

Statistical Mechanics

William F. Barnes

June 21, 2020

Contents

1	Introduction	3
2	Microcanonical Ensemble	5
	2.1 Microstates and Macrostates	5
	2.2 Ergodic Hypothesis	6
	2.3 Two Microcanonical Systems in Contact	7
	2.4 Paramagnetism I	9
	2.5 Einstein Solid	12
	2.6 Quantum Ideal Gas	16
3	Canonical Ensemble	19
	3.1 Helmholtz Free Energy Minimum	19
	3.2 Boltzmann Factor and Partition Function	20
	3.3 Non-interacting Particles	20
	3.4 Observables	21
	3.5 Derivations	22
	3.6 Canonical Ideal Gas	24
	3.7 Simple Harmonic Oscillator	28
	3.8 Two-State System	32
	3.9 Paramagnetism II	32
	3.10 Problems	35

Appendix

Hypersphere

Consider a d -dimensional space mapped by orthogonal coordinates x_j . Defining a radius R such that

$$\sum_{i=1}^d x_i^2 < R^2 ,$$

the resulting manifold is a d -dimensional sphere.

Volume

A hyperspherical volume can be separated into a radial component and an angular component as

$$V_d = \int_{\sum_{i=1}^d x_i^2 < R^2} dx_1, \dots, dx_d = \int_0^R r^{d-1} dr \int d\Omega_{d-1} = \frac{R^d}{d} \int d\Omega_{d-1} .$$

To proceed, recall the classic Gaussian integral identity

$$\sqrt{\pi} = \int_0^\infty e^{-x^2} dx ,$$

and multiply d copies together to write

$$(\sqrt{\pi})^d = \int_{-\infty}^\infty e^{-x_1^2} dx_1 \cdot \int_{-\infty}^\infty e^{-x_2^2} dx_2 \cdots \int_{-\infty}^\infty e^{-x_d^2} dx_d = \int_0^\infty r^{d-1} e^{-r^2} dr \int d\Omega_{d-1} .$$

From the study of gamma functions, we pick out the identity

$$\int_0^\infty r^{d-1} e^{-r^2} dr = \frac{\Gamma(d/2)}{2}$$

to find

$$\int d\Omega_{d-1} = \frac{2(\sqrt{\pi})^d}{\Gamma(d/2)} ,$$

and the volume thus far reads

$$V_d = \frac{R^d}{d} \frac{2(\sqrt{\pi})^d}{\Gamma(d/2)} .$$

Recalling two more gamma function identities

$$\frac{\Gamma(d/2)}{2} = \frac{\Gamma(d/2 + 1)}{d} \qquad \Gamma(z) = (z - 1)!$$

the volume of the hypersphere resolves to:

$$V_d = \frac{R^d \pi^{d/2}}{(d/2)!} \tag{1}$$

Testing equation (1) for $d = 1, d = 2, d = 3, d = 4$, we find:

$$V_1 = \frac{R\sqrt{\pi}}{(1/2)!} = 2R \qquad V_2 = \pi R^2$$

$$V_3 = \frac{R^3\pi\sqrt{\pi}}{(3/2)!} = \frac{4\pi R^3}{3} \qquad V_4 = \frac{R^4\pi^2}{2}$$

Surface Area

The surface area of the hypersphere can be derived from the volume by noticing that in any number of dimensions, an R -derivative of a spherical volume equals the surface area according to

$$A_{d-1} = \frac{dV_d}{dR}.$$

Substituting equation (1), the surface area is

$$A_{d-1} = \frac{d}{R} V_d. \tag{2}$$

To get an equation with matching indexes, it's easy to show:

$$A_d = \frac{d+1}{R} V_{d+1} \qquad A_d = V_d \frac{2\sqrt{\pi}(d/2)!}{(d/2-1/2)!}$$

Testing equation (2) for $d = 1, d = 2, d = 3, d = 4$, we find:

$$A_0 = 2 \qquad A_1 = 2\pi R$$

$$A_2 = 4\pi R^2 \qquad A_3 = 2R^3\pi^2$$

1 Introduction

Statistical mechanics studies 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 (big and small), and also redundant to a simpler *statistical* analysis. A formal statistical analysis of physics delivers all of the familiar results of elementary thermodynamics, along with many new insights into classical and quantum systems.

We gain traction by making a broad connection that the classical entropy of a system has something to do with the ‘order’ or ‘organization’ of the parts constituting that system.

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 :

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

The next 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 contained in the natural log term, which in this case is a dimensionless ratio of volumes - that is, 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 :

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

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

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

Extensive and Intensive Variables

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 becomes addition:

$$\begin{aligned}\Omega_T &= \Omega_1 \Omega_2 \\ \ln \Omega_T &= \ln \Omega_1 + \ln \Omega_2\end{aligned}$$

Recasting 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:

$$S = K \ln \Omega \tag{3}$$

2 Microcanonical Ensemble

A physical system with fixed energy, volume, and number of particles is a *microcanonical ensemble*.

