

Statistical Mechanics
MANUSCRIPT

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Chapter 1

Statistical Mechanics

1 Introduction

Statistical mechanics concerns with the behavior of matter and energy when the number of parts in a system is very large. It begins by admitting that any attempt to keep a ledger of the position and momentum of *every* particle in a system, even on a computer, becomes intractable beyond certain limits. Also, one can imagine a grand mechanical ledger being redundant to a simpler *statistical* analysis.

Entropy

Recall from elementary thermodynamics that Carnot successfully identified an entirely reversible thermodynamic cycle composed of isothermal and adiabatic processes. In one cycle of a so-called Carnot engine, all instances of heat energy Q transferred to the system divided by the temperature T at each instance,

sums to zero:

$$\sum_{\text{Carnot cycle}} \frac{Q}{T} = 0$$

Traversing an open path or an irreversible path in PV -space will give a non-zero result on the right, identified as the entropy:

$$\sum \frac{Q}{T} = \Delta S$$

In the differential limit, the sum becomes an integral of over small increments dQ/T :

$$\Delta S = \int \frac{dQ}{T}$$

Another exhibit comes from analyzing free expansion of ideal gas from an initial volume into confined vacuum. For initial volume V_i of gas that expands freely into a final volume V_f , the entropy change simplifies to:

$$\Delta S = NK \ln \left(\frac{V_f}{V_i} \right) = K \ln \left(\frac{V_f^N}{V_i^N} \right)$$

Note that all information about the system is enclosed in the natural logarithm, which in this case is a dimensionless ratio of volumes - just a number.

Configurations

A system of one particle confined to a volume only large enough to contain that particle has no options for change, and we say there is only one available *configuration* in the system. If the system volume is doubled, there are suddenly *two* available configurations - the particle can occupy either half of the available volume. It clearly follows that the number of configurations available to a single-particle system scales with

the volume of the system. Start adding more particles, and the number of configurations grows rapidly. The total number of configurations available to a system is called the combinatoric *multiplicity*, denoted Ω (Greek Omega).

Distinguishability

An important consideration is whether any two members in a system are *distinguishable* or *indistinguishable*. For instance, the number of configurations of two identical letters XX is precisely one - it would be *physically* redundant to swap the order of each X and claim a second configuration. However, if given the distinguishable pair X_1X_2 , then it is *not* futile to swap each member, giving X_2X_1 as the second configuration.

The multiplicity of a system having two particles occupying any of N available volume units is easy to write. The first particle has all N ‘choices’ of empty volume units, so we begin with $\Omega_1 = N$. The second particle can’t choose from all N volume units, but instead $N - 1$, indicating $\Omega_2 = N - 1$.

If the particles are distinguishable, the total multiplicity is simply the product of Ω_1 and Ω_2 :

$$\Omega_{\text{dist}} = \Omega_1\Omega_2 = N(N - 1)$$

For particles that are identical though, it follows that Ω_{dist} over-counts the multiplicity by a factor of 2. The total multiplicity is then:

$$\Omega_{\text{indist}} = \frac{N(N - 1)}{2}$$

Extensive and Intensive

Recall from elementary thermodynamics that a system exhibits two classes of variables - extensive and intensive. *Extensive* quantities, such as mass, volume, and energy, scale when resizing the system. By contrast, *intensive* quantities, such as density and temperature, don’t scale by resizing the system.

In a class of its own, the multiplicity is *super-extensive*, meaning it grows by multiplication. In order to ‘knock down’ the multiplicity into an everyday extensive quantity, the most natural maneuver is to take the logarithm of Ω , so that multiplication

$$\Omega_T = \Omega_1\Omega_2$$

becomes addition:

$$\ln(\Omega_T) = \ln(\Omega_1) + \ln(\Omega_2)$$

Rethinking Entropy

Our walk-through of combinatorics suggests an information-based definition of entropy for two reasons. (i) For an ideal gas expanding freely into vacuum, we found that entropy is equal to the Boltzmann constant K times the natural log of some number that has to do with configurations. (ii) The natural log of the multiplicity is an extensive quantity. It follows that entropy shall be *defined* generally as K times the natural log of the multiplicity:

$$S = K \ln(\Omega) \quad (1.1)$$

2 Microcanonical Ensemble

A thermodynamic system that is not allowed to exchange volume V , number of particles N , or energy U with its environment is a *microcanonical ensemble*. One should recall from elementary thermodynamics that the entropy S of such a system can only increase with time, which is indeed the case here. The entropy is crucial to calculate, as the myriad of thermodynamic variables are computed from S or its derivatives.

Microstate

In a microcanonical ensemble, consider an instantaneous ‘snapshot’ of the whole system, and write the position and momentum of *every* particle involved, within the Heisenberg limit $\Delta x \Delta p \geq \hbar$. Such a (potentially enormous) body of information is called a *microstate*.

A fundamental assumption of the microcanonical ensemble is that *all microstates are equally accessible*. This is to say that microstates are uniformly sampled by the system as time evolves.

Macrostate

System-wide, or otherwise ‘global’ quantities of the system are called *macrostates*. One can readily imagine that many, sometimes an *infinite* number of microstates can correspond to one macrostate. For instance, a box of gas in the macrostate with fixed pressure, fixed volume, and fixed temperature, can correspond to very many microstates. A corollary to this is that any observed macrostate, such as the air density in a room, is one corresponding to the greatest number of microstates.

Ergodic Hypothesis

A fundamental assumption of microcanonical ensemble theory is the *ergodic hypothesis*, stating that the time-average \bar{x} of an observable is equivalent to the ensemble average $\langle x \rangle$ of the observable. We demonstrate this by considering a simple harmonic oscillator of mass m having position $q(t)$ and momentum $p(t)$ at fixed energy E obeying the (Hamiltonian) differential equation

$$H(q, p) = \frac{p^2}{2m} + \frac{m\omega^2}{2}q^2,$$

solved by:

$$\begin{aligned} q(t) &= A \cos(\omega t) \\ p(t) &= -m\omega A \sin(\omega t) \\ A &= \sqrt{\frac{2E}{m\omega^2}} \end{aligned}$$

We easily calculate the time-average of the mean-square position $q(t)^2$ using the definition

$$\overline{q^2} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T q(t)^2 dt,$$

which comes out to

$$\overline{q^2} = \lim_{T \rightarrow \infty} \frac{A^2}{T} \int_0^T \frac{\cos(2\omega t) + 1}{2} dt = \frac{A^2}{2} = \frac{E}{m\omega^2}.$$

We next calculate the ensemble average $\langle q^2 \rangle$ using

$$\langle q^2 \rangle = \frac{\int q^2 \rho(q, p) dq dp}{\int \rho(q, p) dq dp},$$

where the density

$$\rho(q, p) \propto \delta(H(q, p) - E)$$

is a Dirac delta function that obeys

$$\int \delta(\phi(y)) dy = \frac{1}{\phi'(y_0)}.$$

Starting with the denominator, find:

$$\begin{aligned} \int \rho(q, p) dq dp &= \int \delta(H(q, p) - E) dq dp \\ &= \int \frac{1}{\left(\frac{\partial H}{\partial p}\right) \Big|_{\frac{p^2}{2m} + \frac{m\omega^2}{2}q^2 - E = 0}} dq \\ &= \int_{\pm} \frac{m dq}{\sqrt{2m(E - m\omega^2 q^2/2)}} \\ &= 2 \int \frac{p dt}{|p|} = \frac{2}{\omega} \int \omega dt = \frac{2}{\omega} \int_0^\pi d\theta \\ &= \frac{2\pi}{\omega} \end{aligned}$$

Moving on to the numerator, the calculation is similar until the last step:

$$\begin{aligned} \int q^2 \rho(q, p) dq dp &= \frac{2}{\omega} \int q^2 \omega dt \\ &= \frac{2A^2}{\omega} \int \cos^2(\omega t) \omega dt \\ &= \frac{2A^2}{\omega} \frac{\pi}{2} = \frac{\pi A^2}{\omega} \end{aligned}$$

Finally, the ensemble average $\langle q^2 \rangle$ comes to

$$\langle q^2 \rangle = \frac{\pi A^2}{\omega} \frac{\omega}{2\pi} = \frac{A^2}{2} = \frac{E}{m\omega^2},$$

matching the time-average.

2.1 Equilibrium

Having fixed volume, number of particles, and energy, the dynamic quantities in the microcanonical ensemble tend to be the temperature T , pressure P , and chemical potential μ .

Thermal Equilibrium

Consider a microcanonical system A having multiplicity Ω_A , internal energy U_A , and entropy $S_A = K \ln(\Omega_A)$, and also a second system B characterized by Ω_B , U_B , and $S_B = K \ln(\Omega_B)$.

When placed in contact, the systems A and B are allowed to exchange internal energy while maintaining a constant total $U_C = U_A + U_B$, with corresponding differential $dU_A = -dU_B$. (The volume and number of particles in each subsystem must remain the same.) The entropy is extensive and obeys $S_C = S_A + S_B$, and meanwhile the multiplicity is super-extensive and follows $\Omega_C = \Omega_A \Omega_B$.

As each system achieves thermal equilibrium, the energies U_A and U_B are not fixed, but instead hover around average values \bar{U}_A and \bar{U}_B . The temperature of each system finds a common value $T_C = T_A = T_B$, which is defined from elementary thermodynamics in terms of S and U :

$$\begin{aligned} T_A &= \left(\frac{\partial S_A}{\partial U_A} \right)_{V_A, N_A, \bar{U}_A}^{-1} \\ T_B &= \left(\frac{\partial S_B}{\partial U_B} \right)_{V_B, N_B, \bar{U}_B}^{-1} \end{aligned}$$

Encoded in the above definitions is the notion that the entropy is maximized at thermal equilibrium.

To proceed, let us choose a dependent variable (from system A for simplicity), and frame the total entropy as

$$S_C(U_A) = K \ln(\Omega_C(U_A)).$$

By Taylor-expanding in the neighborhood $U_A \approx \bar{U}_A$, the entropy becomes

$$S_C(U_A) \approx S_C(\bar{U}_A) + \left(\frac{\partial S_C}{\partial U_A} \right)_{\bar{U}_A} (U_A - \bar{U}_A) + \frac{1}{2!} \left(\frac{\partial^2 S_C}{\partial U_A^2} \right)_{\bar{U}_A} (U_A - \bar{U}_A)^2 + \dots,$$

where we stop expanding after at least second order, because the first-order coefficient is identically zero:

$$\begin{aligned} \left(\frac{\partial S_C}{\partial U_A} \right)_{\bar{U}_A} &= \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = \frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} \\ &= \frac{1}{T_A} - \frac{1}{T_B} = 0 \end{aligned}$$

The second-order coefficient is recast by brute force, giving

$$\begin{aligned} \left(\frac{\partial^2 S_C}{\partial U_A^2} \right)_{\bar{U}_A} &= \frac{\partial}{\partial U_A} \left(\frac{\partial S_C}{\partial U_A} \right) = \frac{\partial}{\partial U_A} \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \\ &= -\frac{1}{T_A^2} \frac{\partial T_A}{\partial U_A} - \frac{1}{T_B^2} \frac{\partial T_B}{\partial U_B}, \end{aligned}$$

which contains the definition of the heat capacity at constant volume for each subsystem near equilibrium. Condensing the second-order coefficient into a variable $-K\sigma_A^{-2}$, we have

$$\left(\frac{\partial^2 S_C}{\partial U_A^2} \right)_{\bar{U}_A} = -\frac{1}{T^2} \left(\frac{1}{(C_V)_A} + \frac{1}{(C_V)_B} \right) = \frac{-K}{\sigma_A^2}.$$

In terms of σ_A^2 , the total entropy near equilibrium reads:

$$S_C(U_A) \approx S_C(\bar{U}_A) - \frac{K}{2\sigma_A^2} (U_A - \bar{U}_A)^2 \quad (1.2)$$

The total multiplicity Ω_C of the combined system is given by inverting the definition $S_C = K(\ln \Omega_C)$, or

$$\Omega_C \approx e^{S_C(\bar{U}_A)/K} e^{-(U_A - \bar{U}_A)^2 / 2\sigma_A^2},$$

which is Gaussian in the U_A -variable. As normalized, the above becomes a probability density

$$p(U_A) = \left(\frac{1}{2\pi\sigma_A^2} \right)^{1/2} e^{-(U_A - \bar{U}_A)^2 / 2\sigma_A^2}.$$

Problem 1

Use the thermodynamic identity $dU = TdS - PdV + \mu dN$ to derive

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

Problem 2

Use Gaussian integrals to show:

$$\begin{aligned} \int_{\text{all } U_A} p(U_A) dU_A &= 1 \\ \langle U_A \rangle &= \bar{U}_A \\ \langle U_A^2 \rangle &= \bar{U}_A^2 + \sigma_A^2 \end{aligned}$$

