\begin{aligned} C &= \frac{\partial}{\partial T} \left(\sum E_i \frac{1}{Z} e^{-\beta E_i} \right) \\ &= \frac{Z \cdot \frac{1}{k_B T^2} \sum E_i^2 e^{-\beta E_i} - \frac{\partial Z}{\partial T} \sum E_i e^{-\beta E_i}}{Z^2} \\ &= \frac{1}{k_B T^2} \langle E^2 \rangle + \frac{\langle E \rangle}{Z} \cdot -\frac{1}{k_B T^2} \frac{\partial Z}{\partial \beta} \\ &= \frac{1}{k_B T^2} \left(\langle E^2 \rangle - \langle E \rangle^2 \right). \end{aligned}$$

In other words, heat capacities correspond to energy fluctuations.

Heat Capacities With Discrete Energy Levels For systems with discrete energies the energy fluctuations must vanish at low temperatures, as only the lowest energy states becomes accessible.

Pressure The pressure is given by

$$p = -\frac{\partial F}{\partial V} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}.$$

Enthalpy The enthalpy is given by

$$H = k_B T^2 \frac{\partial \ln Z}{\partial T} + \frac{V}{\beta} \frac{\partial \ln Z}{\partial V} = k_B T \left(T \frac{\partial \ln Z}{\partial T} + V \frac{\partial \ln Z}{\partial V} \right).$$

Gibbs Free Energy The Gibbs free energy is given by

$$G = k_B T \left(-\ln Z + V \frac{\partial \ln Z}{\partial V} \right).$$

The Equipartition Theorem Suppose that some degree of freedom x , which may take any value, of a system without degenerate microstates only appears in the Hamiltonian as a term $\alpha|x|^\nu$. Its contribution to the internal energy is

$$\begin{aligned} \langle \alpha|x|^\nu \rangle &= \frac{\int_{-\infty}^{\infty} dx \alpha|x|^\nu e^{-\beta\alpha|x|^\nu}}{\int_{-\infty}^{\infty} dx e^{-\beta\alpha|x|^\nu}} \\ &= \frac{\int_0^{\infty} dx \alpha x^\nu e^{-\beta\alpha x^\nu}}{\int_0^{\infty} dx e^{-\beta\alpha x^\nu}}. \end{aligned}$$

Defining

$$I_\nu = \int_0^{\infty} dx e^{-\beta\alpha x^\nu}$$

we can write

$$\langle \alpha|x|^\nu \rangle = -\frac{1}{I_\nu} \frac{dI_\nu}{d\beta} = -\frac{d \ln I_\nu}{d\beta}.$$

We have

$$\begin{aligned} I_\nu &= \int_0^{\infty} du \frac{1}{\nu\beta\alpha} x^{1-\nu} e^{-u} \\ &= \frac{1}{\nu\beta\alpha} \int_0^{\infty} du \left(\frac{u}{\beta\alpha} \right)^{\frac{1}{\nu}-1} e^{-u} \\ &= \frac{1}{\nu} \left(\frac{1}{\beta\alpha} \right)^{\frac{1}{\nu}} \int_0^{\infty} du u^{\frac{1}{\nu}-1} e^{-u} \\ &= \beta^{-\frac{1}{\nu}} \frac{\Gamma\left(\frac{1}{\nu}\right)}{\nu\alpha^{\frac{1}{\nu}}}. \end{aligned}$$

From this we obtain

$$\langle \alpha|x|^\nu \rangle = \frac{1}{\nu\beta} = \frac{1}{\nu} k_B T.$$

Examples of such degrees of freedom (assuming a sufficient number of states is thermally available, which may not be the case for systems with a quantum nature) are

- translations, rotations and vibrations in a gas.
- vibrations in a crystal.

