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.

Contents

1   Handy Mathematics

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

$$\mathrm{d}f = \vec{\boldsymbol{\nabla}} f \cdot \mathbf{r}.$$

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

$$\mathrm{d}x = \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z + \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y, \ \mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y.$$

Combining these yields

$$\mathrm{d}x = \left(\frac{\partial x}{\partial z}\right)_y \left(\left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y\right) + \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y$$

$$= \left(\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y\right) \mathrm{d}x + \left(\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x + \left(\frac{\partial x}{\partial y}\right)_z\right) \mathrm{d}y.$$

This implies

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

which can be combined to yield

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

2   Combinatorics

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

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

3   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.

Types of Work   The following discussions will focus on gaseous systems, where all work is manifest as expansions and compressions. Before doing that, we should specify how work terms work. They are generally of the form

$$\text{d\kern-0.5exW} = X \, \mathrm{d}x \, ,$$

where X is an intensive generalized force and x an extensive generalized displacement. For gases, 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.

Heat Capacity of a Gas   The work required to compress a gas is $\text{d\kern-0.5exW} = -p \, \mathrm{d}V$. The change in internal energy for a gas is

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V \, ,$$

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

$$\text{d\kern-0.5exQ} = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\left(\frac{\partial U}{\partial V}\right)_T + p\right) \mathrm{d}V \, .$$

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

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

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

Adiabatic Index   The adiabatic index is defined as

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

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

$$\mathrm{d}U = \text{d\kern-0.5exQ} + \text{d\kern-0.5exW}.$$

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

To prove that Kelvin's statement implies Clausius', we introduce a Kelvin violater 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_l from the cold reservoir and leaving heat Q_h in the cold reservoir. The combination of these two systems thus transfer heat Q_l from the cold reservoir to the hot reservoir with no other results, violating Kelvin's statement.

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.

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_l 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 $\text{d}Q_i$ being supplied at every stage. The total work performed during the cycle is given by

$$W = \sum \text{d}Q_i.$$

Now suppose that the heat at each point is supplied by a Carnot engine operating between temperatures T and T_i. One can show that for a Carnot engine the ratio of heat to temperature at which the heat is exchanged is constant. This implies

$$\frac{\text{d}Q_i}{T_i} = \frac{\text{d}Q_i + \text{d}W_i}{T}$$

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

$$W + \sum đW_i \leq 0.$$

Hence

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

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

$$\int đQ \frac{1}{T} \leq 0.$$

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

Entropy   As we have seen, the integral

$$\int đQ \frac{1}{T}$$

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

$$dS = \frac{đQ}{T}$$

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

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

This holds for two arbitrary points, meaning

$$dS \geq \frac{đQ}{T}.$$

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 we obtain

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

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

Natural Variables For Internal Energy   Our restatement of the first law implies that U is most naturally written as a function of S and V (naturally it could be written in terms of other variables too, but you would have to change variables from S and V in order to do that). This implies

$$\left(\frac{\partial U}{\partial S} \right)_V = T, \quad \left(\frac{\partial U}{\partial V} \right)_S = -p.$$

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

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

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 reciprocity theorem to obtain

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{p}{T}\,\mathrm{d}V\,.$$

This implies

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

Enthalpy The enthalpy is defined as

$$H = U + pV.$$

We have

$$\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_i\,\mathrm{d}N_i + p\,\mathrm{d}V + V\,\mathrm{d}p = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu_i\,\mathrm{d}N_i\,,$$

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

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

Helmholtz Free Energy The Helmholtz free energy is defined as

$$F = U - TS.$$

We have

$$\mathrm{d}F = \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_i\,\mathrm{d}N_i - T\,\mathrm{d}S - S\,\mathrm{d}T = -p\,\mathrm{d}V - S\,\mathrm{d}T + \mu_i\,\mathrm{d}N_i\,,$$

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

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

Gibbs Free Energy The Gibbs free energy is defined as

$$G = H - TS.$$

We have

$$\mathrm{d}G = \mathrm{d}H - T\,\mathrm{d}S - S\,\mathrm{d}T = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu_i\,\mathrm{d}N_i - T\,\mathrm{d}S - S\,\mathrm{d}T = V\,\mathrm{d}p - S\,\mathrm{d}T + \mu_i\,\mathrm{d}N_i\,,$$

implying that G is a function of T and p, 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

$$\Phi_{\mathrm{G}} = F - \mu N.$$

We have

$$\mathrm{d}\Phi_{\mathrm{G}} = -p\,\mathrm{d}V - S\,\mathrm{d}T + \mu\,\mathrm{d}N - \mu\,\mathrm{d}N - N\,\mathrm{d}\mu = -p\,\mathrm{d}V - S\,\mathrm{d}T - N\,\mathrm{d}\mu\,,$$

implying that Φ_{G} is a function of V, T and μ, as well as

$$S = -\left(\frac{\partial \Phi_{\mathrm{G}}}{\partial T}\right)_{V,\mu}, \quad p = -\left(\frac{\partial \Phi_{\mathrm{G}}}{\partial V}\right)_{T,\mu}, \quad N = -\left(\frac{\partial \Phi_{\mathrm{G}}}{\partial \mu}\right)_{T,V}.$$