Problem 3

From elementary thermodynamics, we know the ideal gas has internal energy $U = 3NKT/2$. For connected systems A and B of total energy U , (i) use the equilibrium condition to write U_A in terms of U , N_A , and N_B . (ii) Solve for σ_A explicitly and show that σ_A/U_A scales with $N^{-1/2}$. Answer:

$$\begin{aligned} T_A &= T_B \\ \frac{2U_A}{3N_A K} &= \frac{2(U - U_A)}{3N_B K} \\ U_A &= U \frac{N_A}{N} \end{aligned}$$

$$\begin{aligned} \frac{1}{\sigma_A^2} &= \frac{3N_A}{2U_A^2} + \frac{3N_B}{2(U - U_A)^2} \\ &= \frac{3N^2}{2U^2} \left(\frac{1}{N_A} + \frac{1}{N_B} \right) = \frac{3}{2U^2} \frac{N^3}{N_A N_B} \end{aligned}$$

$$\begin{aligned} \frac{\sigma_A}{U_A} &= \sqrt{\frac{3}{2}} \frac{U \sqrt{N_A N_B}}{N \sqrt{N}} \frac{N}{U N_A} \\ &= \sqrt{\frac{3}{2}} \sqrt{\frac{N_B}{N_A}} \frac{1}{\sqrt{N}} \propto \frac{1}{\sqrt{N}} \end{aligned}$$

Mechanical Equilibrium

Extending the previous example, consider a composite microcanonical system C made from two systems A, B that are allowed to exchange energy and volume (but not particles). In particular, we have

$$\begin{aligned} 0 &= dU_A - dU_B \\ 0 &= dV_A - dV_B \\ 0 &= dN_A = dN_B \end{aligned}$$

such that

$$\begin{aligned} \Omega_C &= \Omega_A(U_A, V_A, N_A) \\ &\quad \times \Omega_B(U_C - U_A, V_C - V_A, N_B). \end{aligned}$$

The system C tends toward thermal equilibrium with $T_A = T_B$ and also mechanical equilibrium with $P_A = P_B$, written as:

$$\begin{aligned} P_A &= T \left(\frac{\partial S_A}{\partial V_A} \right)_{U_A, N_A, \bar{V}_A} \\ P_B &= T \left(\frac{\partial S_B}{\partial V_B} \right)_{U_B, N_B, \bar{V}_B} \end{aligned}$$

Using $S_C = K \ln(\Omega_C)$ and Taylor-expanding in the neighborhood $V_A \approx \bar{V}_A$, the entropy is approximately

$$S_C(V_A) \approx S_C(\bar{V}_A) + \left(\frac{\partial S_C}{\partial V_A} \right)_{\bar{V}_A} (V_A - \bar{V}_A) + \frac{1}{2!} \left(\frac{\partial^2 S_C}{\partial V_A^2} \right)_{\bar{V}_A} (V_A - \bar{V}_A)^2 + \dots,$$

and we draw attention to the first-order coefficient:

$$\begin{aligned} \left(\frac{\partial S_C}{\partial V_A} \right)_{\bar{V}_A} &= \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} \\ &= \frac{P_A - P_B}{T} = 0 \end{aligned}$$

Problem 4

Use the thermodynamic identity $dU = TdS - PdV + \mu dN$ to derive

$$P = T \left(\frac{\partial S}{\partial V} \right)_{U, N}.$$

Diffusive Equilibrium

A system allowed to exchange energy, volume, and particles will tend toward diffusive equilibrium. For this situation, the thermodynamic identity $dU = TdS - PdV + \mu dN$ readily leads to

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U, V},$$

which must be the same for each subsystem A, B .

2.2 Microcanonical Paramagnetism

Magnetic Materials

A simple application of microcanonical ensemble theory is *paramagnetism*. Magnetism is a phenomenon caused by circulating electric currents in matter or vacuum. Most solids generally fall into one of three categories: paramagnetic, diamagnetic, or ferromagnetic.

Ferromagnetic materials have the strongest coupling to magnetic phenomena, and are most familiar to everyday experience. Inside a ferromagnetic material, atoms are arranged into macroscopic *domains*, wherein electrons orbit their respective nuclei such that the angular momentum vector of each electron points the same way. A strong permanent magnet consists of many domains, where any given cluster of domains has a net magnetic moment that is strong in a direction we decide to call ‘north’.

Paramagnetic materials exhibit weak affinity to magnetism, and do not carry permanent magnetic fields. A paramagnetic material responds attractively to an external magnetic field, wherein electrons inside the material align their axis of orbit in order to increase the total magnetic field near the paramagnet. It follows that a paramagnetic material is attracted to an external field and moves toward it.

A diamagnetic material acts in the opposite manner as a paramagnet - it tries to oppose an external magnetic field and is repelled from it. These phenomena only occur when the temperature of the material is low enough, otherwise thermal noise prevents domain alignment.

Paramagnet in External Field

Consider a large- N paramagnetic material of fixed volume made of non-interacting spin $1/2$ particles, each having magnetic moment $\vec{\mu} = 2\mu_B \vec{S}$, where μ_B is the Bohr magneton and \vec{S} is the spin of a given particle. When an external magnetic field $\vec{B} = +B\hat{z}$ is applied, a number N_\uparrow particles tend to align their spin axis along the external field’s direction, where a minority N_\downarrow of particles go against the field. (At low temperatures or in strong fields, none of the spin vectors support an angle with respect to \hat{z} .) The paramagnet in turn acts as a two-state system with total internal energy $U = -N_\uparrow\mu B + N_\downarrow\mu B$ among its $N = N_\uparrow + N_\downarrow$ particles.

As a two-state system, the multiplicity Ω in terms of U and N reads

$$\begin{aligned} \Omega(U, N) &= \frac{N!}{N_\uparrow! N_\downarrow!} \\ &= \frac{N!}{\left(\frac{N}{2} - \frac{U}{2\mu B}\right)! \left(\frac{N}{2} + \frac{U}{2\mu B}\right)!}. \end{aligned} \quad (1.3)$$

Proceeding carefully, let $x = U/2\mu B$ and apply Stirling’s approximation

$$n! \approx \left(\frac{n}{e}\right)^n \sqrt{2\pi n}$$

to arrive at

$$\Omega(x, N) \approx \frac{N^N \sqrt{N/2\pi}}{\left(\frac{N^2}{4} - x^2\right)^{N/2} \left(\frac{N}{2} - x\right)^{-x} \left(\frac{N}{2} + x\right)^x \sqrt{\frac{N^2}{2} - x^2}},$$

which is more easily handled if we take the natural

logarithm:

$$\begin{aligned} \ln(\Omega(U, N)) &\approx N \ln(N) + \frac{1}{2} \ln\left(\frac{N}{2\pi}\right) \\ &\quad - \left(\frac{N+1}{2}\right) \ln\left(\frac{N^2}{4} - x^2\right) \\ &\quad + x \left(\ln\left(\frac{N}{2} - x\right) - \ln\left(\frac{N}{2} + x\right)\right) \end{aligned} \quad (1.4)$$

Proceed by Taylor-expanding inside the ln-terms, using the approximation that $N \gg x$. Doing so, we find

$$\begin{aligned} \ln\left(\frac{N}{2} \pm x\right) &\approx \ln\left(\frac{N}{2}\right) \pm \frac{2x}{N} \\ \ln\left(\frac{N^2}{4} - x^2\right) &\approx 2 \ln\left(\frac{N}{2}\right) - \left(\frac{2x}{N}\right)^2, \end{aligned}$$

and the multiplicity boils down to (ignoring the last very small term)

$$\ln(\Omega(U, N)) \approx N \ln(2) + \ln\sqrt{\frac{2}{\pi N} - \frac{2x^2}{N} + \frac{2x^2}{N^2}}.$$

While already in the $\ln(\Omega)$ domain, multiply by the Boltzmann constant to write the entropy of the two-state paramagnet

$$S = K \left(N \ln(2) + \frac{1}{2} \ln\left(\frac{2}{\pi N}\right) - \frac{U^2}{2N\mu^2 B^2} \right), \quad (1.5)$$

which decreases as more spins align. The corresponding multiplicity is

$$\Omega(U, N) = 2^N \sqrt{\frac{2}{\pi N}} e^{-2(U/2\mu B)^2/N}. \quad (1.6)$$

Note that by dividing out the total multiplicity (total number of microstates) 2^N , Ω becomes a Gaussian probability density in the dimensionless quantity $U/2\mu B$:

$$p(U/2\mu B, N) = \sqrt{\frac{2}{\pi N}} e^{-2(U/2\mu B)^2/N}$$

Having fixed volume and number of particles, the formula $1/T = (\partial S/\partial U)_{V,N}$ gives the temperature as

$$KT = -\frac{N}{U} \mu^2 B^2,$$

which has a minus sign to balance out the overall negativity of U . This relation is handy near $U = 0$, but completely ignores the boundary cases $U = \pm N\mu B$.

To refine the calculation, we must return to Equation (1.4) without using Taylor expansion. Instead of

writing a massively ugly formula for the entropy, go straight to the temperature calculation by taking a derivative with respect to $x = U/2\mu B$, which yields

$$\frac{\partial S}{\partial x} = K \left(\frac{x}{\frac{N^2}{4} - x^2} + \ln\left(\frac{\frac{N}{2} - x}{\frac{N}{2} + x}\right) \right),$$

where the first term has been ignored due to the factor of N^{-2} . This is equivalent to leaving out the $\sqrt{2\pi N}$ -like terms in Stirling's approximation. Adjusting for U instead of x , we find

$$KT = \frac{2\mu B}{\ln\left(\frac{N\mu B - U}{N\mu B + U}\right)}, \quad (1.7)$$

which equals zero at the boundaries $U = \pm N\mu B$.

Negative Temperature

Curiously, a two-state paramagnet *can have negative temperature* if conditions are right. If the system is prepared so that most spins oppose the external magnetic field, the temperature is indeed negative, however not colder than absolute zero. The temperature undergoes a major discontinuity as the energy passes through $U = 0$, at which point the temperature is ambiguously either/and $T = -\infty$ or $T = \infty$. If the energy is a small positive number $U \approx \mu B$, the temperature is around $-\infty$ (spins alternate up and down). If the energy is instead negative with $U \approx -\mu B$, the temperature is approximately ∞ . This is not so far-fetched, because a paramagnet that can still manage $U = 0$ despite the external B -field should be quite hot!

2.3 Entropic Spring

Consider a stretchable material classified as a polymer chain, such as a rubber band, that is maintained under tension F in the x -direction. In particular, we imagine the chain made of $N \gg 1$ links, each of length a and connected end-to-end, oriented as follows: (i) The N_{\parallel} links oriented parallel to x each contribute a to the total length of the chain. (ii) The N_{\perp} links oriented perpendicular to x do not contribute to the length L of the chain. Using the variables on hand, we write

$$L = Nx,$$

where

$$x = a \frac{N_{\parallel}}{N}.$$

Such a setup is the *entropic spring model*. Let us also assume that the system is in an environment of fixed temperature T . Since each link doesn't 'care'

about the orientation of other links, the internal energy is taken as $U = 0$. The relevant thermodynamic potential is in fact the Gibbs free energy in the form

$$G = -FL - TS,$$

where $-FL$ is playing the one-dimensional role of PV . The negative sign occurs because pressure is usually a push from outside the system. The force F in this case is a pull.

As a microcanonical system, we can write the multiplicity of links parallel to x :

$$\Omega(N_{\parallel}, N) = \frac{N!}{N_{\parallel}!(N - N_{\parallel})!}$$

The next target is the entropy, which first requires Stirling's approximation to arrive at

$$\Omega(N_{\parallel}, N) \approx N \ln(N) - N_{\parallel} \ln(N_{\parallel}) - (N - N_{\parallel}) \ln(N - N_{\parallel}),$$

to which $S = K \ln(\Omega)$ is readily applied.

The Gibbs free energy is minimized at equilibrium. For this, we calculate

$$\begin{aligned} \frac{dG}{dL} &= \frac{d}{dL} (-FL - TS)_{x=\langle x \rangle} \\ 0 &= -F - KT \left(\frac{d\Omega}{dN_{\parallel}} \frac{dN_{\parallel}}{dL} \right)_{x=\langle x \rangle}, \end{aligned}$$

simplifying to an equation of state

$$F = \frac{-KT}{a} \ln \left(\frac{a}{\langle x \rangle} - 1 \right).$$

We next solve for $\langle x \rangle$ and subsequently write the length of the chain as $\langle L \rangle = N \langle x \rangle$ while under force:

$$\langle L \rangle = \frac{Na}{1 + e^{-Fa/KT}}$$

The case $F = 0$ corresponds to $a = 2\langle x \rangle$, or $N = 2N_{\parallel}$. This means that without any force, statistically half of the links are in the parallel orientation. Using $L = Nx$, it follows that the rest length L_0 of the chain is

$$L_0 = \frac{Na}{2}.$$

Define

$$\Delta = \langle L \rangle - L_0$$

so the equation of state becomes

$$F = \frac{-KT}{a} \ln \left(\frac{Na - 2\Delta}{Na + 2\Delta} \right).$$

For small Δ , we note that

$$\ln \left(\frac{Na - 2\Delta}{Na + 2\Delta} \right) \approx \frac{-4\Delta}{Na},$$

and the above simplifies to a Hookean regime:

$$F = \frac{4KT}{Na^2} (\langle L \rangle - L_0)$$

Note the effective spring constant is proportional to temperature, as one might expect for a polymer. Metals, on the other hand, lose stiffness at high temperature.

