

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

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

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

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.

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

$$dU = dQ + dW.$$

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.

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

$$dW = X dx,$$

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 $dW = -p dV$. The change in internal energy for a gas is

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

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

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

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 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_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.

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 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

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

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

$$\int \mathrm{d}Q \frac{1}{T}$$

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

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T}$$

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

$$\int_A^B \mathrm{d}Q \frac{1}{T} + \int_B^A \mathrm{d}Q_{\text{rev}} \frac{1}{T} \leq 0 \implies \int_A^B \mathrm{d}Q \frac{1}{T} \leq \int_A^B \mathrm{d}Q_{\text{rev}} \frac{1}{T}.$$

This holds for two arbitrary points, meaning

$$\mathrm{d}S \geq \frac{\mathrm{d}Q}{T}.$$

Considering a thermally isolated system, we obtain

$$\mathrm{d}S \geq 0.$$

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

$$\mathrm{d}U = T \mathrm{d}S - p \mathrm{d}V.$$

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 can be written as a function of S and V .

Enthalpy The enthalpy is defined as

$$H = U + pV.$$

We have

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

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

$$\left(\frac{\partial H}{\partial S} \right)_p = T, \quad \left(\frac{\partial H}{\partial p} \right)_S = V.$$

Helmholtz Free Energy The Helmholtz free energy is defined as

$$F = U - TS.$$

We have

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

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

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

Gibbs Free Energy The Gibbs free energy is defined as

$$G = H - TS.$$

We have

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

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

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

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 dQ is supplied to the system during some process, the entropy change satisfies $T_0 dS \geq dQ$. 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

$$dW \geq dA.$$

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.

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 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. 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, 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.

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 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 particles 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 has maximal multiplicity.

The Boltzmann constant Consider two systems which are not in contact. The total energy and multiplicity is given by

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

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

$$\partial_{E_1} \Omega = \Omega_2 \frac{d\Omega_1}{dE_1} + \Omega_1 \frac{d\Omega_2}{dE_2} \frac{dE_2}{dE_1}.$$

The total energy is fixed, yielding

$$\frac{1}{\Omega_1} \frac{d\Omega_1}{dE_1} = - \frac{1}{\Omega_2} \frac{d\Omega_2}{dE_2},$$

which we can rewrite as

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

We define this 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 , so that the bath has energy $E - \varepsilon$. For each energy, only one configuration is available for the small system. Taylor expanding the multiplicity yields

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

with solution

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

This exponential factor is called the Boltzmann factor.

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

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

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

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

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

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 , V and E preserved.

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

Grand Canonical Ensembles The grand canonical ensemble has μ , 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

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

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

$$\frac{1}{2}nf(v)\sin\theta\,dv\,d\theta$$

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 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

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

Per unit area this number becomes

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

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

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

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

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

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 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 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

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

This has the solution

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

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

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

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

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

Alternatively, in terms of temperature,

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

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

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} dx \alpha x^2 e^{-\beta \alpha x^2}}{\int_{-\infty}^{\infty} dx e^{-\beta \alpha x^2}}.$$

One can show that this is equal to

$$\langle E \rangle = \frac{1}{2} k_B T.$$

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 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 length

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

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