2.1 Microstates and Macrostates

Consider any system of any size undergoing (almost) any kind of dynamics. At any instant in time, we imagine an instantaneous 'snapshot' of the whole system, and write the position and momentum of *every* particle (to the limit $\Delta x \Delta p \geq \hbar$) involved. Such a (potentially enormous) body of information is called a *microstate*.

It requires little to imagine that microstates in a dynamic system are changing continuously. However, when we ‘zoom back out’, the ‘global’ characteristics of the system typically undergo change more slowly, despite the vast internal meandering through microstates. System-wide quantities of the system are called *macrostates*.

One immediate corollary of the microstate vs. macrostate dichotomy is that many (sometimes infinite) microstates could give rise to the same macrostate. A probabilistic insight indicates that the macrostate physically observed in a system is the one corresponding to the greatest number of microstates.

2.2 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:

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

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:

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

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

$$\begin{aligned}
\int q^2 \rho(q, p) dq dp &= \frac{2}{\omega} \int q^2 \omega dt = \frac{2A^2}{\omega} \int \cos^2(\omega t) \omega dt \\
&= \frac{2A^2}{\omega} \int_0^\pi \cos^2(\theta) d\theta = \frac{2A^2}{\omega} \frac{\pi}{2} = \frac{\pi A^2}{\omega}
\end{aligned}$$

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.

2.3 Two Microcanonical Systems in Contact

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’, 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 of a common value $T_C = T_A = T_B$, which is defined from elementary thermodynamics in terms of S and U :

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

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:

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

The second-order coefficient can be reinterpreted by brute force, giving

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

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:

$$S_C(U_A) \approx S_C(\bar{U}_A) - \frac{K}{2\sigma_A^2} (U_A - \bar{U}_A)^2 \quad (4)$$

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

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

Using Gaussian integrals, it's easy 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 1

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 $N^{-1/2}$.

Solution 1

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

2.4 Paramagnetism I

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

$$\Omega(U, N) = \frac{N!}{N_{\uparrow}!N_{\downarrow}!} = \frac{N!}{\left(\frac{N}{2} - \frac{U}{2\mu B}\right)! \left(\frac{N}{2} + \frac{U}{2\mu B}\right)!}. \quad (5)$$

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 log:

$$\begin{aligned} \ln \Omega(U, N) \approx N \ln N + \frac{1}{2} \ln \left(\frac{N}{2\pi}\right) - \\ \left(\frac{N+1}{2}\right) \ln \left(\frac{N^2}{4} - x^2\right) + x \left(\ln \left(\frac{N}{2} - x\right) - \ln \left(\frac{N}{2} + x\right)\right) \end{aligned} \quad (6)$$

Let us place a mental bookmark at equation (6), and proceed for now by Taylor-expanding inside the ln-terms, using the approximation that $N \gg x$. In 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)

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

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

$$S = K \left(N \ln 2 + \frac{1}{2} \ln \left(\frac{2}{\pi N}\right) - \frac{U^2}{2N\mu^2 B^2} \right), \quad (7)$$

which decreases as more spins align. The corresponding multiplicity is

$$\Omega(U, N) = 2^N \sqrt{\frac{2}{\pi N}} e^{-2(U/2\mu B)^2/N}. \quad (8)$$

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 (6) but proceed 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

$$KT = \frac{2\mu B}{\ln \left(\frac{N\mu B - U}{N\mu B + U} \right)}, \quad (9)$$

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!

Two-State Partition Function (Preview)

Reverting to our N_\uparrow, N_\downarrow notation, the ratio inside the logarithm in equation (9) 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

$$\frac{N_\uparrow}{N} = \frac{e^{\mu B/KT}}{e^{\mu B/KT} + e^{-\mu B/KT}} \quad \frac{N_\downarrow}{N} = \frac{e^{-\mu B/KT}}{e^{\mu B/KT} + e^{-\mu B/KT}}.$$

By introducing new nomenclature, the above relations can be unified to foreshadow our study of Boltzmann statistics. 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

$$g(\epsilon) = \frac{1}{Z} e^{-\epsilon/KT} \quad \epsilon(N_{\uparrow,\downarrow}) = \mp\mu B ,$$

where the exponential term is called a *Boltzmann factor*, and Z is called the *partition function*, defined as the sum over all possible Boltzmann factors.

2.5 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.

Internal Energy

The total energy E of an Einstein solid is the sum

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

which is *not* zero when all excitation numbers n_i are zero. 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 (it will always be there), so we ignore it in the same way we ignore the rest mass-energy mc^2 in many other calculations. The internal energy of an Einstein solid subtracts off the zero-point energy, and is given by:

$$U = E - E_0 = \hbar\omega \sum_{i=1}^N n_i \quad (10)$$

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 (•). Taking a system with $N = 4$ as an example, we depict the unique ground state by four empty spaces (three slashes) and no dots:

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

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

$$\bullet||| \qquad | \bullet || \qquad || \bullet | \qquad ||| \bullet ,$$

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 configurations to arrange two dots among the slashes

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

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:

$$\Omega(u, N) = \frac{(N - 1 + u)!}{u!(N - 1)!} \qquad (11)$$

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

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

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

$$S = K \left(N \ln \left(1 + \frac{u}{N} \right) + u \ln \left(1 + \frac{N}{u} \right) \right), \quad (12)$$