2.4 Einstein Solid

Using quantum mechanics, an accurate and precise description of matter is 'easy' enough to attain for simple systems such as isolated atoms, simple harmonic oscillators, and perfect crystals. Choosing how to model a system is a careful game, because we want to capture the physically interesting phenomena, while filtering out details that won't factor into the investigation.

In a model called the *Einstein solid*, matter is assumed to consist of N non-interacting quantum harmonic oscillators, with each oscillator having energy

$$\epsilon_i(n_i) = \hbar\omega \left(n_i + \frac{1}{2} \right) \quad n_i = 0, 1, 2, \dots,$$

where ω is the angular vibration frequency, and n_i is the quantum excitation level of the i th oscillator, having allowed values 0, 1, 2, etc. The Einstein solid model allows us to ignore nucleons, electrons, spin, momentum, and so on.

Total Energy

The total energy E of an Einstein solid is the sum

$$E = \sum_{i=0}^N \epsilon_i(n_i) = \hbar\omega \sum_{i=0}^N \left(n_i + \frac{1}{2} \right),$$

which is *not* zero when all excitation numbers n_i are zero.

Zero-Point Energy

The ground-state quantity

$$E_0 = \frac{1}{2} N \hbar\omega$$

is called the *zero-point energy*, and is thermodynamically inaccessible. An oscillator cannot lose or modify its zero-point energy without destroying the system, so we ignore it in the same way we ignore the rest mass-energy mc^2 in calculations.

Internal Energy

The internal energy of an Einstein solid subtracts off the zero-point energy, and is given by:

$$U = E - E_0 = \hbar\omega \sum_{i=1}^N n_i \quad (1.8)$$

Multiplicity

Begin with a ground-state Einstein solid with zero internal energy. If we add some integer number u of energy units $\hbar\omega$ to the system, the internal energy of the solid jumps to $U = u\hbar\omega$. The particular distribution of energy units among individual oscillators is not defined, which means we must track *all* possible configurations available to the system, captured by the multiplicity $\Omega(U, N)$.

To proceed, we shall depict the boundary between two oscillators as a vertical slash ($|$), and one energy unit $\hbar\omega$ as a dot (\bullet). Taking a system with $N = 4$ as an example, we depict the unique ground state by four empty spaces (three slashes) and no dots:

$$U = 0 \quad ||| \quad \Omega(0, 4) = 1$$

If we add one energy unit to the system, we find exactly four ways to arrange the dot between various slashes

$$\bullet||| \quad |\bullet|| \quad ||\bullet| \quad |||\bullet,$$

so we conclude there are four configurations available, or $\Omega(1, 4) = 4$. That is, any one of the four oscillators has $n_j = 1$ while $n_{i \neq j} = 0$. Adding a second energy unit to the system, the internal energy becomes $U = 2\hbar\omega$, and there are ten ways to arrange two dots among the slashes

$$\begin{array}{cccccc} \bullet\bullet||| & \bullet|\bullet|| & \bullet||\bullet| & \bullet|||\bullet & |\bullet\bullet|| \\ |\bullet|\bullet| & |\bullet||\bullet & ||\bullet\bullet| & ||\bullet|\bullet & |||\bullet\bullet, \end{array}$$

so we write $\Omega(2, 4) = 10$, and we could continue this way for any number of oscillators containing any number of energy units.

In the pictorial representation of the Einstein solid, there are $N - 1$ slashes and $u = U/\hbar\omega$ dots, or $N - 1 + u$ total symbols. Framing the problem this way, we may borrow directly from two-state analysis to write the multiplicity (think of dots and slashes as heads and tails on a coin). Of the $N - 1 + u$ symbols, u of them contribute to the internal energy. The multiplicity is exactly:

$$\Omega(u, N) = \frac{(N - 1 + u)!}{u!(N - 1)!} \quad (1.9)$$

To anticipate calculations that follow, we may as well eliminate the factorial terms using Stirling's approximation

$$\ln(n!) \approx n \ln n - n + \ln \sqrt{2\pi n},$$

so the multiplicity becomes

$$\begin{aligned} \ln(\Omega(u, N)) &= (N - 1) \ln \left(1 + \frac{u}{N - 1} \right) \\ &+ u \ln \left(1 + \frac{N - 1}{u} \right) \\ &+ \frac{1}{2} \ln \left(\frac{N - 1 + u}{2\pi u (N - 1)} \right). \end{aligned}$$

In the large- N limit, the final term will be negligible compared to the first two. Of course, $N - 1$ may also be replaced by N . Assuming further that $u \gg N$, the natural log of the multiplicity is approximately

$$\ln(\Omega(u, N)) \approx N(1 + \ln(u/N)),$$

implying

$$\Omega(u, N) \approx \left(\frac{ue}{N} \right)^N.$$

Thermodynamic Properties

With the natural log of the the multiplicity on hand, multiply by the Boltzmann constant to write the entropy of an N -particle Einstein solid

$$S = K \left(N \ln \left(1 + \frac{u}{N} \right) + u \ln \left(1 + \frac{N}{u} \right) \right), \quad (1.10)$$

where the internal energy is $U = u\hbar\omega$.

Having fixed volume and number of particles, the formula $1/T = (\partial S/\partial U)_{V, N}$ gives the temperature as

$$KT = \frac{\hbar\omega}{\ln(1 + N\hbar\omega/U)}.$$

In the $u \gg N$ limit, this resolves to a formula for the average energy per element in the solid:

$$KT = \frac{U}{N}$$

In light of the equipartition theorem, the left side is the sum of two factors $KT/2$, as the harmonic oscillator has two degrees of freedom. In the limit that u cannot be assumed to be much greater than N , we may still solve for U/N to derive the *Planck* result for the average energy per oscillator

$$\frac{U}{N} = \frac{\hbar\omega}{\exp(\hbar\omega/KT) - 1},$$

reproducing the $u \gg N$ case for high temperatures.

Solving for the internal energy U in terms of T comes out to

$$U = \frac{N\hbar\omega}{e^{\hbar\omega/KT} - 1}.$$

A temperature derivative of U gives the heat capacity at constant volume:

$$C_V = \frac{dU}{dT} = \frac{N(\hbar\omega)^2 e^{\hbar\omega/KT}}{KT^2 (e^{\hbar\omega/KT} - 1)^2}$$

Combined Solids

Consider a combined Einstein solid composed of two equal-volume subsystems A and B such that

$$\begin{aligned} N/2 &= N_A = N_B \\ U_A &= \frac{U}{2} + Q \\ U_B &= \frac{U}{2} - Q, \end{aligned}$$

where $U = u\hbar\omega$ is the total internal energy and N is the total number of particles. The quantity Q is a small energy imbalance between the two systems, defined as q counts of $\hbar\omega$. Taking the trivial case $q = 0$, the entropy of each $S_j(u_j, N_j, q)$ of subsystem reads

$$S_A\left(\frac{u}{2}, \frac{N}{2}, 0\right) = S_B\left(\frac{u}{2}, \frac{N}{2}, 0\right) = \frac{S(u, N, 0)}{2},$$

which is half of the total entropy, indicating the multiplicity to be

$$\Omega(u, N, 0) = \Omega\left(\frac{u}{2}, \frac{N}{2}, 0\right)^2.$$

The next job is to develop the nontrivial case $\Omega(u, N, q)$ for relatively small q . Begin by splitting the multiplicity inspired from Equation (1.10) to account for subsystems A and B ,

$$\begin{aligned} \Omega(u, N, q) &= \left(1 + \frac{u/2 + q}{N/2}\right)^{N/2} \left(1 + \frac{u/2 - q}{N/2}\right)^{N/2} \\ &\quad \left(1 + \frac{N/2}{u/2 + q}\right)^{u/2 + q} \left(1 + \frac{N/2}{u/2 - q}\right)^{u/2 - q}, \end{aligned}$$

simplifying to, in the small- q limit:

$$\Omega(u, N, q) = \Omega(u, N, 0) e^{-2Nq^2/u^2} \quad (1.11)$$

Dividing away the Ω -term and introducing a new normalization constant $A(u, N)$, the multiplicity becomes a Gaussian distribution in the q -variable:

$$p(u, N, q) = A(u, N) e^{-2Nq^2/u^2},$$

where the normalization constant is determined by

$$\begin{aligned} 1 &= A(u, N) \int_{-\infty}^{\infty} e^{-2Nq^2/u^2} dq \\ A(u, N) &= \sqrt{\frac{2N}{\pi u^2}}. \end{aligned}$$

This allows calculations of $\langle q \rangle$, $\langle q^2 \rangle$, and the peak width (or standard deviation or variance):

$$\begin{aligned} \langle q \rangle &= A(u, N) \int_{-\infty}^{\infty} q e^{-2Nq^2/u^2} dq = 0 \\ \langle q^2 \rangle &= A(u, N) \int_{-\infty}^{\infty} q^2 e^{-2Nq^2/u^2} dq = \frac{u^2}{4N} \\ \sigma_q &= \sqrt{\langle q^2 \rangle - \langle q \rangle^2} = \frac{u}{2\sqrt{N}} \end{aligned}$$

To express everything in terms of the dimensionless quantities u_A and u_B , start by writing

$$u_A = \frac{u}{2} + q \quad u_B = \frac{u}{2} - q$$

$$u_A^2 = \frac{u^2}{4} - uq + q^2 \quad u_B^2 = \frac{u^2}{4} - uq + q^2,$$

and use the ‘sum of the averages’ rule on each quantity (noting that u is already an average), accounting for the results above:

$$\begin{aligned} \langle u_k \rangle &= \frac{u}{2} \pm \langle q \rangle = \frac{u}{2} \\ \langle u_k^2 \rangle &= \frac{u^2}{4} \pm u \langle q \rangle + \langle q^2 \rangle = \frac{u^2}{4} + \frac{u^2}{4N} \\ \sigma_{u_A} &= \sigma_{u_B} = \sigma_q \end{aligned}$$

2.5 Quantum Ideal Gas

The ideal gas is defined as a collection of non-interacting particles occupying a container, which happens to be a generalization of a well-studied ‘confined quantum particle’ system (the infinite well). Consider a one-dimensional ‘box’ of length L occupied by a single particle of mass m . The walls at $x = 0$ and $x = L$ are impenetrable. The behavior of the particle is determined by the Schrodinger equation, namely

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right) \psi(x, t),$$

where ψ is the wavefunction of the particle, and V is the potential energy of the particle, which is zero inside the box.

The confined-particle solution to the Schrodinger equation is

$$\psi(x, t) = \sqrt{\frac{2}{L}} e^{-iet/\hbar} \sin(kx),$$

where the particle's energy ϵ and wavenumber

$$k = \frac{p}{\hbar}$$

are related by

$$\epsilon = \frac{\hbar^2 k^2}{2m}.$$

Explicitly, these are:

$$\epsilon = \frac{n^2 \hbar^2}{8mL^2}$$

and

$$k = \frac{n\pi}{L}$$

The number n is any positive nonzero integer. (Exclude the negative k -branch as we are dealing with standing-wave solutions.)

Generalizing the container to be three dimensional by $L \rightarrow L^3$, it's readily shown that the particle's energy becomes

$$\epsilon = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2).$$

Increasing the number of particles from one to N , the total internal energy U becomes the sum

$$U = \sum_{j=1}^N \epsilon_j,$$

which motivates inquiry into the total excitation number among all particles, which we define as a 'dimensionless energy' quantity:

$$(N^*)^2 = \sum_{j=1}^N (n_x^2 + n_y^2 + n_z^2) = \frac{8mL^2 U}{\hbar^2}$$

Multiplicity

The number of microstates Ω that correspond to an ideal gas of given energy U with fixed volume $L^3 = V$ and number of particles N must begin as the integral over all possible position and momentum states as:

$$\Omega = \frac{1}{N!} \frac{\int dx_1 \dots dx_{3N} \int dp_1 \dots dp_{3N}}{h^{3N}} \quad (1.12)$$

The factor of $1/N!$ has been inserted to account for the indistinguishability of ideal gas particles, and Planck's constant $h = 2\pi\hbar$ is present for normalization purposes. This is simply a generalization of the $N = 1$ case, where the number of microstates available to a single particle is the product of 'space bins'

and 'momentum bins', simplified by the Heisenberg uncertainty relation

$$\Omega_1 = \frac{L_x L_p}{\Delta x \Delta p} \approx \frac{L_x L_p}{h}.$$

The position integral is easy to evaluate, as we simply get N multiples of the volume V of the gas, or

$$\int dx_1 \dots dx_{3N} = V^N.$$

The momentum integral is less obvious. First recast the dp_i factors in terms of the integers n_i , and write

$$\Omega = \frac{1}{N!} \frac{V^N}{h^{3N}} \left(\frac{\hbar\pi}{L} \right)^{3N} \int dn_1 \dots dn_{3N}.$$

The remaining integral is the surface area of a hypersphere having $3N - 1$ dimensions and radius N^* . As it turns out, such an integral resolves to:

$$\int dn_1 \dots dn_{3N} = \frac{2\pi^{3N/2} (N^*)^{3N-1}}{(3N/2 - 1)!}$$

The anticipated multiplicity of the ideal gas of energy U and fixed volume V and particle number $N \gg 1$ reads

$$\Omega(U, V, N) = \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(3N/2)!} (2mU)^{3N/2} \quad (1.13)$$

Problem 5

A container of volume V is filled with one mole of ideal gas. Calculate the probability that a region with volume $V/1000$ will be completely void of particles. Answer:

$$P = \frac{\Omega(U, V \frac{999}{1000}, N)}{\Omega(U, V, N)} = \left(\frac{999}{1000} \right)^{6 \times 10^{23}} \approx 0$$

Entropy

With the multiplicity in hand, take the natural logarithm and multiply by the Boltzmann constant K to attain the entropy of the ideal gas. (Of course, use Stirling's approximation to handle the factorials.) After doing so, we find

$$S = NK \left(\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right), \quad (1.14)$$

a result known as the *Sackur-Tetrode* equation.