Availability and Equilibrium The availability is a more general quantity which can be defined appropriately for systems with given constraints. Its differential will give 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. If heat $\mathrm{d}Q$ is supplied to the system during some process, the entropy change satisfies $T_0\,\mathrm{d}S \geq \mathrm{d}Q$. The first law implies

$$\mathrm{d}Q = \mathrm{d}U - \mathrm{d}W - (-p_0\,\mathrm{d}V),$$

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

$$T_0\,\mathrm{d}S \geq \mathrm{d}U - \mathrm{d}W - (-p_0\,\mathrm{d}V),$$
$$\mathrm{d}W \geq \mathrm{d}U - T_0\,\mathrm{d}S + p_0\,\mathrm{d}V\,.$$

Defining the availability for this case as

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

implies

$$\mathrm{d}W \geq \mathrm{d}A\,.$$

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

$$\mathrm{d}A \leq 0.$$

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

$$\mathrm{d}A = \mathrm{d}U + p_0\,\mathrm{d}V - T_0\,\mathrm{d}S = \mathrm{d}(U + p_0 V - T_0 S) = \mathrm{d}G\,.$$

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

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

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

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 satement:** 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. We have

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

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

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

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

near absolute zero, which implies

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

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.

Reinterpretation of the Chemical Potential and Grand Potential Consider a system 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

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

and setting $\lambda = 1$ yields

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

and thus that μ is the Gibbs free energy per particle. This also implies

$$\Phi_{\mathrm{G}} = -pV.$$

Chemical Potential Without Particle Conservation For certain systems, there are no conservation laws for the number of particles. For such systems, equilibrium corresponds to $\mu = 0$.

Gaseous Reactions

4   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 studies is $N_{\mathrm{A}} = 6.022 \times 10^{23}$.

Molar Mass The molar mass of a substance is defined as $M = mN_{\mathrm{A}}$, 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. $= 1.66 \times 10^{-27}$ 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   Consider two systems which are not in contact. The total energy and multiplicity is given by

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

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

$$\partial_{E_1}\Omega = \Omega_2\frac{\mathrm{d}\Omega_1}{\mathrm{d}E_1} + \Omega_1\frac{\mathrm{d}\Omega_2}{\mathrm{d}E_2}\frac{\mathrm{d}E_2}{\mathrm{d}E_1}.$$

The total energy is fixed, yielding

$$\frac{1}{\Omega_1}\frac{\mathrm{d}\Omega_1}{\mathrm{d}E_1} = \frac{1}{\Omega_2}\frac{\mathrm{d}\Omega_2}{\mathrm{d}E_2},$$

which we can rewrite as

$$\frac{\mathrm{d}\ln\Omega_1}{\mathrm{d}E_1} = \frac{\mathrm{d}\ln\Omega_2}{\mathrm{d}E_2}.$$

We define this to be equal to $\frac{1}{k_\mathrm{B}T}$.

The Boltzmann Factor   Consider a thermal bath in contact with a small system. The energy of the small system is ε, so that the bath has energy $E - \varepsilon$. For each energy, only one cunfiguration is available for the small system. Taylor expanding the multiplicity yields

$$\ln\Omega(E - \varepsilon) \approx \ln\Omega(E) - \varepsilon\frac{\mathrm{d}\ln\Omega}{\mathrm{d}E} = \ln\Omega(E) - \frac{\varepsilon}{k_\mathrm{B}T},$$

with solution

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

This exponential factor is called the Boltzmann factor.

We note that the probability of finding the small system in the macrostate with energy ε is, according to the fundamental hypothesis, proportional to $e^{-\frac{\varepsilon}{k_\mathrm{B}T}}$.

The Statistical Basis For Entropy   We can use what we have seen in thermodynamics to show that

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

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

$$S = k_\mathrm{B}\ln\Omega.$$

The Boltzmann Factor With Varying Particle Number Consider a system with energy U and N particles exchanging energy and particles with a smaller system with energy ε and n particles. The entropy of the reservoir is

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

Somehow this implies

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

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 $S_{\text{tot}} = k_{\text{B}} \ln N$, 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

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

This yields

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

5   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.

6   Gases

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

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

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 $v_i + \mathrm{d}v_i$ is equal to $g(v_i)\,\mathrm{d}v_i$.

It can be shown that

$$\langle v_i \rangle = 0, \ \langle |v_i| \rangle = \sqrt{\frac{2k_\mathrm{B} T}{m}}, \ \langle v_i^2 \rangle = \frac{k_\mathrm{B} T}{m}.$$

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 $v + \mathrm{d}v$ is

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

where the quadratic factor arises due to the integration volume.