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

$$N = N_A + N_B \qquad U_A = \frac{U}{2} + Q \qquad U_B = \frac{U}{2} - Q,$$

where U is the total internal energy N is the total number of particles, and 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 (12) to account for subsystems A and B ,

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

simplifying to, in the small- q limit:

$$\Omega(u, N, q) = \Omega(u, N, 0) e^{-2Nq^2/u^2} \quad (13)$$

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

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

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

$$\begin{aligned} u_A &= \frac{u}{2} + q & u_B &= \frac{u}{2} - q \\ u_A^2 &= \frac{u^2}{4} - uq + q^2 & u_B^2 &= \frac{u^2}{4} - uq + q^2, \end{aligned}$$

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

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

2.6 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

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

where the particle’s energy ϵ and wavenumber $k = p/\hbar$ are related by $\epsilon = \hbar^2 k^2 / 2m$. Explicitly, these are:

$$\epsilon = \frac{n^2 \hbar^2}{8mL^2} \qquad k = \frac{n\pi}{L}$$

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:

$$\Omega = \frac{1}{N!} \frac{\int dx_1, \dots, dx_{3N} \int dp_1, \dots, dp_{3N}}{h^{3N}} \tag{14}$$

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^* . Consulting the Appendix, find that 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

$$\Omega(U) = \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{N! (3N/2)!} (2mU)^{3N/2} \quad (15)$$

Problem 2

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.

Solution 2

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

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

$$S = NK \left(\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right), \quad (16)$$

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*.

State Variables

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

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

to derive three relations:

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

The first two relations are trivial to evaluate after inserting equation (16), recovering well-known results for the ideal gas

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

The chemical potential also simplifies:

$$\mu = -KT \ln \left(\frac{S}{N} - \frac{5}{2} \right) = -KT \ln \left[\frac{V}{N} \left(\frac{4\pi m}{3Nh^2} \frac{3}{2} NKT \right)^{3/2} \right] = -KT \ln \left(\frac{V}{N\lambda_0^3} \right) ,$$

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

$$\lambda_0 = \frac{h}{\sqrt{2\pi mKT}} . \quad (17)$$

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 (15) 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

$$U = \frac{\alpha}{2}NKT \quad PL^\alpha = NKT .$$

Problem 3

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 $U_3 = U - U_2$.

Solution 3

$$\Omega = \left(\sqrt{U - U_2}\right)^{3N_3} \left(\sqrt{U_2}\right)^{2N_2} f(L, N_2, N_3)$$
$$\left(\frac{\partial S}{\partial U_2}\right)_{L^2, N} = 0 \quad \rightarrow \quad \bar{U}_2 = \frac{N_2 U}{N_2 + 3N_3/2}, \quad \bar{U}_3 = \frac{3N_3 U/2}{N_2 + 3N_3/2}$$

3 Canonical Ensemble

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

3.1 Helmholtz Free Energy Minimum

For two canonical systems A and B that combine to a composite system C , the total multiplicity in terms of U_A reads

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

Taking the log 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 $U_A \approx 0$, we find

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

and 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 such a system seeks to minimize. Therefore we deduce

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

is a formula for the Helmholtz free energy.

3.2 Boltzmann Factor and Partition Function

Returning to the first-order relation

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

re-use the identity $\partial \ln \Omega_B / \partial U_B = 1/KT$ and raise both sides as a power of e as follows:

$$e^{\ln \Omega_C(U_A)} \approx e^{\ln \Omega_A(U_A)} e^{-U_A/KT}$$

$$\Omega_C(U_A) \approx \Omega_A(U_A) e^{-U_A/KT}$$

$$\Omega_C(U_A) \propto e^{-U_A/KT}$$

Remarkably, the multiplicity is proportional to $\exp(-U_A/KT)$, a term known as the *Boltzmann factor*. Introducing a normalization constant Z , it follows that the probability of the system having energy state U_j is

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

The normalization constant Z is called the (canonical) *partition function*, given by

$$Z = \sum_{\text{all states } j} e^{-U_j/KT}.$$

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

$$Z = \sum_{\text{all energies}} g(U_j) e^{-U_j/KT},$$

where $g(U_j)$ 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

$$Z = \int_{\text{all energies}} g(U) e^{-U/KT} dU.$$

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

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

where $H(x, p)$ is the Hamiltonian of the system.

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:

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

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

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

3.4 Observables

We found that the probability of finding a system in energy state U_j is given by

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

which normalizes to unity as

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

Further insight from probability and statistics tells us that any observable macrostate Q can be calculated from

$$\langle Q \rangle = \sum_j \hat{Q} \text{Pr}(k) = \frac{1}{Z} \sum_j \hat{Q} e^{-U_j/KT} ,$$

where $\langle Q \rangle$ is the ensemble average (brackets usually omitted), and \hat{Q} is the corresponding operator.