As a historical note, the pioneers of statistical mechanics hadn't developed the insight to slip the factor of $1/N!$ into the multiplicity. The entropy they were calculating was wrong, namely the factor of $5/2$ incorrectly appeared as $3/2$, a mistake remembered as the *Gibbs paradox*.

Problem 6

Write the multiplicity Ω of the ideal gas in terms of the thermal de Broglie wavelength. Answer:

$$\Omega = \frac{2(3N/2)^{3N/2}}{N!(3N/2)!} \left(\frac{V}{\lambda_0^3}\right)^N$$

State Variables

From elementary thermodynamics, take the so-called first thermodynamic identity

$$dU = TdS - PdV + \mu dN$$

to derive three relations:

$$\begin{aligned} \left(\frac{\partial S}{\partial U}\right)_{V,N} &= \frac{1}{T} \\ \left(\frac{\partial S}{\partial V}\right)_{U,N} &= \frac{P}{T} \\ \left(\frac{\partial S}{\partial N}\right)_{U,V} &= -\frac{\mu}{T} \end{aligned}$$

The first two relations are trivial to evaluate after inserting equation (1.14), recovering well-known results for the ideal gas:

$$\begin{aligned} U &= \frac{3}{2}NKT \\ PV &= NKT \\ H &= U + PV = \frac{5}{2}NKT \end{aligned}$$

From the above we calculate the heat capacity at constant volume and at constant pressure:

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3}{2}NK \\ C_P &= \left(\frac{\partial H}{\partial T}\right)_{P,N} = \frac{5}{2}NK \end{aligned}$$

The chemical potential also simplifies:

$$\begin{aligned} \mu &= -KT \ln \left(\frac{S}{N} - \frac{5}{2}\right) \\ &= -KT \ln \left(\frac{V}{N} \left(\frac{4\pi m \cancel{V}^3}{3N\hbar^2} \frac{3}{2}NKT\right)^{3/2}\right) \\ &= -KT \ln \left(\frac{V}{N\lambda_0^3}\right) \end{aligned}$$

Length λ_0 is known as the *thermal de Broglie wavelength*, namely

$$\lambda_0 = \frac{h}{\sqrt{2\pi mKT}}. \quad (1.15)$$

Accounting for dilute (non-ideal) solutions, we tack on a constant μ_0 to the chemical potential to write

$$\mu = \mu_0 - KT \ln \left(\frac{V}{N\lambda_0^3}\right),$$

or as a function of pressure,

$$\mu = \mu_0 + KT \ln \left(\frac{P}{P_0}\right),$$

where $P_0 = KT/\lambda_0^3$.

Other Dimensions

The ideal gas multiplicity equation (1.13) can be condensed via

$$\Omega(U, V, N) = (L^3)^N U^{3N/2} f(N),$$

where generalizing the number of dimensions from 3 to α , we get

$$\Omega(U, V, N) = L^{\alpha N} U^{\alpha N/2} f(N).$$

Proceeding in analog to the three-dimensional case, the state variables for a gas occupying α dimensions are related by:

$$\begin{aligned} U &= \frac{\alpha}{2}NKT \\ PL^\alpha &= NKT \end{aligned}$$

Problem 7

Write the multiplicity of an ideal gas occupying an α -dimensional box with side length L . Answer:

$$\Omega(U) = \frac{L^{\alpha N}}{h^{\alpha N}} \frac{2\pi^{\alpha N/2}}{N!(\alpha N/2)!} (2mU)^{\alpha N/2}$$

Problem 8

Consider a three-dimensional ideal gas consisting of N_3 particles occupying a volume L^3 that can exchange energy (but not matter) with a two-dimensional ideal gas consisting of N_2 particles on a surface of area L^2 . Let the total energy U of the system equal the sum $U_3 + U_2$, the energies of the individual subsystems. Find (i) the total number of microstates of the system as a function of E_2 , and find (ii) the equilibrium value of U_2 and $U_3 = U - U_2$. Answer:

$$\Omega = \left(\sqrt{U - U_2}\right)^{3N_3} \left(\sqrt{U_2}\right)^{2N_2} f(L, N_2, N_3)$$

$$\left(\frac{\partial S}{\partial U_2}\right)_{L^2, N} = 0$$

$$\bar{U}_2 = \frac{N_2 U}{N_2 + 3N_3/2}$$

$$\bar{U}_3 = \frac{3N_3 U/2}{N_2 + 3N_3/2}$$

3 Canonical Ensemble

A physical system with constant volume V and constant number of particles N in an environment of fixed temperature T is a *canonical ensemble*. The internal energy U is not constant.

Helmholtz Free Energy

Consider two canonical systems A and B that combine to a composite system C , where the internal energies sum to a constant $U = U_A + U_B$ such that $dU_B = -dU_A$.

The total multiplicity in terms of U_A reads

$$\Omega_C(U_A) = \Omega_A(U_A) \Omega_B(U - U_A) .$$

Taking the natural logarithm of both sides gives

$$\ln(\Omega_C(U_A)) = \ln(\Omega_A(U_A)) + \ln(\Omega_B(U - U_A)) .$$

Evaluating to first order near $U_A \approx 0$ and $U_B \approx U$, we find

$$\ln(\Omega_C(U_A)) \approx \ln(\Omega_A(U_A)) - U_A \frac{\partial \ln(\Omega_B)}{\partial U_B} .$$

Multiplying through by K converts the above to an entropy equation

$$S_C(U_A) \approx S_A(U_A) - U_A \left(\frac{\partial S_B}{\partial U_B} \right)_{V, N, U_B \approx U} ,$$

where the derivative term is identically equal to $1/T$. So far then, we have

$$-TS_C(U_A) \approx U_A - TS_A(U_A) .$$

From elementary thermodynamics, note the right side is simply the Helmholtz free energy of system A , and happens to be the quantity that the canonical ensemble seeks to minimize. Therefore we deduce

$$A = -KT \ln(\Omega_C(U_A))$$

is a formula for the Helmholtz free energy. Moreover, we see that A is minimized when the combined entropy is maximized.

3.1 Boltzmann Factor

Returning to the first-order cononical ensemble relation

$$\ln \Omega_C(U_A) \approx \ln \Omega_A(U_A) - U_A \frac{\partial \ln \Omega_B}{\partial U_B}$$

for connected systems, use the identity

$$\frac{\partial \ln(\Omega_B)}{\partial U_B} = \frac{1}{KT}$$

and exponentiate both sides:

$$\begin{aligned} e^{\ln \Omega_C(U_A)} &\approx e^{\ln \Omega_A(U_A)} e^{-U_A/KT} \\ \Omega_C(U_A) &\approx \Omega_A(U_A) e^{-U_A/KT} \\ \Omega_C(U_A) &\propto e^{-U_A/KT} \end{aligned}$$

Note too that $\Omega_A \ll \Omega_C$ and could have been ignored. The final term on the right is known as the *Boltzmann factor*.

For a second motivation, recall the entropy of the universe is the sum of the system entropy plus that of its environment:

$$dS_{\text{uni}} = \left(\frac{1}{T} (dU + PdV - \mu dN) \right)_{\text{sys}} + dS_{\text{env}}$$

We are in the regime of constant N , and any change dV is much less than dU for the system or the environment. Near equilibrium with $dS_{\text{uni}} = 0$, we can write the above equation for two neighboring states 1, 2 as

$$0 = \frac{\Delta U_{\text{sys}}}{T} + \Delta S_{\text{env}} .$$

To continue, recall from elementary statistics that the ratio

$$\left(\frac{\Omega(2)}{\Omega(1)} \right)_{\text{env}} = \left(\frac{\text{Pr}(2)}{\text{Pr}(1)} \right)_{\text{env}}$$

holds, which says the probability $P(j)$ of finding the environment in state j is proportional to the number of corresponding microstates available in the environment.

Using the definition $S = K \ln(\Omega)$, we derive

$$\begin{aligned} \left(\frac{\text{Pr}(2)}{\text{Pr}(1)} \right)_{\text{env}} &= e^{(S(2) - S(1))/K} \\ &= e^{-(U(2) - U(1))/KT} , \end{aligned}$$

or

$$\left(\frac{\text{Pr}(2)}{\text{Pr}(1)} \right)_{\text{env}} = \left(\frac{e^{-(U(2))/KT}}{e^{-(U(1))/KT}} \right)_{\text{sys}} .$$

From this, we deduce that the probability of finding the system in state j is (once again) proportional to the Boltzmann factor:

$$\text{Pr}(j) \propto e^{-U(j)/KT}$$

Two-State Paramagnet

Recall that a two-state paramagnet in an external magnetic field has N total particles where N_\uparrow particles align with the external field, and N_\downarrow oppose the field such that $N = N_\uparrow + N_\downarrow$. The internal energy of the system is given by $U = -N_\uparrow\mu B + N_\downarrow\mu B$.

In the N_\uparrow, N_\downarrow notation, the ratio inside the logarithm in Equation (1.7) is equivalent to the ratio N_\uparrow/N_\downarrow . Solving for this, we get

$$\frac{N_\uparrow}{N_\downarrow} = e^{2\mu B/KT},$$

where using $N = N_\uparrow + N_\downarrow$, we find

$$\begin{aligned} \frac{N_\uparrow}{N} &= \frac{e^{\mu B/KT}}{e^{\mu B/KT} + e^{-\mu B/KT}} \\ \frac{N_\downarrow}{N} &= \frac{e^{-\mu B/KT}}{e^{\mu B/KT} + e^{-\mu B/KT}}. \end{aligned}$$

Each ratio $N_{\uparrow,\downarrow}/N$ can be interpreted as the probability $g_{\uparrow,\downarrow}$ of finding a random particle in the up- or down-state, and the energy of any one particle shall be denoted ϵ such that $\epsilon(N_\uparrow) = -\mu B$ and $\epsilon(N_\downarrow) = \mu B$. The above pair of equations reduces to

$$\text{Pr}(\epsilon) = \frac{1}{Z} e^{-\epsilon/KT}$$

such that

$$\epsilon(N_{\uparrow,\downarrow}) = \mp\mu B,$$

where the exponential term is the Boltzmann factor and

$$Z = e^{\mu B/KT} + e^{-\mu B/KT}$$

is the normalization constant.

3.2 Partition Function

Converting from the multiplicity Ω to a probability is done by dividing by a normalization constant Z . In terms of the Boltzmann factor, the probability of the system having energy state U_j is

$$\text{Pr}(j) = \frac{1}{Z} e^{-U_j/KT}, \quad (1.16)$$

where Z is called the canonical *partition function*, given by

$$Z = \sum_j e^{-U_j/KT}, \quad (1.17)$$

such that the probability obeys the normalization condition

$$1 = \sum_j \text{Pr}(j).$$

If more than one microstate corresponds to the same energy U_j , then the sum may be recast over all energies by introducing a degeneracy factor as

$$Z = \sum_j g(j) e^{-U_j/KT},$$

where $g(j)$ is a dimensionless number that counts the number of states for a given energy.

Supposing U_A lives on a continuous energy spectrum instead of a discrete one, the sum becomes an integral according to

$$Z = \int g(U) e^{-U/KT} dU.$$

Recasting over position- and momentum-space, and generalizing to α dimensions, the partition function is

$$Z = \frac{1}{h^\alpha} \int \int e^{-H(x,p)/KT} d^\alpha x d^\alpha p, \quad (1.18)$$

where $H(x,p)$ is the Hamiltonian of the system. Compare to Equation (1.12).

3.3 Non-interacting Particles

Consider a system of two particles A and B having internal energy $U = U_A(s_A) + U_B(s_B)$, where $s_{A,B}$ denotes the state of particle A, B respectively.