The Ideal Gas We will now study the statistical mechanics of an ideal gas. We will do this by considering the gas as a set of non-interacting free quantum particles in an $L \times L \times L$ box. The single-state wave function is

$$\psi = \left(\frac{2}{L}\right) \sin(k_x x) \sin(k_y y) \sin(k_z z),$$

where each quantum number is given by $k_i = \frac{\pi}{L} n_i$. Representing each possible state in a 3-dimensional space where each point represents a state, the available states of the system occupy the first octant, each state taking up a cube with dimensions $\frac{\pi}{L}$. The number of states with wave vector of length k to $k + dk$ is given by $\frac{1}{8} 4\pi k^2 dk$. Defining the density of states g as the number of states in a small k -interval divided by the interval length and the volume occupied by each state implies

$$g(k) = \frac{\frac{1}{2}\pi k^2}{\left(\frac{\pi}{L}\right)^3} = \frac{V k^2}{2\pi^2}.$$

The single-particle partition function can now be calculated as

$$Z_1 = \int_0^\infty dk e^{-\beta E} g(k) = \int_0^\infty dk e^{-\beta \frac{\hbar^2 k^2}{2m}} \frac{V k^2}{2\pi^2} = \frac{V}{2\pi^2} \int_0^\infty dk e^{-\beta \frac{\hbar^2 k^2}{2m}} k^2 = \frac{V}{\hbar^3} \left(\frac{mk_B T}{2\pi}\right)^{\frac{3}{2}}.$$

We can now define the quantum concentration

$$n_Q = \frac{1}{\hbar^3} \left(\frac{mk_B T}{2\pi}\right)^{\frac{3}{2}}$$

and the thermal wavelength

$$\lambda_{th} = \frac{1}{n_Q^{\frac{1}{3}}},$$

allowing us to write

$$Z_1 = V n_Q = \frac{V}{\lambda_{th}^3}.$$

The partition function for the entire system can be written as

$$Z_N = \frac{1}{N!} \frac{V^N}{\lambda_{th}^{3N}}$$

assuming that the number of thermally accessible energy levels is much larger than the density of particles, i.e. $\frac{N}{V} \ll n_Q$.

It is now time to derive thermodynamic properties of the system. We have

$$U = \frac{3}{2} k_B T, \quad p = \frac{N k_B T}{V}, \quad S = N k_B \left(\frac{5}{2} - \ln \left(\frac{N}{V} \lambda_{th}^3 \right) \right), \quad G = N k_B T \ln \left(\frac{N}{V} \lambda_{th}^3 \right).$$

Heat Capacity of a Diatomic Gas A major challenge of classical thermodynamics was explaining the behaviour of the heat capacity of diatomic gases. A diatomic ideal gas has translational, vibrational and rotational degrees of freedom. Classical equipartition theory would imply their heat capacity to be $C_V = \frac{7}{2} k_B T$, but this was only observed after heating above a certain temperature.

To understand this we have to study diatomic gases with quantum mechanics. We find that higher rotational energy levels are only thermally accessible for temperatures close to or above $\frac{\hbar^2}{2Ik_B}$, and vibrational levels close to or above $\frac{\hbar\omega}{k_B}$.

6.3 The Grand Canonical Ensemble

The Grand Canonical Partition Function For a system which may exchange energy and particles with its surroundings, we define the grand canonical partition function

$$\mathcal{Z} = \sum e^{-\beta(E_i - \mu N_i)},$$

which may be written as

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N.$$

Number of Particles The number of particles is given by

$$N = \frac{1}{\mathcal{Z}} \sum N_i e^{-\beta(E_i - \mu N_i)} = \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta \mu} = k_B T \frac{\partial \ln \mathcal{Z}}{\partial \mu}.$$

Internal Energy The internal energy is given by

$$U = \frac{1}{\mathcal{Z}} \sum E_i e^{-\beta(E_i - \mu N_i)} = \frac{1}{\mathcal{Z}} \left(-\frac{\partial \mathcal{Z}}{\partial \beta} + \sum \mu N_i e^{-\beta(E_i - \mu N_i)} \right) = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} + \mu N.$$