It can be shown that

$$\langle v \rangle = \sqrt{\frac{8k_\mathrm{B} T}{\pi m}}, \ \langle v^2 \rangle = \frac{3k_\mathrm{B} T}{m}$$

and that f has a maximum for

$$v = \sqrt{\frac{2k_\mathrm{B} T}{m}}.$$

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

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

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 Consider a wall with area A with a gas on one side. In a time interval $\mathrm{d}t$ the molecules travelling at angle θ to the wall normal sweep out a volume $A\cos\theta v \, \mathrm{d}t$. This means that the number of molecules hitting the wall during $\mathrm{d}t$ is given by

$$A\cos\theta v \, \mathrm{d}t \cdot \frac{1}{2} n f(v) \sin\theta \, \mathrm{d}v \, \mathrm{d}\theta \,.$$

Per unit area this number becomes

$$\cos\theta v \, \mathrm{d}t \cdot \frac{1}{2} n f(v) \sin\theta \, \mathrm{d}v \, \mathrm{d}\theta \,.$$

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

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

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

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

Integrating this, the total pressure is

$$p = \frac{1}{3} n m \langle v^2 \rangle = n k_\mathrm{B} T.$$

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

$$pV = N k_\mathrm{B} T.$$

Dalton's Law For a mixture of ideal gases, the partial pressures of each gas can be added. This is 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 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 thu 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

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

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

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

7 Statistical Physics

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 possible microstates of the system.

Properties of the Partition Function

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

$$U = \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}}$$
$$= \frac{-\frac{\mathrm{d}Z}{\mathrm{d}\beta}}{Z}$$
$$= -\frac{\partial \ln Z}{\partial \beta}.$$

Alternatively, in terms of temperature,

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

Entropy We have

$$\ln P_i = \ln\left(\frac{e^{-\beta E_i}}{Z}\right) = -\beta E_i - \ln Z.$$

The definition of entropy from probability thus implies

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

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

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

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

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

Distinguishability   For distinguishable particles one can show that

$$Z_N = Z_1^N.$$

However, for indistinguishable particles, an issue arises due to overcounting of states where two particles have equal energies. However, if these states can be ignored, we can solve the overcounting problem by writing

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

The Equipartition Theorem   Suppose that some degree of freedom x, which may take any value, of a system only appears in the Hamiltonian as a quadratic term αx^2. Its contribution to the internal energy is

$$\langle E \rangle = \frac{\int\limits_{-\infty}^{\infty} \mathrm{d}x \, \alpha x^2 e^{-\beta \alpha x^2}}{\int\limits_{-\infty}^{\infty} \mathrm{d}x \, e^{-\beta \alpha x^2}}.$$

One can show that this is equal to

$$\langle E \rangle = \frac{1}{2} k_{\mathrm{B}} T.$$

Examples of such degrees of freedom 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 sate, 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 $k+\mathrm{d}k$ is given by $\frac{1}{8} 4\pi k^2 \, \mathrm{d}k$. 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

$$Z_1 = \int\limits_0^{\infty} \mathrm{d}k \, e^{-\beta E} g(k) = \int\limits_0^{\infty} \mathrm{d}k \, e^{-\beta \frac{\hbar^2 k^2}{2m}} \frac{V k^2}{2\pi^2} = \frac{V}{2\pi^2} \int\limits_0^{\infty} \mathrm{d}k \, e^{-\beta \frac{\hbar^2 k^2}{2m}} k^2 = \frac{V}{\hbar^3} \left(\frac{m k_{\mathrm{B}} T}{2\pi} \right)^{\frac{3}{2}}.$$

We can now define the quantum concentration

$$n_{\mathrm{Q}} = \frac{1}{\hbar^3} \left(\frac{m k_{\mathrm{B}} T}{2\pi} \right)^{\frac{3}{2}}$$

and the thermal length

$$\lambda_{\mathrm{th}} = \frac{1}{n_{\mathrm{Q}}^{\frac{1}{3}}},$$

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. $\frac{N}{V} << n_Q$.

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

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

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 (I think).

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 $\frac{\hbar^2}{2 I k_B}$, and vibrational levels close to or above $\frac{\hbar \omega}{k_B}$.

The Grand Canonical Partition Function   For a system which may exchange energy and particles with its surroundings, we have

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

This defines the grand canonical partition function

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

which may be written as

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

8   Quantum Statistical Mechanics

Distinguishability   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 changing the positions of two quantum particles in a quantum state 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 do 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 Canonical 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. If this system is set in thermal contact with a heat bath, this implies that the occupancy of each state will vary due to the heat exchange, which is why such systems belong to the grand canonical ensemble. The grand canonical partition function for such a system is of the form

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

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.

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. The total energy and the number of particles may be expressed as sums over particle numbers, allowing us to write

$$\mathcal{Z} = \sum_{n_1} \cdots \sum_{n_\infty} e^{n_i \beta(\mu - E_i)}$$

$$= \prod_i \left(\sum_{n_i} e^{n_i \beta(\mu - E_i)} \right),$$

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.

The Bose-Einstein and Fermi-Dirac Distributions When considering the statistics of quantum gases, we will base our work on distribution functions describing the mean occupancy of a given energy level. 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

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

for bosons and

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

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