Distinguishable Particles

If particle A is somehow different than particle B , they are a *distinguishable* pair. The combined partition function $Z_{\text{indist.}}$ must involve the sum over all states s_A, s_B such that:

$$\begin{aligned} Z_{\text{dist.}} &= \sum_{s_A} \sum_{s_B} e^{-(U_A(s_A) + U_B(s_B))/KT} \\ &= \sum_{s_A} e^{-U_A(s_A)/KT} \sum_{s_B} e^{-U_B(s_B)/KT} \\ &= Z_A Z_B \end{aligned}$$

Evidently the combined partition function is the product $Z_A Z_B$, which easily generalizes to N particles:

$$Z_{\text{indist.}} = \prod_{k=1, \dots, N} Z_k$$

Indistinguishable Particles

Particles that are identical have a curious implication for physical systems: there is no discernible way to know if distinguishable particles trade places. From combinatorial arguments, it follows that the partition function for indistinguishable particles must be

$$Z_{\text{indist.}} = \frac{1}{N!} \prod_{k=1, \dots, N} Z_k .$$

Problem 9

Consider two groups A , B of non-interacting indistinguishable particles. Show that the total partition function is

$$Z = \left(\frac{1}{N_A!} z_{1_A}^{N_A} \right) \left(\frac{1}{N_B!} z_{1_B}^{N_B} \right) ,$$

where $z_{1_A}^{N_A}$, $z_{1_B}^{N_B}$ are the one-particle partition functions of each group.

Two-State System

A ubiquitous and nontrivial partition function applies to the two-state system. For a special case, suppose a single particle can occupy two energy levels $U = \pm\epsilon$, and these are the only two states (no degeneracy). For this we write the partition function

$$z_1 = e^{-\epsilon/KT} + e^{\epsilon/KT} = 2 \cosh \left(\frac{\epsilon}{KT} \right) .$$

Now, let us introduce a second distinguishable particle with access to the same energy levels $U = \pm\epsilon$, and the two particles do not interact. The combined energy of the system can be any of -2ϵ , 0 , 2ϵ . The ground state however is not unique, as there are two distinct ways for $\pm\epsilon + \pm\epsilon$ to sum to zero. Thus, the two-particle partition function is

$$z_2 = e^{2\epsilon/KT} + 2e^0 + e^{-2\epsilon/KT} ,$$

simplifying to

$$z_2 = 2^2 \cosh^2 \left(\frac{\epsilon}{KT} \right) = z_1^2 ,$$

which we'd expect for distinguishable particles. For a total of N distinguishable particles, the partition function is

$$Z = z_1^N = 2^N \cosh^N \left(\frac{\epsilon}{KT} \right) .$$

3.4 Observables

Borrowing more from probability theory, we have that an *observable* variable X has an ensemble average $\langle X \rangle$ that is calculated via

$$\langle X \rangle = \sum_j \hat{X}_j \text{Pr}(j) ,$$

where \hat{X}_j is the corresponding operator. The brackets on $\langle X \rangle$ are often omitted for brevity.

Internal Energy

The internal energy U of a canonical system is straightforwardly written as an ensemble average:

$$\langle U \rangle = \frac{1}{Z} \sum_j U_j e^{-U_j/KT}$$

This can be simplified considerably. Begin by noticing

$$U = \frac{-1}{Z} \sum_j \left(\frac{\partial}{\partial (KT)^{-1}} e^{-U_j/KT} \right) ,$$

or

$$U = \frac{-1}{Z} \frac{\partial}{\partial (KT)^{-1}} Z .$$

Using the chain rule, we finally have:

$$U = - \frac{\partial}{\partial (KT)^{-1}} \ln(Z) \quad (1.19)$$

Problem 10

Calculate the internal energy of a two-state system consisting of N distinguishable particles. Examine the extreme temperature limits $T \rightarrow \infty$, $T \rightarrow 0$ and compare the first result to the high-temperature formula for a two-state paramagnet. Answer:

$$\begin{aligned} U &= -N\epsilon \tanh(\epsilon/KT) \\ U_{T \rightarrow \infty} &= \frac{-N\epsilon^2}{KT} \\ U_{T \rightarrow 0} &= -N\epsilon \end{aligned}$$

Energy Fluctuations

In many scenarios, the internal energy is sharply-peaked around its average value $\langle U \rangle$, where we approximate the profile to be Gaussian, i.e.

$$\text{Pr}(U) = \tilde{A} e^{-(U - \langle U \rangle)^2 / 2\sigma^2} ,$$

where \tilde{A} is a normalization constant.

Meanwhile, the continuous probability in terms of the Boltzmann factor is

$$\text{Pr}(U) = g(U) e^{-U/KT} .$$

Equating these and taking the natural logarithm we find

$$\ln(g(U)) - \frac{U}{KT} = \ln(\tilde{A}) - \frac{(U - \langle U \rangle)^2}{2\sigma^2} .$$

Taking a single partial derivative with respect to U , and then evaluating at $U \rightarrow \langle U \rangle$, the above gives

$$\frac{1}{KT} = \frac{\partial}{\partial U} \ln(g(U)) \Big|_{U \rightarrow \langle U \rangle}.$$

The second-order derivative is more interesting. Carrying this out, we find

$$-\frac{1}{KT^2} \frac{\partial T}{\partial U} = \frac{\partial}{\partial U} \left(\frac{\partial}{\partial U} \ln(g(U)) \Big|_{U \rightarrow \langle U \rangle} \right) - \frac{1}{\sigma^2},$$

where $\partial T / \partial U$ is the reciprocal of the heat capacity at constant volume, letting us conclude

$$\sigma = \sqrt{KT^2 C_V}.$$

For example, an ideal gas at about $300^\circ C$ has $KT \approx (1/40)$ eV (electron-volts). The fluctuation width σ evaluates to about 2×10^{10} eV, making $\sigma/U \approx 10^{-12}$.

Entropy

To work out the entropy of the canonical ensemble, note first that despite the energies U_j not being equal, all states j are equally-accessible. From this, we reason that probability of finding the system in one particular state is the reciprocal of the multiplicity:

$$\text{Pr}(j) = \frac{1}{\Omega}$$

By definition, the entropy is calculated from

$$\langle S \rangle = \sum_j \hat{S} \text{Pr}(j),$$

where the operator \hat{S} is given by

$$\hat{S} = K \ln(\Omega) = -K \ln(\text{Pr}(j)).$$

Proceed by substitution and write

$$S = -K \sum_j \ln \left(\frac{1}{Z} e^{-U_j/KT} \right) \frac{1}{Z} e^{-U_j/KT},$$

and simplify to find

$$S = \frac{K}{Z} \ln(Z) \sum_j e^{-U_j/KT} + \frac{1}{T} \langle U \rangle.$$

Solving for $U - TS$, also known as the Helmholtz free energy, we derive a powerful relationship to the partition function:

$$A = -KT \ln(Z) \quad (1.20)$$

Beta Parameter

The quantity $(KT)^{-1}$ is sufficiently ubiquitous to warrant its own abbreviation, namely

$$\beta = \frac{1}{KT}. \quad (1.21)$$

This makes the internal energy easier to write, as Equation (1.19) reduces to

$$U = -\frac{\partial}{\partial \beta} \ln(Z).$$

Take a T -derivative across Equation (1.21) to write a useful identity:

$$\frac{d\beta}{dT} = \frac{-1}{KT^2} = \frac{-\beta}{T}$$

Problem 11

It's easy to show from the thermodynamic identity

$$dA = -SdT - PdV + \mu dN$$

that various derivatives of the Helmholtz free energy yield variables of state:

$$\begin{aligned} -S &= \left(\frac{\partial A}{\partial T} \right)_{V,N} \\ -P &= \left(\frac{\partial A}{\partial V} \right)_{T,N} \\ \mu &= \left(\frac{\partial A}{\partial N} \right)_{T,V} \end{aligned}$$

Simplify or otherwise verify each of the above. Answer:

$$\begin{aligned} S &= \frac{\partial}{\partial T} (KT \ln(Z)) \\ &= K \ln(Z) + KT \frac{\partial}{\partial \beta} \ln(Z) \left(\frac{d\beta}{dT} \right) \\ &= \frac{-A + U}{T} \end{aligned}$$

$$\begin{aligned} P &= KT \frac{\partial}{\partial V} \ln(Z) \\ &= \frac{1}{Z} \sum_j \left(-\frac{\partial U_j}{\partial V} \right) e^{-U_j/KT} = \langle P \rangle \end{aligned}$$

$$\begin{aligned} \mu_{\text{dist.}} &= -KT \frac{\partial}{\partial N} \ln(z_1^N) \\ &= KT \ln \left(\frac{1}{z_1} \right) \end{aligned}$$

$$\begin{aligned}
\mu_{\text{indist.}} &= -KT \frac{\partial}{\partial N} \ln \left(\frac{z_1^N}{N!} \right) \\
&= -KT \ln(z_1) + KT \ln(N!) \\
&\approx -KT \ln(z_1) + KT \frac{\partial}{\partial N} (N \ln(N) - N) \\
&= KT \ln \left(\frac{N}{z_1} \right)
\end{aligned}$$

3.5 Applications

Entropic Spring

In the entropic spring model, we consider a polymer chain of $N \gg 1$ links under a tension force F along the x -direction, where any link orients either parallel or perpendicular to x . Links parallel to x contribute length a to the chain, with total length L . Links perpendicular to x do not contribute to length.

We then write two energy values

$$\begin{aligned}
\epsilon_{\parallel} &= -Fa \\
\epsilon_{\perp} &= 0,
\end{aligned}$$

and thus the partition function of a single link is given by

$$z_1 = 1 + e^{Fa/KT}.$$

Let $\langle x \rangle$ equal the average length per segment. Using the definition, we proceed with:

$$\begin{aligned}
\langle x \rangle &= \sum_{k=\parallel, \perp} \hat{x}(k) \text{Pr}(k) \\
&= \frac{(0)1 + (a)e^{Fa/KT}}{1 + e^{Fa/KT}} \\
&= \frac{a}{1 + e^{-Fa/KT}}
\end{aligned}$$

Using $\langle L \rangle = N \langle x \rangle$, we find the average length to be

$$\langle L \rangle = \frac{Na}{1 + e^{-Fa/KT}}.$$

In the high-temperature limit, the above readily reduces to

$$\langle L \rangle = L_0 + \frac{NFa^2}{4KT},$$

where $L_0 = Na/2$ corresponds to zero force applied. Solve for F to recover a Hookean statement:

$$F = \frac{4KT}{Na^2} (\langle L \rangle - L_0)$$

Equipartition Theorem

In elementary thermodynamics, one references the idea of equipartition of energy to explain, for instance, factors like $3/2$ as it appears in the internal

energy equation $U = (3/2)NKT$ for the ideal gas. In particular, one has that the internal energy per molecule gains a factor $KT/2$ for each independent quadratic degree of freedom.

The plan is to prove that the equipartition theorem is a special case of a case where molecules are governed by the Hamiltonian

$$H(x, p) = H(p) + bx^\alpha.$$

For a single molecule, write the partition function using Equation (1.18):

$$z_1 = \frac{1}{h} \int e^{-H(p)/KT} dp \int e^{-bx^\alpha/KT} dx$$

Let the momentum integral be represented by a function $f(T, V)$ (absorbing the Planck factor as well). Also let $w = bx^\alpha/KT$ such that $dw = \alpha bx^{\alpha-1} dx/KT$. With this we attain

$$z_1 = f(T, V) \frac{1}{\alpha} \left(\frac{KT}{b} \right)^{1/\alpha} \int_0^\infty w^{1/\alpha-1} e^{-w} dw.$$

The final integral doesn't need to be explicitly evaluated, but nonetheless can be shortened to $\Gamma(1/w)$.

Generalizing to N total particles, the partition function is written

$$Z = F(T, V, N) \left(\frac{KT}{b} \right)^{N/\alpha} \left(\frac{\Gamma(1/w)}{w} \right)^N,$$

where $F(T, V, N)$ is another arbitrary function that contains at least f and an optional factor of $N!$ that depends on the distinguishability of molecules.

With Z on hand, we next compute the internal energy using Equation (1.19). Anticipating the derivative, note that the term involving the gamma function is strictly numerical and is ignored. The F -term has unknown T -dependence, however we can ignore this as well, as it is purely a kinetic term while we're interested in internal energy only. Thus we need to calculate

$$U = -\frac{\partial}{\partial (KT)^{-1}} \ln \left(\left(\frac{KT}{b} \right)^{N/\alpha} \right),$$

or

$$U = \frac{N}{\alpha} \frac{\partial}{\partial \beta} \ln(\beta b),$$

finally yielding

$$\frac{U}{N} = \frac{KT}{\alpha}.$$

That is, the energy per particle is generally equal to KT/α , where $\alpha = 2$ generates the equipartition theorem.