Entropy The entropy is given by

$$\begin{aligned} S &= -k_B \sum P_i \ln P_i \\ &= k_B \sum \frac{1}{\mathcal{Z}} e^{-\beta(E_i - \mu N_i)} \cdot (\beta(E_i - \mu N_i) - \ln \mathcal{Z}) \\ &= \frac{U}{T} - \frac{\mu N}{T} - k_B \sum P_i \ln \mathcal{Z} \\ &= \frac{U - \mu N + k_B T \ln \mathcal{Z}}{T}. \end{aligned}$$

Grand Potential The grand potential is given by

$$\Phi_G = U - TS - \mu N = -k_B T \ln \mathcal{Z}.$$

7 Quantum Statistical Mechanics

Distinguishability and Exchange Symmetry The concepts developed in this chapter will be based on the concepts of distinguishability. Classical particles are distinguishable, but quantum particles are not. As is postulated ad hoc in non-relativistic quantum mechanics, the operation of exchanging the two quantum particles with each other has a certain symmetry depending on the type of considered particles. Boson states are symmetric under exchange, and fermions are antisymmetric.

The Pauli Exclusion Principle Consider a many-particle state of fermions where two particles occupy the same state. Exchanging these two particles does not modify the total state. Combining this with the requirement that the state be antisymmetric under particle exchange implies that such a state cannot exist for fermions. This gives rise to the Pauli exclusion principle, which states that two indistinguishable fermions cannot occupy the same quantum state.

Quantum Grand Partition Functions Consider a system with a set of quantum states with energies E_i occupied by n_i particles each. Such a system would correspond to a set of non-interacting particles. The partition function for such a system is

$$Z = \sum_{\text{States}} e^{-\beta \sum n_i (E_i - \mu)} = \sum_{\text{States}} e^{\beta(\mu N - \sum n_i E_i)}.$$

A first question might be what happened to the factor $N!$ signifying that the particles are indistinguishable - after all, we said that distinguishability would be important. The answer is that the occupancy numbers themselves are not quantum numbers directly defining any state, but rather numbers defining the composition of the states. Due to the (anti)symmetry of the total state, it must be that any set of occupancy numbers can only correspond to a single quantum state, and thus there is no overcounting.

Computing this sum for any significant N is very difficult, as fixing one occupation number leaves constraints on the next, making the computation very intricate. However, the grand canonical partition function for such a system is of the form

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{\text{States}} e^{\beta(\mu N - \sum n_i E_i)}.$$

The sum over states is a sum over all configurations such that the sum of all occupancy numbers is equal to N . Combining this with the summation over N yields that this sum may be replaced by a sum over all conceivable occupancy configurations, removing the intricacies in the canonical ensemble. Furthermore, we have

$$\begin{aligned}\mathcal{Z} &= \sum_{n_1} \dots \sum_{n_\infty} e^{n_i \beta(\mu - E_i)} \\ &= \prod_i \left(\sum_{n_i} e^{n_i \beta(\mu - E_i)} \right),\end{aligned}$$

where the summation is performed over all possible values of the quantum numbers.

At this point we must specify what kinds of particles are discussed in order to proceed. For bosons n_i may be any positive integer, yielding

$$\mathcal{Z} = \prod_i \left(\frac{1}{1 - e^{\beta(\mu - E_i)}} \right),$$

whereas for fermions n_i may only be 0 or 1, yielding

$$\mathcal{Z} = \prod_i \left(1 + e^{\beta(\mu - E_i)} \right).$$

We can also write

$$\ln \mathcal{Z} = \pm \sum_i \ln \left(1 \pm e^{\beta(\mu - E_i)} \right),$$

where the $+$ is for fermions and the $-$ is for bosons.