The internal energy U and entropy S of a canonical system are easy to write as statistical observables by exploiting the chain rule:

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

$$S = -K \sum_j \ln(\text{Pr}(j)) \text{Pr}(j) = \frac{U}{T} + K \ln Z$$

Solving for $U - TS$, we identify a new formula for the Helmholtz free energy:

$$A = -KT \ln Z$$

From elementary thermodynamics, recall that the pressure of a canonical system can be calculated from the Helmholtz free energy:

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,N} = \frac{1}{Z} \sum_j \left(- \frac{\partial U_j}{\partial V} \right)_{T,N} e^{-U_j/KT} = \langle P \rangle$$

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:

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

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

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

Equating these and taking the 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 inverse 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 $2 \times 10^{10} eV$, making $\sigma/U \approx 10^{-12}$.

3.5 Derivations

Several tools from elementary thermodynamics that were quietly placed on the shelf without derivation are finally accounted for here.

Equipartition Theorem

In familiar form, the equipartition theorem tells us that the average internal energy per particle in a system is equal to f multiples of $KT/2$, where f is the number of quadratic degrees of freedom. If the Hamiltonian contains a non-quadratic potential term, the factor of 2 generalizes to match the power of the potential.

To begin, consider a system of N particles subject to the Hamiltonian

$$H(x, p) = H_0(p) + bx^m.$$

As an integral in one-dimensional position- and momentum phase space, the partition function for a single particle is

$$Z_1 = \frac{1}{h} \int e^{-bx^m/KT} dx \int e^{-H_0(p)/KT},$$

where the integral involving $H_0(p)$ is condensed as some unknown (and unneeded) function $f(T, V)$. Letting $z = bx^m/KT$ such that $dz = mbx^{m-1} dx/KT$, we have

$$\begin{aligned} Z_1 &= f(T, V) \frac{1}{m} \left(\frac{KT}{b}\right)^{1/m} \int_0^\infty z^{1/m-1} e^{-z} dz \\ &= f(T, V) \frac{1}{m} \left(\frac{KT}{b}\right)^{1/m} \Gamma\left(\frac{1}{m}\right), \end{aligned}$$

where a gamma function identity has replaced the final integral. Generalizing to N particles, we write

$$Z = \tilde{f}(T, V, N) \left(\frac{\Gamma(1/m)}{m}\right)^N \left(\frac{KT}{b}\right)^{N/m},$$

where $\tilde{f}(T, V, N)$ implies an optional factor of $1/N!$, depending on whether particles are distinguishable.

Noting that the equipartition theorem deals with internal energy only, the kinetic term $H_0(p)$ need not be specified, nor must we evaluate a gamma function. Only the term including b matters, thus we use the formula for $U(Z)$ above, giving

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

and we finish the proof by taking the ratio U/N :

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

Maxwell Speed Distribution

The ideal gas model alone has little to say about the distribution of molecular speeds within the gas, however one formula was ‘borrowed’ from statistical mechanics that we finally derive here. The Maxwell speed distribution

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

gives the probability of finding an ideal gas particle with speed within the interval $[v_1, v_2]$ equals the area under $D(v)$ curve spanning that interval, or

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

To derive $D(v)$, assume ideal gas is a canonical ensemble, and write the elementary notion that the probability of a particle having *some* speed between zero and infinity is one:

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

where A is a normalization constant. Since the integrals take place in a three-dimensional velocity domain, let us convert from Cartesian coordinates to spherical coordinates. By symmetry, the angular component integrates out to 4π , and the radial part of $dv_x dv_y dv_z$ becomes $v^2 dv$. Finally, note that the energy in an ideal gas is purely kinetic, so we substitute $U = mv^2/2$ as

$$\begin{aligned} 1 &= A \int_0^{\infty} e^{-mv^2/2KT} 4\pi v^2 dv \\ 1 &= A \cdot 4\pi \left(\frac{2KT}{m}\right)^{3/2} \int_0^{\infty} e^{-x^2} x^2 dx \\ 1 &= A \cdot \left(\frac{2\pi KT}{m}\right)^{3/2} , \end{aligned}$$

where the Gaussian integral identity

$$\int_0^{\infty} e^{-x^2} x^2 dx = \frac{\sqrt{\pi}}{4}$$

has been used. Solving for A and substituting back into the normalization condition gives

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

indicating the $D(v)$ function was correct.

3.6 Canonical Ideal Gas

Partition Function

We begin by calculating Z_1 , the partition function of a single particle in three dimensions, given by

$$Z_1 = \frac{1}{h^3} \int \int e^{-H(x,p)/KT} d^3x d^3p ,$$

where the Hamiltonian is purely kinetic, namely $H(p) = p^2/2m$. The spatial integral trivially evaluates to the volume V , and the momentum integral can be transformed to spherical coordinates to give us

$$Z_1 = \frac{V}{h^3} \int_0^{\infty} e^{-p^2/2mKT} 4\pi p^2 dp ,$$

which contains the same integral (up to the constant m) encountered in the Maxwell speed distribution derivation. So far then

$$Z_1 = \frac{V}{h^3} (2\pi mKT)^{3/2} ,$$

where generalizing to N particles, we note that ideal gas constituents are indistinguishable. The ideal gas partition function is

$$Z = \frac{1}{N!} Z_1^N = \frac{1}{N!} \frac{V^N}{h^{3N}} (2\pi mKT)^{3N/2} = \frac{1}{N!} \left(\frac{V}{\lambda_0^3} \right)^N .$$