Maxwell Speed Distribution

In an ideal gas, the probability of observing a particle with speed v in the interval $v_1 < v < v_2$ is given by

$$P(v_1 < v < v_2) = \int_{v_1}^{v_2} D(v) dv ,$$

where $D(v) dv$ is the Maxwell speed distribution:

$$D(v) dv = \left(\frac{m}{2\pi KT} \right)^{3/2} 4\pi v^2 e^{-mv^2/KT} dv$$

The derivation of $D(v)$ begins with slipping the kinetic energy of a particle into the Boltzmann factor

$$e^{-U/KT} = e^{-mv^2/2KT} ,$$

which is the basis for the normalization condition

$$1 = A \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-mv^2/2KT} dv_x dv_y dv_z ,$$

with A constant. The integral is over all of velocity space in three-dimensional Cartesian coordinates. Switching to spherical coordinates and noticing the lack of an angular variable, the above reduces to

$$1 = A \int_0^{\infty} e^{-mv^2/2KT} 4\pi v^2 dv .$$

Next let $w^2 = mv^2/2KT$ to write

$$1 = 4\pi A \left(\frac{2KT}{m} \right)^{3/2} \int_0^{\infty} w^2 e^{-w^2} dw ,$$

and notice the remaining Gaussian integral is resolved via

$$\int_0^{\infty} w^2 e^{-w^2} dw = \frac{\sqrt{\pi}}{4} .$$

This allows solving for A and the form for $D(v)$ is recovered.

3.6 Canonical Ideal Gas

The ideal gas system can be analyzed as a micro-canonical ensemble.

Partition Function

For a single particle in a volume V , the partition function is

$$z_1 = \frac{1}{h^3} \int d^3x \int e^{-p^2/2mKT} d^3p .$$

The spatial integral trivially evaluates to V . The momentum integral can be recast in spherical coordinates:

$$z_1 = \frac{V}{h^3} 4\pi \int_0^{\infty} p^2 e^{-p^2/2mKT} dp$$

Next let $w^2 = p^2/2mKT$ to write

$$z_1 = \frac{V}{h^3} 4\pi (2mKT)^{3/2} \int_0^{\infty} w^2 e^{-w^2} dw ,$$

where the remaining Gaussian integral resolves to $\sqrt{\pi}/4$. For z_1 , we finally have

$$z_1 = \frac{V}{h^3} (2\pi mKT)^{3/2} .$$

The single-particle partition function can be recast in terms of the thermal de Broglie wavelength using Equation (1.15). With this, z_1 is simply

$$z_1 = \frac{V}{\lambda_0^3} .$$

For a gas of N indistinguishable particles, the total partition function is

$$Z = \frac{1}{N!} (z_1)^N .$$

State Variables

The internal energy per particle of the ideal gas is calculated from Equation (1.19) via

$$\frac{U}{N} = -\frac{\partial}{\partial (KT)^{-1}} \ln(z_1) ,$$

or

$$U = N \frac{\partial}{\partial \beta} \ln \left(\frac{h^3}{V} \left(\frac{\beta}{2\pi m} \right)^{3/2} \right) = \frac{3}{2} NKT ,$$

as expected.

Calculating the Helmholtz free energy A from the partition function Z requires Stirling's approximation to write

$$\ln(Z) \approx -N \ln(N) + N + N \ln \left(\frac{V}{\lambda_0^3} \right)$$

such that

$$A = -NKT \left(1 + \ln \left(\frac{V}{N\lambda_0^3} \right) \right) , \quad (1.22)$$

or equivalently,

$$A = -NKT \ln \left(\frac{eV}{N\lambda_0^3} \right) .$$

Using $A = U - TS$, the entropy readily simplifies to

$$S = NK \left(\ln \left(\frac{V}{N\lambda_0^3} \right) + \frac{5}{2} \right) ,$$

in agreement with the Sackur-Tetrode Equation (1.14). One may alternatively calculate the entropy from

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V,N}.$$

Explicitly:

$$\begin{aligned} S &= \frac{-A}{T} - 3NKT \frac{d}{dT} \ln(\lambda_0) \\ &= \frac{-A}{T} + \frac{3}{2}NKT \frac{d}{dT} \ln \left(\frac{2\pi mKT}{h^2} \right) \\ &= (U - A)/T \end{aligned}$$

Recalling that the V -derivative of A is $-P$, i.e.,

$$-P = \left(\frac{\partial A}{\partial V} \right)_{T,N},$$

insert Equation (1.22) to recover the ideal gas law

$$PV = NKT.$$

The T -derivative of U is the heat capacity:

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

Finally, the chemical potential for indistinguishable particles is given by

$$\mu = KT \ln \left(\frac{N}{z_1} \right) = -KT \ln \left(\frac{V}{N\lambda_0^3} \right),$$

in agreement with the microcanonical analysis.

Relativistic Gas

When a particle moves relativistically with momentum p , the kinetic energy $T = p^2/2m$ is replaced by $T = pc$, where c is the speed of light. Otherwise following the same derivation that applies to the canonical ideal gas, one finds the partition function of a single particle of relativistic ideal gas to be

$$z_1 = 4\pi V \left(\frac{KT}{hc} \right)^3 \int_0^\infty w^2 e^{-w} dw,$$

where the remaining integral resolves to 2. If the gas is made of indistinguishable particles, the total partition function is

$$Z = \frac{1}{N!} \left(8\pi V \left(\frac{KT}{hc} \right)^3 \right)^N.$$

Problem 12

Suppose a relativistic ideal gas comprised of $3N$ particles is confined to a one-dimensional channel of length L . Show that the partition function is:

$$Z = \frac{1}{(3N)!} \left(2L \left(\frac{KT}{hc} \right) \right)^{3N}$$

Gas in Gravity

Consider an ideal gas of $N \gg 1$ molecules of mass m at temperature T in a cylinder of base area B and height L .

Suppose too that each molecule is subject to Earth's local gravity and is some height $z < L$ above the ground. The single-particle partition function is written

$$z_1 = \frac{B}{h^3} \int_0^L e^{-mgz/KT} dz \int e^{-p^2/2mKT} d^3p,$$

which contains a new Boltzmann factor $e^{-mgz/KT}$, where mgz is the gravitational potential energy of the particle.

Handling each integral separately, we have

$$\int_0^L e^{-mgz/KT} dz = \left(\frac{KT}{mg} \right) \left(1 - e^{-mgL/KT} \right),$$

along with

$$\frac{1}{h^3} \int e^{-p^2/2mKT} d^3p = \left(\frac{2\pi mKT}{h^2} \right)^{3/2} = \frac{1}{\lambda_0^3},$$

so the single-particle partition function is

$$z_1 = \frac{V}{\lambda_0^3} \left(\frac{KT}{mgL} \right) \left(1 - e^{-mgL/KT} \right).$$

Per standard ideal gas analysis, we take all particles as indistinguishable and write the total partition function as

$$Z = \frac{1}{N!} (z_1)^N.$$

To anticipate energy calculations, it helps to write the natural logarithm of the partition function as

$$\ln(Z) = Z_0 + N \ln \left(\frac{1 - e^{-mgL/\beta}}{mgL/\beta} \right),$$

where Z_0 applies to the unperturbed ideal gas. Then, the Helmholtz free energy is

$$A = A_0 - NKT \ln \left(\frac{1 - e^{-mgL/KT}}{mgL/KT} \right),$$

where A_0 applies to the unperturbed ideal gas.

The internal energy U is calculated straightforwardly from Equation (1.19), leading to

$$U = U_0 + NKT - \frac{NmgL}{1 - e^{-mgL/KT}},$$

where U_0 applies to the unperturbed ideal gas. From the above we discern the following limits:

$$U_{L \rightarrow \infty} = \frac{5}{2} NKT$$

$$U_{mgL \ll KT} = U_0$$

The volume derivative of the Helmholtz free energy is related to the pressure, and we use this to calculate the force at the top of the cylinder:

$$F = BP = -\frac{\mathcal{B}}{\mathcal{B}} \left(\frac{\partial A}{\partial L} \right)_{T,N}$$

$$= NKT \frac{\partial}{\partial L} \left(\ln \left(\frac{BL}{N\lambda_0^3} \right) + \ln \left(\frac{1 - e^{-mgL/KT}}{mgL/KT} \right) \right)$$

$$= \frac{NKT}{L} \left(\frac{mgL/KT}{e^{mgL/KT} - 1} \right)$$

From the above we discern the following limits:

$$F_{L \rightarrow \infty} = 0$$

$$F_{mgL \ll KT} = \frac{NKT}{L}$$

The average height $\langle z \rangle$ of a molecule from the base of the cylinder is calculated via

$$\langle z \rangle = \frac{1}{z_g} \int_0^L z e^{-mgz/KT} dz,$$

where normalization is achieved by

$$z_g = \int_0^L e^{-mgz/KT} dz.$$

Instead of a brute-force calculation, notice that a tricky derivative of the Boltzmann factor gets the same job done. In particular:

$$\langle z \rangle = \frac{1}{z_g} \left(\frac{-KT}{m} \right) \int_0^L \frac{\partial}{\partial g} \left(e^{-mgz/KT} \right) dz$$

$$= \left(\frac{-KT}{m} \right) \frac{\partial}{\partial g} \ln(z_g)$$

Notice too that z_g was evaluated previously, and we could substitute into the above and carry on with precision. In the approximation $L \rightarrow \infty$, as one may use for Earth's atmosphere, then z_g reduces to KT/mg , thus

$$\langle z \rangle \approx \left(\frac{-KT}{m} \right) \frac{\partial}{\partial g} \ln \left(\frac{KT}{mg} \right) = \frac{KT}{mg}.$$

Problem 13

If the average thickness of Earth's atmosphere is 10 km, use $g = 9.8 \text{ m/s}^2$ and $T = 300 \text{ K}$ to estimate the mass of a molecule of air. Answer: $m \approx 4.23 \times 10^{-26} \text{ kg}$

Interacting Particles

Consider a gas of N particles whose interactions are governed by a homogeneous function of the n th degree:

$$W(\lambda \vec{r}_1, \dots, \lambda \vec{r}_N) = \lambda^n W(\vec{r}_1, \dots, \vec{r}_N)$$

Due to the scale invariance inherent to V , one may claim the partition function to have the form

$$Z(T, V) = T^a f(VT^b),$$

where f is an arbitrary function, and a, b are functions of N and n .

Putting $Z(T, V)$ through the meat grinder, we first find

$$\ln(Z) = a \ln(T) + \ln(f(VT^b)),$$

betraying the Helmholtz free energy, internal energy, and pressure of such a gas:

$$A = -KT(a \ln(T) + \ln(f(VT^b)))$$

$$U = -\frac{\partial}{\partial \beta} \ln(Z) = KT \left(a + \frac{f'}{f} b VT^b \right)$$

$$P = -\left(\frac{\partial A}{\partial V} \right)_{T,N} = KT \left(\frac{f'}{f} T^b \right)$$

Eliminating the f' -dependence from the above yields the equation of state:

$$U = aKT + bPV$$

This is as far as we get without getting dirty. Now we work toward finding a, b by first writing the partition function of a single particle:

$$z_1 = \int_0^V e^{-\lambda^n W/KT} d^3x \int e^{-p^2/2mKT} d^3p$$

Proceed with the substitutions

$$x \rightarrow x'\lambda$$

$$p \rightarrow p'\lambda^{n/2}$$

so z_1 becomes

$$z_1 = \left(\lambda^3 \int_0^{V/\lambda^3} e^{-\lambda^n W/KT} d^3x' \right)$$

$$\times \left(\lambda^{3n/2} \int e^{-\lambda^n p'^2/2mKT} d^3p' \right),$$

or, accounting for all N particles,

$$Z = \lambda^{3N(1+n/2)} Z(T\lambda^{-n}, V\lambda^{-3}).$$

Using the given formula for the partition function, we further have

$$Z = \lambda^{3N(1+n/2)} (T\lambda^{-n})^a f\left((V\lambda^{-3})(T\lambda^{-n})^b\right).$$

In order to retain $Z(T, V) = T^a f(VT^b)$, it can only follow that

$$a = 3N \left(\frac{1}{n} + \frac{1}{2} \right)$$

$$b = \frac{-3}{n}.$$

In terms of n , the equation of state now reads

$$\frac{n}{3}U + PV = NKT \left(1 + \frac{n}{2} \right).$$

Van der Waals Model

The Van der Waals model is a generalized ideal gas model that introduces an effective volume

$$V \rightarrow V - Nb,$$

where b is a constant pertaining to the gas. Also, the Leonard-Jones attraction between particles imparts an average energy

$$\epsilon = \frac{-aN}{V},$$

where a is another constant.

Using the standard apparatus, we find the relevant partition function to be

$$Z = \frac{1}{N!} \left(\frac{V - Nb}{\lambda_0^3} e^{aN/VKT} \right)^N$$

and furthermore

$$\ln(Z) \approx N + N \ln \left(\frac{V - Nb}{N\lambda_0^3} \right) + \frac{aN^2}{VKT}.$$

The internal energy is the negative β -derivative of $\ln(Z)$, which trivially works out to

$$U = U_0 - \frac{aN^2}{V},$$

where U_0 applies to the unperturbed ideal gas. Next, the Helmholtz free energy is

$$A = -NKT \left(1 + \ln \left(\frac{V - Nb}{N\lambda_0^3} \right) \right) - \frac{aN^2}{V},$$

or equivalently

$$A = A_0 - NKT \ln \left(1 - \frac{Nb}{V} \right) - \frac{aN^2}{V},$$

where A_0 applies to the unperturbed ideal gas.