Constraints on the Chemical Potential At this point it is wise to explicitly state a constraint which is often placed on the chemical potential, namely that it is chosen such that the number of particles does not change when either V or T are varied.

The Bose-Einstein and Fermi-Dirac Distributions When considering the statistics of quantum gases, we will base our work on distribution functions written in terms of energy rather than occupancy. This choice is highly analogous to, say, converting from the Maxwell-Boltzmann velocity distribution to a corresponding speed distribution for ideal gases. We have

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial E_i} = \frac{e^{\beta(\mu - E_i)}}{1 \pm e^{\beta(\mu - E_i)}} = \frac{1}{e^{\beta(E_i - \mu)} \pm 1}.$$

As there is a one-to-one correspondence between a given occupancy number and the corresponding energy, we can now write the distribution functions as

$$f(E) = \frac{1}{e^{\beta(E - \mu)} - 1}$$

for bosons and

$$f(E) = \frac{1}{e^{\beta(E - \mu)} + 1}$$

for fermions. These functions are called the Bose-Einstein and Fermi-Dirac distribution functions.

Note that the Bose-Einstein distribution imposes a constraint on the chemical potential, as it becomes singular if the chemical potential is greater than the lowest available energy state.

The Density of States In all problems to be studied, we will consider particles in a periodic cube. For such particles the components of the wave vector are of the form

$$k_i = \frac{2\pi}{L} n, \quad n = 0, \pm 1, \pm 2, \dots$$

where L is the dimension of the cube. In addition, there is a spin degeneracy, hence termed $\eta(s)$, such that the density of states in k -space is

$$\rho(\mathbf{k}) = \eta(s) \frac{1}{\left(\frac{2\pi}{L}\right)^3} = \eta(s) \frac{V}{8\pi^3}.$$

In terms of the length of the wave vector we have

$$\rho(k) = \eta(s) \frac{V}{8\pi^3} \cdot 4\pi k^2 = \eta(s) \frac{V}{2\pi^2} k^2.$$

To express this in terms of the energy, we use the dispersion relation

$$E = \frac{\hbar^2 k^2}{2m},$$

which yields that the density of states is

$$\rho(E) = \frac{1}{\frac{\hbar^2 k(E)}{m}} \cdot \eta(s) \frac{V}{2\pi^2} k^2(E) = \frac{\eta(s)}{2\pi^2} \frac{mV}{\hbar^2} \frac{\sqrt{2mE}}{\hbar} = \frac{\eta(s)}{(2\pi)^2} V \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E}.$$

We can also compute the number of states with energy less than E , which is given by

$$\begin{aligned} \sigma(E) &= \int_0^E d\varepsilon \rho(\varepsilon) \\ &= \frac{\eta(s)}{(2\pi)^2} V \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^E d\varepsilon \sqrt{\varepsilon} \\ &= \frac{2}{3} \frac{\eta(s)}{(2\pi)^2} V \left(\frac{2mE}{\hbar^2} \right)^{\frac{3}{2}}. \end{aligned}$$

The Non-Interacting Quantum Gas Consider a fluid of non-interacting quantum particles. The state of the system is characterized by a set of possible wave vectors, and each wave vector state has a degeneracy of $2s + 1$, where s is the spin of each particle. The partition function can thus be written as

$$\mathcal{Z} = \prod_{\mathbf{k}} \mathcal{Z}_{\mathbf{k}}^{2s+1}$$

where

$$\mathcal{Z}_{\mathbf{k}} = (1 \pm e^{-\beta(E_{\mathbf{k}} - \mu)})^{\pm 1}.$$

The partition function of a quantum gas is thus given by

$$\begin{aligned} \ln \mathcal{Z} &= \pm \sum_{\mathbf{k}} \ln(1 \pm e^{-\beta(E_{\mathbf{k}} - \mu)}) \\ &= \pm \int_0^\infty dE \rho(E) \ln(1 \pm e^{-\beta(E - \mu)}) \\ &= \mp \int_0^\infty dE \sigma(E) \frac{\mp \beta e^{-\beta(E - \mu)}}{1 \pm e^{-\beta(E - \mu)}} \\ &= \beta \int_0^\infty dE \frac{\sigma(E)}{e^{\beta(E - \mu)} \pm 1}, \end{aligned}$$

where the top sign is for fermions and the bottom for bosons.