Internal Energy

It's well-established that the internal energy of the ideal gas obeys $U = 3NKT/2$, which is easily verified by calculating U/N according to

$$\frac{U}{N} = -\frac{\partial}{\partial (KT)^{-1}} \ln Z_1 = \frac{3}{2}KT .$$

Entropy

With the partition function in hand, we calculate the entropy to be

$$\begin{aligned} S &= \frac{U}{T} + K \ln Z \\ &= \frac{3}{2}NK - \cancel{K \ln(N!)} - NK \ln N + NK + NK \ln \left(\frac{V}{\lambda_0^3} \right) \\ &= \frac{5}{2}NK + NK \ln \left(\frac{V}{N\lambda_0^3} \right) , \end{aligned}$$

matching the Sackur-Tetrode equation. Note the internal energy $U = 3NKT/2$ has been used, along with Stirling's approximation to handle the factorial.

Helmholtz Free Energy

Using $A = U - TS$ or $A = K \ln Z$, the Helmholtz free energy comes out to

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

Equation of State

The proper derivative of A , namely $-P = (\partial_A/\partial_V)_{T,N}$, delivers the ideal gas law:

$$PV = NKT$$

Relativistic Gas

For relativistic speeds, the kinetic energy per particle is no longer given by $E = p^2/2m$, but instead $E = pc$.

Problem 4

Consider an ‘ideal’ gas made of N particles that move at relativistic speeds in a three-dimensional volume V . Find the partition function.

Solution 4

$$Z_1 = 4\pi V \left(\frac{KT}{hc}\right)^3 \int_0^\infty e^{-x} x^2 dx \qquad Z = \frac{1}{N!} \left(8\pi V \left(\frac{KT}{hc}\right)^3\right)^N$$

Problem 5

Consider an ‘ideal’ gas made of $3N$ particles that move at relativistic speeds in a one-dimensional channel L . Find the partition function.

Solution 5

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

Ideal Gas in Gravity

Problem 6

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 . The molecules are subject to Earth’s gravitational field. (a) Compute the partition function of this system, and compute the internal energy. Examine the limits $L \rightarrow \infty$ and $L \ll KT/mg$. (b) Compute the force acting on the top of the cylinder. (c) In the limit $L \rightarrow \infty$, find the average distance of the molecules from the base. (d) In terms of $g = 9.8 m/s^2$ and $T = 300 K$ for the atmosphere, and assuming the thickness of the atmosphere is $10 km$, estimate the mass of an air molecule.

Solution 6

$$Z = \frac{1}{N!} \left[\frac{B}{h^3} \int_0^L e^{-mgz/KT} dz \int e^{-p^2/2mKT} d^3p \right]^N = \frac{1}{N!} \left(\frac{V}{\lambda_0^3} \frac{(1 - e^{-mgL/KT})}{mgL/KT} \right)^N$$
$$U = -\frac{\partial}{\partial (KT)^{-1}} \ln Z = \frac{5}{2} NKT + \frac{NmgL}{1 - e^{-mgL/KT}}$$
$$U_{g \rightarrow 0} = \frac{3}{2} NKT \qquad U_{KT \gg mgL} = \frac{3}{2} NKT \qquad U_{L \rightarrow \infty} = \frac{5}{2} NKT$$

$$\begin{aligned} \frac{F_{top}}{B} = P &= - \left(\frac{\partial A}{\partial V} \right)_{T,N} = KT \frac{1}{B} \frac{\partial}{\partial L} \ln Z = \frac{NKT}{V} \left(\frac{mgL/KT}{e^{mgL/KT} - 1} \right) \\ \langle z \rangle &= \frac{\int_0^L e^{-mgz/KT} z dz}{\int_0^L e^{-mgz/KT} dz} \Bigg|_{L \rightarrow \infty} = \frac{-KT}{m} \frac{\partial}{\partial g} \ln Z_1 \Bigg|_{L \rightarrow \infty} = \frac{KT}{mg} \\ m &= \frac{K_B \cdot 300 K}{10 km \cdot 9.8 m/s^2} = 4.23 \times 10^{-26} kg \end{aligned}$$

Interacting Particles

Problem 7

Consider a gas of N classical particles whose interactions are a homogeneous function of the n^{th} degree: $V(\lambda \vec{r}_1, \dots, \lambda \vec{r}_N) = \lambda^n V(\vec{r}_1, \dots, \vec{r}_N)$. This scale invariance causes the partition function to be of the form $Z_N(T, V) = T^{\alpha_1} f(VT^{\alpha_2})$, where f is some unknown function. (a) Compute α_1 and α_2 . (b) Compute the pressure and the internal energy of such a gas. (c) Eliminate the dependence on f , and derive an equation of state. Check that it reduces to $PV = NKT$ for $n = 0$.