Using $A = U - TS$, the entropy is given by

$$S = \frac{U_0 - A_0}{T} + NK \ln \left(1 - \frac{Nb}{V} \right),$$

or equivalently

$$S = NK \left(\ln \left(\frac{V - Nb}{N\lambda_0^3} \right) + \frac{5}{2} \right),$$

which is not dependent on a .

Let P_0 equal the pressure of the unperturbed ideal gas. Then, the pressure in the Van der Waals model is

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,N}$$

$$P = P_0 + \frac{NKT}{1 - Nb/V} \left(\frac{Nb}{V^2} \right) - \frac{aN^2}{V^2}.$$

Simplifying delivers the famed Van der Waals equation:

$$\left(P + \frac{aN^2}{V^2} \right) (V - Nb) = NKT$$

In conditions of constant temperature and constant number of particles, the thermodynamic identity $dG = -SdT + VdP + \mu dN$ can be integrated via

$$G = \int VdP.$$

Writing the Van der Waals equation as

$$P = \frac{NKT}{V - Nb} - \frac{aN^2}{V^2},$$

we have

$$dP = \frac{-NKT}{(V - Nb)^2} dV + \frac{2aN^2}{V^3} dV.$$

Carrying out the integral gives the Gibbs free energy up to an integration constant that is not a function of volume or pressure:

$$G = -NKT \ln(V - Nb)$$

$$+ \frac{N^2bKT}{V - Nb} - \frac{2aN^2}{V} + C(T)$$

Problem 14

Calculate the Gibbs free energy of the Van der Waals gas using $G = U + PV - TS$. Use the result to show that the integration constant in the Gibbs free energy is given by

$$C(T) = NKT \ln(N\lambda_0^3).$$

Internal Freedom

Consider a gas of N non-interacting particles with internal degrees of freedom. Each particle has an internal spectrum of energies ϵ_j with degeneracies g_j , where $j = 0, 1, 2, \dots, n$.

The single-particle partition function is

$$z_1 = \left(\frac{V}{\lambda_0^3} \right) z_{\text{int}},$$

where

$$z_{\text{int}} = \sum_{j=0}^n g(\epsilon_j) e^{-\epsilon_j/KT}.$$

As a gas of indistinguishable particles, the total partition function is

$$Z = \frac{1}{N!} \left(\frac{V}{\lambda_0^3} z_{\text{int}} \right)^N.$$

Letting A_0, U_0, S_0 equal the unperturbed Helmholtz free energy, internal energy, and entropy, we have:

$$A = A_0 - NKT \ln(z_{\text{int}})$$

$$U = U_0 + NKT^2 \frac{\partial}{\partial T} \ln(z_{\text{int}})$$

$$S = S_0 + NK \ln(z_{\text{int}}) + NKT \frac{\partial}{\partial T} \ln(z_{\text{int}})$$

If z_{int} is not a function of the volume, then the ideal gas law still holds:

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,N} = \frac{NKT}{V}$$

This makes quick work of the enthalpy

$$H = U + PV = \frac{5}{2} NKT + NKT \frac{\partial}{\partial T} \ln(z_{\text{int}}),$$

and now the heat capacities can be worked out:

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T} \right)_{V,N} \\ &= \frac{3}{2} NK + 2NKT \partial_T \ln(z_{\text{int}}) \\ &\quad + NKT^2 \partial_{TT} \ln(z_{\text{int}}) \end{aligned}$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P,N} = C_V + NK$$

3.7 Simple Harmonic Oscillator

The simple harmonic oscillator (SHO) is any system characterized by an attractive potential

$$V(x) = \frac{m\omega^2 x^2}{2},$$

where motion is sinusoidally centered around $x = 0$, m is the mass, and ω is the angular frequency of the oscillator.

By approximating solid materials as a collection of harmonic oscillators, it follows that each oscillator is fixed in place, in which case all particles are distinguishable. Moreover, the volume is approximately constant, and the pressure is identically zero.

Classical Oscillator System

A classical system consisting of N identical simple harmonic oscillators is governed by the Hamiltonian

$$H = \sum_{j=1}^N \left(\frac{p_j^2}{2m} + \frac{m\omega^2 x_j^2}{2} \right),$$

where x_j, p_j are the position and momentum of the j th oscillator.

For a single oscillator, the partition function is straightforwardly calculated:

$$\begin{aligned} z_1 &= \frac{1}{h} \int_{-\infty}^{\infty} e^{-m\omega^2 x^2/2KT} dx \int_{-\infty}^{\infty} e^{-p^2/2mKT} dp \\ &= \frac{1}{h} \sqrt{\frac{2KT}{m\omega^2}} \sqrt{2mKT} \left(\int_{-\infty}^{\infty} e^{-w^2} dw \right)^2 \end{aligned}$$

The parenthesized Gaussian integral resolves to $\sqrt{\pi}$. Also remembering $\hbar = h/2\pi$, the single-oscillator partition function reduces to

$$z_1 = \frac{KT}{\hbar\omega} = (\beta\hbar\omega)^{-1}.$$

Generalizing to N distinguishable oscillators, the total partition function is given by

$$Z = z_1^N = \left(\frac{KT}{\hbar\omega} \right)^N = (\beta\hbar\omega)^{-N}.$$

With the partition function on hand, we swiftly calculate the Helmholtz free energy A and the internal energy U :

$$A = -KT \ln(Z) = NKT \ln \left(\frac{\hbar\omega}{KT} \right)$$

$$U = - \frac{\partial}{\partial \beta} \ln(Z) = NKT$$

The entropy of the classical SHO system is given by

$$\begin{aligned} S &= - \left(\frac{\partial A}{\partial T} \right)_{V,N} = \frac{U - A}{T} \\ &= NK \left(1 - \ln \left(\frac{\hbar\omega}{KT} \right) \right) \end{aligned}$$

Having no pressure, the enthalpy is no different from the internal energy:

$$H = U + PV = NKT$$

Using $G = H - TS$, we find the Gibbs free energy to be the same as the Helmholtz free energy:

$$G = NKT \ln \left(\frac{\hbar\omega}{KT} \right)$$

Finally, the chemical potential is given by:

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{T,V} = \frac{G}{N} = KT \ln \left(\frac{\hbar\omega}{KT} \right)$$

Problem 15

Calculate the grand free energy

$$\Phi = U - TS - \mu N$$

for the classical SHO system. Answer: 0

Quantum Oscillator System

A system of simple harmonic oscillators can be analyzed as a quantum system. Using the same potential energy $V(x) = m\omega^2 x^2/2$, all dynamics are given by the Schrodinger equation, with a notable result being the energy ϵ_n of the oscillator as a function of excitation number n :

$$\epsilon_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

Using $\exp(\epsilon_n/KT)$ as the Boltzmann factor, the partition function z_1 of a single oscillator is

$$z_1 = \sum_{n=0}^{\infty} e^{-\epsilon_n/KT} = e^{-\hbar\omega/2KT} \sum_{n=0}^{\infty} \left(e^{-\hbar\omega/KT} \right)^n,$$

which accounts for all energies accessible to the oscillator. The final sum is a geometric series, and z_1 simplifies as

$$z_1 = \frac{e^{-\hbar\omega/2KT}}{1 - e^{-\hbar\omega/KT}} = \frac{1}{2 \sinh(\hbar\omega/2KT)}.$$

Accounting for all N particles, the partition function for a canonical ensemble of quantum oscillators is

$$Z = \frac{e^{-N\hbar\omega/2KT}}{(1 - e^{-\hbar\omega/KT})^N} = \left(2 \sinh \left(\frac{\hbar\omega}{2KT} \right) \right)^{-N}.$$

With the partition function on hand, we calculate the Helmholtz free energy A and the internal energy U :

$$\begin{aligned} A &= N \left(\frac{\hbar\omega}{2} + KT \ln \left(1 - e^{-\hbar\omega/KT} \right) \right) \\ &= NKT \ln \left(2 \sinh \left(\frac{\hbar\omega}{2KT} \right) \right) \\ U &= N\hbar\omega \left(\frac{1}{e^{\hbar\omega/KT} - 1} + \frac{1}{2} \right) \\ &= N\hbar\omega \coth \left(\frac{\hbar\omega}{2KT} \right) \end{aligned}$$

The combination $1/(e^{\hbar\omega/KT} - 1)$ is significant enough to warrant its own symbol, for which we reserve the *occupation number* $\langle n \rangle$:

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/KT} - 1}$$

In terms of the occupation number, the internal energy is written

$$U = N\hbar\omega \left(\langle n \rangle + \frac{1}{2} \right),$$

which is in many ways analogous to the energy formula ϵ_n .

Let $\langle n \rangle = 0$ correspond to the zero point energy U_0 , particularly

$$U_0 = \frac{N\hbar\omega}{2}.$$

Then, the energies on hand become

$$\begin{aligned} A &= U_0 + KT \ln \left(1 - e^{-\hbar\omega/KT} \right) \\ U &= U_0 + N\hbar\omega \langle n \rangle. \end{aligned}$$

Using $A = U - TS$, the entropy works out to be

$$S = \frac{N\hbar\omega}{T} \langle n \rangle - NK \ln \left(1 - e^{-\hbar\omega/KT} \right).$$

To recover the classical results, take the limit $KT \gg \hbar\omega$ so the occupation number becomes

$$\langle n \rangle_{KT \gg \hbar\omega} \approx \frac{KT}{\hbar\omega}.$$

Problem 16

Calculate the enthalpy H , Gibbs free energy G , chemical potential μ , and grand free energy Φ of the quantum oscillator system and show that each reduces to its classical analog at high temperature.

Quantum Oscillator Gas

Consider an ideal gas where each indistinguishable particle is a quantum harmonic oscillator. For such a system we begin with the partition function of the gas

$$Z = \frac{1}{N!} \left(\frac{V}{\lambda_0^3} z_{\text{int}} \right)^N,$$

where

$$z_{\text{int}} = \frac{1}{2 \sinh(\hbar\omega/2KT)}.$$

We showed previously that the internal energy is given by

$$U = U_0 + NKT^2 \frac{\partial}{\partial T} \ln \left(\frac{1}{2 \sinh(\hbar\omega/2KT)} \right),$$

simplifying as:

$$\begin{aligned} U &= U_0 + N \frac{\partial}{\partial \beta} \ln \left(2 \sinh \left(\frac{\beta \hbar \omega}{2} \right) \right) \\ &= \frac{3}{2} NKT + \frac{1}{2} N \hbar \omega \coth \left(\frac{\hbar \omega}{2KT} \right) \end{aligned}$$

The heat capacity at constant volume is the T -derivative of the above, thus we have, after simplifying:

$$C_v = \frac{3}{2} NK + NK \frac{(\hbar\omega/2KT)^2}{\sinh^2(\hbar\omega/2KT)}$$

From the heat capacity we discern the following limits:

$$\begin{aligned} C_V(T \rightarrow 0) &= \frac{3}{2} NK \\ C_V(T \rightarrow \infty) &= \frac{5}{2} NK \end{aligned}$$

3.8 Canonical Paramagnetism

Classical Paramagnet

Consider a ‘solid’ system of distinguishable non-interacting particles in conditions of fixed temperature T and fixed external magnetic field $\vec{B} = B\hat{z}$. In the classical model, each particle’s magnetic moment $\vec{\mu}$ may orient at an arbitrary angle θ with respect to the z -axis, having energy

$$U = -\vec{\mu} \cdot \vec{B} = \mu_z B_z = -\mu B \cos(\theta).$$

With momentum playing no role in magnetization, the partition function for a single particle in the system is written as a spatial integral over the shell of a three-sphere:

$$z_1 = 2\pi \int_0^\pi e^{\mu B \cos(\theta)/KT} \sin(\theta) d\theta$$

Quickly solve this by letting $x = \mu B \cos(\theta)/KT$ to find

$$z_1 = \frac{4\pi KT}{\mu B} \sinh \left(\frac{\mu B}{KT} \right).$$

The average magnetization $\langle \mu_z \rangle$ of a single particle is written:

$$\langle \mu_z \rangle = \frac{2\pi}{z_1} \int_0^\pi \mu \cos(\theta) e^{\mu B \cos(\theta)/KT} \sin(\theta) d\theta$$

Using the same substitution, the integral resolves to

$$\langle \mu_z \rangle = \mu \left(\coth \left(\frac{\mu B}{KT} \right) - \frac{KT}{\mu B} \right),$$

an application of the *Langevin function*.

In the high-temperature limit, the parenthesized quantity reduces to $\mu B/3KT$, known as the *Curie law*, which states that the magnetization of a paramagnetic particle is proportional to B and inversely proportional to T :

$$\langle \mu_z \rangle \propto \frac{\mu^2}{K} \frac{B}{T}$$

The factor before B/T is called the *Curie constant* for the given material.