The grand potential of such a quantum gas is given by

$$\Phi_G = -k_B T \ln \mathcal{Z} = - \int_0^\infty dE \frac{\sigma(E)}{e^{\beta(E-\mu)} \pm 1},$$

or, by using the density of states, we have

$$\Phi_G = - \frac{2}{3} \frac{\eta(s)}{(2\pi)^2} V \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty dE \frac{E^{\frac{3}{2}}}{e^{\beta(E-\mu)} \pm 1}.$$

The total number of occupied states may be computed in two ways. The first is

$$\begin{aligned} N &= \sum_{\mathbf{k}} n_{\mathbf{k}} \\ &= \sum_{\mathbf{k}} k_B T \frac{\partial \ln Z_{\mathbf{k}}}{\partial \mu} \\ &= k_B T \int_0^\infty dE \rho(E) \frac{\partial \ln Z_{\mathbf{k}}}{\partial \mu}. \end{aligned}$$

The second is

$$N = \frac{\partial \ln \mathcal{Z}}{\partial \beta \mu}.$$

We now use the fact that the integrand in $\ln Z$ is of the form $\sigma(E)f(\beta(E-\mu))$. For such a function we have

$$\partial_{\beta \mu} = -\partial_{\beta E} = -k_B T \partial_E,$$

yielding

$$\begin{aligned} N &= \frac{\partial}{\partial \beta \mu} \left(\beta \int_0^\infty dE \frac{\sigma(E)}{e^{\beta(E-\mu)} \pm 1} \right) \\ &= \beta \int_0^\infty dE \sigma(E) \frac{\partial}{\partial \beta \mu} \left(\frac{1}{e^{\beta(E-\mu)} \pm 1} \right) \\ &= - \int_0^\infty dE \sigma(E) \frac{\partial}{\partial E} \left(\frac{1}{e^{\beta(E-\mu)} \pm 1} \right) \\ &= \int_0^\infty dE \frac{\rho(E)}{e^{\beta(E-\mu)} \pm 1}. \end{aligned}$$

The internal energy is given by

$$\begin{aligned}
U &= \mu N - \frac{\partial \ln Z}{\partial \beta} \\
&= \mu \int_0^\infty dE \frac{\rho(E)}{e^{\beta(E-\mu)} \pm 1} - \frac{\partial}{\partial \beta} \left(\beta \int_0^\infty dE \frac{\sigma(E)}{e^{\beta(E-\mu)} \pm 1} \right) \\
&= \int_0^\infty dE \frac{\mu \rho(E)}{e^{\beta(E-\mu)} \pm 1} - \int_0^\infty dE \frac{\sigma(E)}{e^{\beta(E-\mu)} \pm 1} - \beta \int_0^\infty dE \sigma(E) \cdot -\frac{(E-\mu)e^{\beta(E-\mu)}}{(e^{\beta(E-\mu)} \pm 1)^2} \\
&= \int_0^\infty dE \frac{\mu \rho(E)}{e^{\beta(E-\mu)} \pm 1} - \int_0^\infty dE \frac{\sigma(E)}{e^{\beta(E-\mu)} \pm 1} + \beta \int_0^\infty dE \sigma(E)(E-\mu) \frac{e^{\beta(E-\mu)}}{(e^{\beta(E-\mu)} \pm 1)^2} \\
&= \int_0^\infty dE \frac{\mu \rho(E)}{e^{\beta(E-\mu)} \pm 1} - \int_0^\infty dE \frac{\sigma(E)}{e^{\beta(E-\mu)} \pm 1} + \int_0^\infty dE (\rho(E)(E-\mu) + \sigma(E)) \frac{1}{e^{\beta(E-\mu)} \pm 1} \\
&= \int_0^\infty dE \frac{E \rho(E)}{e^{\beta(E-\mu)} \pm 1},
\end{aligned}$$