Solution 7

$$\begin{aligned} Z_N(T, V) &= \lambda^{3N} \int_0^{L/\lambda} d^{3N}x \int e^{(-\sum_i p_i^2/2mKT - \lambda^n V/KT)} d^{3N}p \\ &= \lambda^{3N} \lambda^{3Nn/2} \int_0^{L/\lambda} d^{3N}x \int e^{-\lambda^n (\sum_i p_i^2/2m + V)/KT} d^{3N}p \\ T^{\alpha_1} f(VT^{\alpha_2}) &= \lambda^{3N(1+\frac{n}{2})} Z_N(T\lambda^{-n}, V\lambda^{-3}) \\ &= \lambda^{3N(1+\frac{n}{2})} \left(\frac{T}{\lambda^n} \right)^{\alpha_1} f \left(V\lambda^{-3} \left(\frac{T}{\lambda^n} \right)^{\alpha_2} \right) \\ &= \lambda^{3N+3Nn/2-n\alpha_1} T^{\alpha_1} f(VT^{\alpha_2} \lambda^{-3-n\alpha_2}) \\ \rightarrow \alpha_1 &= 3N \left(\frac{1}{n} + \frac{1}{2} \right) \quad \alpha_2 = -\frac{3}{n} \end{aligned}$$

$$\begin{aligned} A &= -KT \ln Z_n = -KT (\alpha_1 \ln T + \ln f(VT^{\alpha_2})) \\ P &= - \left(\frac{\partial A}{\partial V} \right)_{T,N} = KT \frac{f'}{f} T^{\alpha_2} = KT^{\alpha_2+1} \frac{f'}{f} \\ U &= - \frac{\partial}{\partial (KT)^{-1}} \ln Z = KT \left(\alpha_1 + \alpha_2 V \frac{f'}{f} T^{\alpha_2} \right) \\ \frac{n}{3} U + PV &= NKT \left(1 + \frac{n}{2} \right) \end{aligned}$$

Van der Waals Equation

In the Van der Waals model, the volume is replaced by

$$V \rightarrow V - Nb,$$

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

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

where a is another constant.

The partition function for a Van der Waals fluid is thus

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

from which the internal energy U computes to

$$U = -\frac{\partial}{\partial (KT)^{-1}} \ln Z = \frac{3}{2}NKT - \frac{aN^2}{V},$$

and the Helmholtz free energy is

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

The entropy is most easily calculated from $A = U - TS$, giving

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

Finally, the equation of state is easily calculated by

$$-P = \left(\frac{\partial A}{\partial V} \right)_{T,N} = -\frac{NKT}{V - Nb} + \frac{aN^2}{V^2},$$

delivering the Van der Waals equation:

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

3.7 Simple Harmonic Oscillator

A simple harmonic oscillator (SHO) is any body bound by an attractive potential

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

whose motions oscillate sinusoidally about the center $x = 0$, where m is the mass and ω is the angular frequency of the oscillator. It follows that solid materials are well-approximated by a canonical ensemble made of distinguishable oscillators. Since each oscillator is locked in place, the volume is constant, and the pressure is identically zero.

Classical SHO

For a system of N harmonic oscillators, the Hamiltonian is

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

where x_j and p_j are the position and momentum of the j^{th} oscillator. The partition function of a single oscillator involves two Gaussian integrals

$$Z_1 = \frac{1}{h} \int_{-\infty}^{\infty} e^{-m\omega^2 x^2/2KT} dx \int_{-\infty}^{\infty} e^{-p^2/2mKT} dp,$$

which simplifies to

$$Z_1 = \frac{1}{h} \sqrt{\frac{2KT}{m\omega^2}} \sqrt{2mKT} \left(\int_{-\infty}^{\infty} e^{-r^2} dr \right)^2 = \frac{2\pi KT}{h \omega} = \frac{KT}{\hbar\omega}.$$

Generalizing to N distinguishable particles, the partition function for the system is

$$Z = Z_1^N = \left(\frac{KT}{\hbar\omega} \right)^N.$$

With the partition function in hand, we may evaluate the internal energy, Helmholtz free energy, enthalpy, entropy, Gibbs free energy, chemical potential, and grand free energy:

$$\begin{aligned} U &= -\frac{\partial}{\partial (KT)^{-1}} \ln Z = NKT \\ A &= -KT \ln Z = NKT \ln \left(\frac{\hbar\omega}{KT} \right) \\ H &= U + PV = U + 0 = NKT \\ S &= -\left(\frac{\partial A}{\partial T} \right)_{V,N} = \frac{U - A}{T} = NK \left(1 - \ln \left(\frac{\hbar\omega}{KT} \right) \right) \\ G &= H - TS = NKT \ln \left(\frac{\hbar\omega}{KT} \right) \\ \mu &= \left(\frac{\partial A}{\partial N} \right)_{T,V} = \frac{G}{N} = KT \ln \left(\frac{\hbar\omega}{KT} \right) \\ \Phi &= -PV = U - TS - \mu N = 0 \end{aligned}$$

Quantum SHO

A quantum mechanical treatment of the simple harmonic oscillator begins with the same potential $V(x) = m\omega^2 x^2/2$, and uses the Schrodinger equation $i\partial_t\psi(x,t) = H\psi(x,t)$ to determine the energy levels of the system, which turn out to be

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

where n is an integer. The Boltzmann factor for a single particle occupying the n^{th} energy level is $\exp(-\epsilon_n/KT)$.