Quantum Two-State Paramagnet

The quantum two-state paramagnet has two energy levels $U = \pm\epsilon$, where $\epsilon = -\mu B$. As a typical two-state system, we know the partition function of a single particle is given by

$$z_1 = 2 \cosh \left(\frac{\mu B}{KT} \right).$$

Made from N distinguishable particles, the total partition function of the quantum two-state paramagnet is

$$Z = z_1^N = 2^N \cosh^N \left(\frac{\mu B}{KT} \right),$$

and the internal energy is easily shown to be

$$U = -N\mu B \tanh \left(\frac{\mu B}{KT} \right).$$

The average magnetization $\langle \mu \rangle$ is straightforwardly calculated via

$$\langle \mu \rangle = \frac{1}{z_1} \sum_{j=1,2} \mu_j e^{-\mu_j B/KT},$$

where $\mu_j = \pm\mu$. One may evaluate the sum manually, or notice that a proper derivative of z_1 emits the same structure:

$$\begin{aligned}\langle\mu\rangle &= \frac{-1}{z_1} \frac{\partial}{\partial(B/KT)} \sum_{j=1,2} e^{-\mu_j B/KT} \\ &= -\frac{\partial}{\partial(B/KT)} \ln(z_1) \\ &= -\mu \tanh\left(\frac{\mu B}{KT}\right)\end{aligned}$$

Quantum Many-State Paramagnet

In a paramagnet exposed to an external magnetic field $\vec{B} = B \hat{z}$, each particle's spin vector has a quantized projection on the z -axis. If a given particle's total spin is J , it follows that the z -projected spin is given by $m_s \hbar$, where m_s is the spin quantum number ranging from $-J$ to J in integer or half-integer steps.

The Hamiltonian of one particle is

$$H = -\mu_z B = -\gamma m_s B,$$

where γ is the *gyromagnetic ratio* of the particle species. For an isolated electron we have $\gamma = g_e \mu_B / \hbar$, where $g_e \approx 2.00$ and μ_B is the *Bohr magneton*, given by $\mu_B = e \hbar / 2m_e$, where m_e is the electron mass and e is the electron charge.

The partition function of a single particle is straightforwardly written as the sum of all possible Boltzmann factors, namely

$$z_1 = \sum_{m_s=-J}^{m_s=J} \left(e^{-\gamma B/KT} \right)^{m_s}.$$

Let $q = \gamma B/KT$ and break apart the sum:

$$\begin{aligned}z_1 &= \sum_{m_s=-J}^{m_s=0} (e^{-q})^{m_s} + \sum_{m_s=0}^{m_s=J} (e^{-q})^{m_s} - 1 \\ &= \sum_0^J (e^q)^x + \sum_0^J (e^{-q})^x - 1\end{aligned}$$

Then, using the geometric series, we have

$$z_1 = \frac{1 - e^{q(J+1)}}{1 - e^q} + \frac{1 - e^{-q(J+1)}}{1 - e^{-q}} - 1,$$

simplifying ultimately to

$$z_1 = \frac{\sinh(\gamma B(J + 1/2)/KT)}{\sinh(\gamma B/2KT)}.$$

By computing the observable $\langle M \rangle \propto \langle \gamma m_s \rangle$, it can be shown that the magnetization of a paramagnet with N particles per unit volume is

$$\langle M \rangle = N \gamma J B_J(x),$$

where $x = \gamma J B/KT$, and the function $B_J(x)$ is called the *Brillouin function*, which is a generalization of the Langevin function as follows:

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$$

If the magnetic field strength B is sufficiently low and the temperature T is sufficiently high, it can be shown that the Curie constant for any J is

$$C = \frac{\partial \langle M \rangle}{\partial B} = \frac{\mu_B^2}{3K} N g_e^2 J(J+1).$$

The special case $J = 1/2$ makes the Brillouin function simplify to $\tanh(x)$, which in the small- x limit reduces to x , matching the previously-found result for the two-state paramagnet.

Classical behavior is recovered from the quantum analysis by allowing the spin vector to occupy the whole continuum of solid angle, accomplished by letting $J \rightarrow \infty$. In this case, the Brillouin function reduces, as expected, to the Langevin function.

4 Grand Canonical Ensemble

So far we have studied in detail the microcanonical ensemble (constant V, N, U) and the canonical ensemble (constant V, N, T). Each of these forbid particles from flowing between the system and the environment.

Naturally, there is another creature called the *grand canonical ensemble* that accounts for systems with non-constant N at constant volume.

Grand Free Energy

Consider two grand canonical systems A and B that combine to a composite system C . The internal energy and number of particles are allowed to flow between the systems, meaning

$$\begin{aligned}U &= U_A + U_B \\ N &= N_A + N_B.\end{aligned}$$

All in terms of A -variables, the entropy of system C reads

$$S_C = S_A(N_A, U_A) + S_B(N - N_A, U - U_A).$$

From the entropy we affirm the condition for thermal equilibrium

$$\begin{aligned}\frac{\partial S_C}{\partial U_A} &= 0 = \left(\frac{\partial S_A}{\partial U_A} \right)_{V_A, N_A} - \left(\frac{\partial S_B}{\partial U_A} \right)_{V_B, N_B} \\ 0 &= \frac{1}{T_A} - \frac{1}{T_B},\end{aligned}$$

along with diffusive equilibrium:

$$\begin{aligned} \frac{\partial S_C}{\partial N_A} = 0 &= \left(\frac{\partial S_A}{\partial N_A} \right)_{U_A, V_A} - \left(\frac{\partial S_B}{\partial N_A} \right)_{U_B, V_B} \\ 0 &= \frac{-\mu_A + \mu_B}{T} \end{aligned}$$

We seek an overall quantity that is minimized at equilibrium in analogy to the Helmholtz and Gibbs free energies. To proceed, write the composite entropy as a Taylor expansion in the vicinity $U_A \approx 0$, $N_A \approx 0$:

$$\begin{aligned} S_C &\approx S_A(U_A, N_A) + S_B(U_B, N_B) \\ &\quad - U_A \left(\frac{\partial S_B}{\partial U_A} \right)_{V_B, N_B} - N_A \left(\frac{\partial S_B}{\partial N_A} \right)_{U_B, V_B} \end{aligned}$$

In the above, we may suppose system B is much larger than system A , so that S_B is essentially a very large constant and is ignored. Replacing derivatives with known quantities, the above tells us

$$S_C(U_A, N_A) \approx S_A - \frac{U_A}{T} + \frac{\mu N_A}{T},$$

or

$$TS_C = TS_A - U_A + \mu N_A.$$

Notice that the remaining quantity on the right is the negative grand free energy of system A , thus we find, dropping the subscript:

$$TS_C = -\Phi = -(U - TS + \mu N)$$

Using the definition $S = K \ln(\Omega)$, conclude that

$$\Phi = -KT \ln(\Omega_C).$$

That is, we find that the system tries to minimize the grand free energy.

4.1 Gibbs Factor

Returning to the first-order grand cononical ensemble relation

$$S_C(U_A, N_A) \approx S_A - \frac{U_A}{T} + \frac{\mu N_A}{T}$$

for connected systems, divide through by K and exponentiate both sides:

$$e^{S_C(U_A)/K} \approx e^{S_A(U_A)/K} e^{(-U_A + \mu N_A)/KT}$$

Note too that $S_A \ll S_C$ and is ignored. The final term on the right is known as the *Gibbs factor*.

For another motivation, one may retrace the development of the canonical ensemble while including the μdN term as it appears in

$$dS_{\text{uni}} = \left(\frac{1}{T} (dU + PdV - \mu dN) \right)_{\text{sys}} + dS_{\text{env}}.$$

This distills to the notion that finding the system in state j is proportional to the Gibbs factor:

$$\Pr(j) \propto e^{(-U(j) + \mu N(j))/KT}$$

Note that $N(j)$ is the number of particles in the system when in state j with energy $U(j)$. If the system has multiple species of particles, make the replacement

$$\mu N \rightarrow \sum_k \mu_k N_k.$$

4.2 Grand Partition Function

Much as the canonical probability relates to the Boltzmann factor, we use the Gibbs factor to write the probability of a particle in state j as

$$\Pr(j) = \frac{1}{Z_G} e^{(-U(j) + \mu N(j))/KT},$$

where z_G is the *grand partition function*:

$$Z_G = \sum_j e^{(-U(j) + \mu N(j))/KT}$$

In terms of the Boltzmann factor, the grand partition function is also written

$$Z_G = \sum_j z_B(j) z_f^{N(j)},$$

where z_B is the Boltzmann factor and z_f is a fugacity term defined as

$$z_f = e^{\mu/KT}.$$

If there are multiple species of particles present, the grand partition function accordingly becomes:

$$\begin{aligned} Z_G &= \sum_j e^{(-U(j) + \mu_1 N_1(j) + \mu_2 N_2(j) + \dots)/KT} \\ &= \sum_j \sum_k e^{(-U(j) + \mu_k N_k(j))/KT} \end{aligned}$$

4.3 Observables

In a statistical system, recall that a variable X has an ensemble average $\langle X \rangle$ that is calculated via

$$\langle X \rangle = \sum_j \hat{X}(j) \Pr(j),$$

where $\hat{X}(j)$ is the corresponding operator.

Internal Energy

The internal energy U of a grand canonical system is straightforwardly written:

$$\langle U \rangle = \frac{1}{Z_G} \sum_j U(j) e^{(-U(j)+\mu N(j))/KT}$$

As with the canonical ensemble analysis, the above can be simplified using a trick of differentiation. Begin by noticing

$$U = \frac{-1}{Z_G} \left(\frac{\partial}{\partial (KT)^{-1}} Z_G \right)_{z_f, V},$$

simplifying (using the chain rule) to:

$$U = - \left(\frac{\partial}{\partial (KT)^{-1}} \ln(Z_G) \right)_{z_f, V} \quad (1.23)$$

Problem 17

Show that the internal energy of the grand canonical ensemble can be written:

$$U = KT^2 \left(\frac{\partial}{\partial T} \ln(Z_G) \right)_{z_f, V}$$

Number of Particles

For a system of N particles, the ensemble average $\langle N \rangle$ at constant V and constant T is calculated via

$$\langle N \rangle = \frac{1}{Z_G} \sum_j N(j) e^{(-U(j)+\mu N(j))/KT}.$$

After simplifying, the above can be written:

$$N = \left(KT \frac{\partial}{\partial \mu} \ln(Z_G) \right)_{V, T} \quad (1.24)$$

Entropy

The statistical entropy is straightforwardly calculated from

$$S = -K \sum_j \ln \left(\frac{1}{Z_G} e^{(-U(j)+\mu N(j))/KT} \right) \\ \times \frac{1}{Z_G} e^{(-U(j)+\mu N(j))/KT},$$

simplifying to

$$S = \frac{U}{T} + K \ln \left(\frac{Z_G}{z_f^N} \right). \quad (1.25)$$

Helmholtz Free Energy

Using the definition $A = U - TS$, one readily reads from Equation (1.25) that the Helmholtz free energy of the grand canonical system is given by:

$$A = -KT \ln \left(\frac{Z_G}{z_f^N} \right) \quad (1.26)$$

Grand Free Energy

Using the definitions $\Phi = U - TS - \mu N$ and $A = U - TS$, we derive a formula for the grand free energy as

$$\Phi = -KT \ln \left(\frac{Z_G}{z_f^N} \right) - NKT \ln \left(e^{\mu/KT} \right),$$

reducing to

$$\Phi = -KT \ln(Z_G). \quad (1.27)$$

Equation of State

Recalling finally that the identity for the grand free energy $\Phi = -PV$ always holds, this combines with Equation (1.27) to make an equation of state:

$$PV = KT \ln(Z_G) \quad (1.28)$$

4.4 Grand Canonical Ideal Gas

For a canonical ideal gas of N particles with volume V at temperature T , recall that the partition function is given by

$$Z_B = \frac{1}{N!} \left(\frac{V}{\lambda_0^3} \right)^N,$$

where λ_0 is the thermal de Broglie wavelength

$$\lambda_0 = \frac{h}{\sqrt{2\pi mKT}}.$$

For the grand canonical ensemble, the corresponding partition function reads:

$$Z_G = \sum_k \frac{1}{N_k!} \left(\frac{V}{\lambda_0^3} \right)^{N_k} z_f^{N_k}$$

The equation for Z_G takes exponential form if we let the upper limit on k go to infinity. To see this, let $y = Vz_f/\lambda_0^3$ so that

$$Z_G = \sum_{k=0}^{\infty} \frac{y^{N_k}}{N_k!} = e^y = e^{Vz_f/\lambda_0^3},$$

or

$$\ln(Z_G) = \frac{Vz_f}{\lambda_0^3}.$$

Immediately from $\ln(Z_G)$, we calculate the internal energy and the pressure we find

$$U = \frac{3}{2}NK \ln(Z_G)$$

$$P = \frac{KT}{V} \ln(Z_G) ,$$

and eliminate the $\ln(Z_G)$ -term to find

$$U = \frac{3}{2}PV .$$

We have yet to show that $\ln(Z_G)$ is equivalent to the number of particles N . Using Equation (1.24),

$$N = \frac{VKT}{\lambda_0^3} \frac{\partial}{\partial \mu} \left(e^{\mu/KT} \right) = \frac{Vz_f}{\lambda_0^3} ,$$

and the equivalence is established.

Problem 18

Show that $N = \ln(Z_G)$ by working backward from the chemical potential of the ideal gas:

$$\mu = -KT \ln \left(\frac{V}{N\lambda_0^3} \right)$$