or alternatively as

$$U = \sum_{\mathbf{k}} n_{\mathbf{k}} E_{\mathbf{k}}.$$

It can be shown that all these quantities are proportional to

$$\mp (k_B T)^n \Gamma(n) \text{Li}(\mp z)$$

where n is the power of E that is integrated.

The Fermi Energy Consider a gas of fermions, a Fermi gas, at $T = 0$. At this temperature, the fermions will fill up states from the lowest energy, $2s + 1$ at a time, until they hit a certain maximal energy, defined to be the Fermi energy. Based on this a more explicit definition of the Fermi energy is

$$E_F = \mu \Big|_{T=0}.$$

At $T = 0$, β is very large. This means that the occupation number for a quantum gas is

$$n_{\mathbf{k}} = \frac{1}{e^{\beta(E_{\mathbf{k}}-\mu)} + 1} \rightarrow \theta(\mu - E_{\mathbf{k}}) = \theta(E_F - E_{\mathbf{k}})$$

where θ is the Heaviside function. We thus obtain

$$N = \int d^3\mathbf{k} g(\mathbf{k})$$

where we integrate over a sphere of radius $k_F = k(E_F)$. This wave vector is called the Fermi wave vector.

The Fermi Temperature The Fermi temperature is defined as

$$T_F = \frac{E_F}{k_B}.$$

The Fermi Surface The Fermi surface is the surface in \mathbf{k} -space made up of points corresponding to states with energy equal to that of the chemical potential.

The Sommerfeld Formula Consider a integral of the form

$$I = \int_0^{\infty} dE \phi(E) f(E), \quad f(E) = \frac{1}{e^{\beta(E-\mu)} + 1}.$$

Introduce the antiderivative ψ of ϕ such that $\psi(0) = 0$. We thus have

$$I = - \int_0^{\infty} dE \psi(E) \frac{df}{dE}.$$

Introducing $x = \beta(E - \mu)$, we can somehow expand ψ as

$$\psi = \sum_{s=0}^{\infty} \left. \frac{d^s \psi}{dx^s} \right|_{x=0} \frac{x^s}{s!},$$

compute

$$\frac{df}{dE} = -\beta \frac{e^x}{(e^x + 1)^2}$$

and write

$$\begin{aligned} I &= \sum_{s=0}^{\infty} \frac{\beta}{s!} \left. \frac{d^s \psi}{dx^s} \right|_{x=0} \int_0^{\infty} dE x^s \frac{e^x}{(e^x + 1)^2} \\ &= \sum_{s=0}^{\infty} \frac{1}{s!} \left. \frac{d^s \psi}{dx^s} \right|_{x=0} \int_{-\beta\mu}^{\infty} dx \frac{x^s e^x}{(e^x + 1)^2}. \end{aligned}$$

If the temperature is much lower than the Fermi temperature, we can extend the integral to $-\infty$, where the odd terms disappear and the even terms take the form

$$\begin{aligned} \int_{-\infty}^{\infty} dx \frac{x^s e^x}{(e^x + 1)^2} &= 2 \int_0^{\infty} dx \frac{x^s e^x}{(e^x + 1)^2} \\ &= 2 \int_0^{\infty} dx \frac{x^s e^{-x}}{(e^{-x} + 1)^2} \\ &= 2 \int_0^{\infty} dx x^s e^{-x} \sum_{m=0}^{\infty} (-1)^m (m+1) e^{-mx} \\ &= 2 \sum_{m=0}^{\infty} (-1)^m (m+1) \int_0^{\infty} dx x^s e^{-(m+1)x} \\ &= 2 \sum_{m=1}^{\infty} (-1)^{m+1} m \int_0^{\infty} dx x^s e^{-mx} \\ &= 2(s!) \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{m^s} \\ &= 2(s!)(1 - 2^{1-s})\zeta(s). \end{aligned}$$