The partition function Z_1 of the single particle is the sum of Boltzmann factors across all n as

$$Z_1 = \sum_{n=0}^{\infty} e^{-\epsilon_n/KT} = e^{-\hbar\omega/2KT} \sum_{n=0}^{\infty} (e^{-\hbar\omega/KT})^n,$$

where the sum is a geometric series obeying

$$\sum_{j=0}^{\infty} x^j = \frac{1}{1-x},$$

allowing a tight expression for Z_1 :

$$Z_1 = \frac{e^{-\hbar\omega/2KT}}{1 - e^{-\hbar\omega/KT}} = \frac{1}{2 \sinh(\hbar\omega/2KT)}$$

For high temperatures, the partition function for a single particle is approximately $KT/\hbar\omega$, matching the classical answer. Generalizing to N distinguishable oscillators, the partition function is

$$Z = Z_1^N = \left(2 \sinh \left(\frac{\hbar\omega}{2KT} \right) \right)^{-N}.$$

For reasons that are especially obvious from Bose-Einstein condensation studies, let us define the occupation number $\langle n \rangle$ as

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

for notational convenience. With the partition function in hand, we may evaluate the internal energy, Helmholtz free energy, enthalpy, entropy, Gibbs free energy, chemical potential, and grand free energy:

$$\begin{aligned} U &= -\frac{\partial}{\partial (KT)^{-1}} \ln Z = N\hbar\omega \left(\frac{1}{2} + \langle n \rangle \right) \\ A &= -KT \ln Z = N \left(\frac{\hbar\omega}{2} + KT \ln (1 - e^{-\hbar\omega/KT}) \right) \\ H &= U + PV = U + 0 = N\hbar\omega \left(\frac{1}{2} + \langle n \rangle \right) \end{aligned}$$

$$\begin{aligned}
S &= - \left(\frac{\partial A}{\partial T} \right)_{V,N} = \frac{U - A}{T} = \frac{N\hbar\omega}{T} \langle n \rangle - NK \ln(1 - e^{-\hbar\omega/KT}) \\
G &= H - TS = \frac{N\hbar\omega}{2} + NK \ln(1 - e^{-\hbar\omega/KT}) \\
\mu &= \left(\frac{\partial A}{\partial N} \right)_{T,V} = \frac{G}{N} = \frac{\hbar\omega}{2} + K \ln(1 - e^{-\hbar\omega/KT}) \\
\Phi &= -PV = U - TS - \mu N = 0
\end{aligned}$$

In the high-temperature limit, each of the above results reduces to the classical limits above.

Problem 8

Consider a gas of non-interacting particles with internal degrees of freedom. Each particle has an internal spectrum of energies $\epsilon_1, \epsilon_2, \dots, \epsilon_n$ with degeneracies g_0, g_1, \dots, g_n . The single-particle partition function can be written as $Z_1 = (V/\lambda_0^3)Z_{int}$, where $Z_{int} = \sum_n g(\epsilon_n) e^{-\epsilon_n/KT}$. (a) Without explicitly computing Z_{int} , derive the expressions for the Helmholtz free energy, the entropy, the internal energy, and the specific heat at constant volume for a system of N of these particles, considered identical. (b) Derive the expression for the pressure, the enthalpy, and the specific heat at constant pressure. (c) Assume that the internal degrees of freedom are those of a quantum simple harmonic oscillator with uniform degeneracy. Derive an expression for Z_{int} , and then evaluate the specific heat at constant volume. Discuss its behavior at extreme temperatures in terms of the equipartition theorem. (d) Instead of a harmonic oscillator model, repeat the previous calculation supposing there are only two allowed energy levels: ϵ_0 with degeneracy g_0 and ϵ_1 with degeneracy g_1 .

Solution 8

$$\begin{aligned}
A &= -KT \ln Z = -NKT \ln \left(\frac{e}{N} \frac{V}{\lambda^3} Z_{int} \right) \\
S &= - \left(\frac{\partial A}{\partial T} \right)_{V,N} = -\frac{A}{T} + \frac{3}{2}NK + NKT \frac{\partial}{\partial T} \ln Z_{int} \\
C_V &= \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{\partial}{\partial T} (A + TS) = \frac{3}{2}NK + 2NKT \partial_T \ln Z_{int} + NKT^2 \partial_{TT} \ln Z_{int} \\
P &= - \left(\frac{\partial A}{\partial V} \right)_{T,N} = \frac{NKT}{V} \\
H &= U + PV = \frac{5}{2}NK + NKT \frac{\partial}{\partial T} \ln Z_{int} \\
C_P &= C_V + NK = \frac{5}{2}NK + 2NKT \partial_T \ln Z_{int} + NKT^2 \partial_{TT} \ln Z_{int} \\
Z_{QSHO} &= \frac{1}{2 \sinh(\hbar\omega/2KT)} \\
C_{V(QSHO)} &= \frac{3}{2}NK + NK \left(\frac{\hbar\omega}{2K} \right)^2 \frac{1}{\sinh^2(\hbar\omega/2KT)}
\end{aligned}$$

$$C_{V(QSHO)}(T \rightarrow 0) = \frac{3}{2}NK \qquad C_{V(QSHO)}(T \rightarrow \infty) = \frac{5}{2}NK$$

$$Z_{2ST} = g_0 e^{-\beta\epsilon_0} + g_1 e^{-\beta\epsilon_1}$$

3.8 Two-State System

The two-state system is immeasurably common in discrete mathematics and quantum mechanics. For many-particle systems, a pure quantum mechanical description is cumbersome to develop, and even worse, excludes the effects of temperature. To solve the many-particle issue and the temperature issue in a single stroke, a statistical analysis is most useful.