We thus finally obtain the Sommerfeld formula

$$\begin{aligned}
I &\approx \sum_{s=0}^{\infty} \frac{1}{s!} \left. \frac{d^s \psi}{dx^s} \right|_{x=0} \int_{-\infty}^{\infty} dx \frac{x^s e^x}{(e^x + 1)^2} \\
&= \sum_{s=0}^{\infty} \frac{1}{(2s)!} \left. \frac{d^{2s} \psi}{dx^{2s}} \right|_{x=0} 2(2s!)(1 - 2^{1-2s})\zeta(2s) \\
&= \psi(x=0) + \frac{\pi^2}{6} \left. \frac{d^2 \psi}{dx^2} \right|_{x=0} + \frac{7\pi^4}{360} \left. \frac{d^4 \psi}{dx^4} \right|_{x=0} + \dots \\
&= \int_0^{\mu} dE \phi + \frac{\pi^2}{6} \left. \frac{d\phi}{dx} \right|_{E=\mu} + \frac{7\pi^4}{360} \left. \frac{d^3 \phi}{dx^3} \right|_{E=\mu} + \dots
\end{aligned}$$

Thermodynamics of the Fermi Gas

Hints of a Phase Transition For a Bose gas it may be shown that

$$\frac{N\lambda_{\text{th}}^3}{\eta(s)V} = \text{Li}_{\frac{3}{2}}(z),$$

which has no solution if

$$\frac{N\lambda_{\text{th}}^3}{\eta(s)V} > \zeta\left(\frac{3}{2}\right).$$

What happens is that the integral approximations of the sums for the macroscopic quantities fails due to the ground state being macroscopically occupied. This occurs at a temperature

$$k_{\text{B}}T_c = \frac{2\pi\hbar^2}{m} \left(\frac{N}{\eta(s)\zeta\left(\frac{3}{2}\right)V} \right)^{\frac{2}{3}}.$$

Corrected Analysis of the Bose Gas Suppose that the total number of occupied states is

$$N = N_0 + N_1$$

where the two terms are the number of particles in the ground state and the number of particles in all other states respectively. Above the critical temperature the ground state is not macroscopically occupied, and we have

$$N_0 = \frac{1}{z^{-1} - 1}, \quad N_1 \approx \frac{\eta(s)V}{\lambda_{\text{th}}^3} \text{Li}_{\frac{3}{2}}(z).$$

To examine what happens below the critical temperature, one can argue that z is close to 1, which yields

$$N_1 = \frac{\eta(s)\zeta\left(\frac{3}{2}\right)}{\lambda_{\text{th}}^3}, \quad N_0 = N \left(1 - \left(\frac{T}{T_c} \right)^3 \right).$$

The Photon Gas We will compute the statistical mechanics of a photon gas using a more crude version of the machinery shown above. For a photon in a three-dimensional cube we have

$$g(k) = 2 \frac{4\pi k^2 V}{8\pi^3} = \frac{k^2 V}{\pi^2}.$$

Using the linear dispersion relation for photons we have

$$g(\omega) = \frac{1}{c} \frac{\omega^2 V}{c^2 \pi^2} = \frac{\omega^2 V}{c^3 \pi^2}.$$

The internal energy for such a photon is given by

$$U_\omega = \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right).$$

We thus obtain

$$U = \int_0^\infty d\omega \frac{\omega^2 V}{c^3 \pi^2} \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right).$$

One issue with this is that the first term diverges, which is typically undesirable. However, we note that its value is independent of temperature, so we conclude that it must correspond to a vacuum energy - an energy which is present in any black body. We thus ignore it to obtain

$$\begin{aligned} U &= \int_0^\infty d\omega \frac{\omega^2 V}{c^3 \pi^2} \hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1} \\ &= \frac{V\hbar}{c^3 \pi^2} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \\ &= \frac{V\hbar}{c^3 \pi^2} \left(\frac{1}{\beta\hbar} \right)^4 \int_0^\infty dx \frac{x^3}{e^x - 1} \\ &= \frac{V}{\hbar^3 c^3 \pi^2} (k_B T)^4 \frac{\pi^4}{15} \\ &= \frac{\pi^2 V k_B^4}{15 \hbar^3 c^3} T^4. \end{aligned}$$

The original integrand, divided by the volume, defines the black-body distribution

$$u_\omega = \frac{\hbar}{c^3 \pi^2} \frac{\omega^3}{e^{\beta\hbar\omega} - 1},$$

which may be rewritten in terms of the wavelength as

$$u_\lambda = \frac{8\pi\hbar c}{\lambda^5} \frac{1}{e^{\frac{\beta\hbar c}{\lambda}} - 1}.$$

The Phonon Gas Phonons are quantized excitations in a crystal lattice. We will now study their statistics.

We first need a dispersion relation. To obtain this, we consider a chain of similar atoms with nearest-neighbour interactions where the displacement of each atom from its equilibrium position is denoted as u_i . Assuming the chain to be infinite and expanding the forces to first order, we obtain

$$m\ddot{u}_n = K(u_{n+1} - u_n) - K(u_n - u_{n-1}) = K(u_{n+1} + u_{n-1} - 2u_n).$$

We are looking for periodic solutions of the form $u_n = C e^{i(kna - \omega t)}$. Inserting this into the equation above yields

$$-m\omega^2 = K(e^{ika} + e^{-ika} - 2) = K(2\cos(ka) - 2) = -4K \sin^2\left(\frac{ka}{2}\right),$$

and thus

$$\omega = 2\sqrt{\frac{K}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|.$$

Studying the dispersion in the long-wavelength limit, we have

$$\omega = 2\sqrt{\frac{K}{m}} \frac{ka}{2} = a\sqrt{\frac{K}{m}} k.$$

This implies a speed for long-wavelength phonons equal to

$$v_s = a\sqrt{\frac{K}{m}}.$$

Next we need a density of states. This is less trivial for phonons than for photons due to the fact that the number of modes is finite - $3N - 6$, to be precise (approximated to $3N$). Two models were proposed. The first is the Einstein model

$$g(\omega) = 3N\delta(\omega - \omega_E),$$

corresponding to all phonons oscillating at the same frequency. As we will see, this makes it natural to define the Einstein temperature

$$T_E = \frac{\hbar\omega_E}{k_B}.$$

The other model starts with the normal k-space density of states

$$g(\mathbf{k}) = \frac{3}{\left(\frac{2\pi}{L}\right)^3} = \frac{3V}{(2\pi)^3}, \quad g(k) = \frac{3V}{(2\pi)^3} 4\pi k^2 = \frac{3V}{2\pi^2} k^2.$$

Using the long-wavelength approximation (which is at least partially valid, as it is those states which are counted first) we obtain

$$g(\omega) = \frac{3V}{2\pi^2 v_s^3} \omega^2.$$

As the number of vibration modes is finite, we are required to introduce the Debye frequency, defined by

$$\int_0^{\omega_D} d\omega g(\omega) = 3N.$$

In three dimensions we obtain

$$\omega_D = \left(\frac{6N\pi^2 v_s^3}{V} \right)^{\frac{1}{3}}.$$

We also introduce the Debye temperature

$$T_D = \frac{\hbar\omega_D}{k_B}.$$

Now we are ready to handle the statistical mechanics of the gas. We have

$$\ln Z = \int_0^{\omega_D} d\omega g(\omega) \ln \left(\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right).$$

For the