The simplest two-state system is a single particle that has two discrete energy levels $U = \pm\epsilon$ at constant temperature T . The partition function is

$$Z_1 = e^{\epsilon/KT} + e^{-\epsilon/KT} = 2 \cosh(\epsilon/KT) .$$

Introducing a second distinguishable particle with the same possible energy states, the total system energy can be any of -2ϵ , 0 , or 2ϵ . The $U = 0$ state however is not unique, as there are two ways for $\pm\epsilon + \pm\epsilon$ to sum to zero. In light of this degeneracy, the partition function for two particles is

$$Z_2 = e^{\epsilon/KT} + 2 e^0 + e^{-\epsilon/KT} = 2^2 \cosh^2(\epsilon/KT) = Z_1^2 ,$$

which is no surprise for distinguishable particles. Generalizing to an N -particle two-state system, the partition function is evidently

$$Z = 2^N \cosh^N(\epsilon/KT) .$$

The internal energy (or any of the myriad of free energies) can be derived from Z , which comes out to

$$U = -\frac{\partial}{\partial (KT)^{-1}} \ln Z = -N\epsilon \tanh(\epsilon/KT) .$$

In the high-temperature limit, the energy and temperature relate by

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

matching the result from our previous study of paramagnetism.

3.9 Paramagnetism II

Using canonical ensemble analysis, we revisit the subject of paramagnetism in the classical and quantum regimes.

Classical Paramagnet

Consider a ‘solid’ system of distinguishable noninteracting particles at temperature T that are subject to a uniform magnetic field $\vec{B} = B\hat{z}$. In the classical model, each particle’s magnetic moment $\vec{\mu}$ may be oriented at an arbitrary angle with respect to \hat{z} . A particle with classical magnetic moment $\vec{\mu}$ in a uniform magnetic field $B\vec{z}$ has potential energy

$$U = -\vec{\mu} \cdot \vec{B} = -\mu_z B_z = -\mu B \cos \theta ,$$

where θ is the angle between $\vec{\mu}$ and the z -axis. We are interested in calculating the magnetization $\langle \mu_z \rangle$ of the material, which is the average z -component of $\vec{\mu}$ per particle. With momentum playing no role in the magnetization, the single-particle partition function is

$$Z_1 = \int_0^\pi e^{\mu B \cos \theta / KT} \sin \theta \, d\theta \, d\phi = 4\pi \frac{KT}{\mu B} \sinh(\mu B / KT) ,$$

which is an integral over a spherical-shell embedded in three-space.

The magnetization $\langle \mu_z \rangle$ is the ensemble average of $\mu \cos \theta$, or

$$\langle \mu_z \rangle = \int_0^\pi \mu \cos \theta e^{\mu B \cos \theta / KT} \sin \theta \, d\theta \, d\phi = \mu \left(\coth(\mu B / KT) - \frac{KT}{\mu B} \right) ,$$

a result known as the *Langevin* function. At high temperatures, the quantity in parenthesis 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 :

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

The factor in front of B/T is called the *Curie constant* for a given material.

Quantum Two-State Paramagnet

We worked previously with the quantum-two state paramagnet having two energy levels $\epsilon = \pm \mu B$. As a canonical ensemble, the partition function is

$$Z = 2^N \cosh(\mu B / KT) ,$$

with total internal energy

$$U = -\frac{\partial}{\partial (KT)^{-1}} \ln Z = -N \mu B \tanh(\mu B / KT) .$$

By taking the derivative of $\ln Z$ with respect to B/KT , we calculate the average magnetization $\langle u \rangle = \langle \mu_z \rangle$. Doing so, we find

$$\langle \mu_z \rangle = -\frac{1}{N} \frac{\partial}{\partial (B/KT)} \ln Z = -\mu \tanh(\mu B / KT) ,$$

which reduces to the classical value for high temperatures.

Quantum Many-State Paramagnet

In a paramagnet exposed to an external magnetic field B , each particle's spin vector has quantized projections on the z -axis. If a given particle's total spin has magnitude J , it follows from standard quantum mechanics that the z -projection of the 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 gyro-magnetic ratio (a constant) of the particle species. For an isolated electron, the gyro-magnetic ratio is $\gamma = g_e \mu_B / \hbar$, where $g_e \approx 2.00$ and μ_B is the Bohr magneton, given by

$$\mu_B = \frac{e \hbar}{2 m_e} ,$$

where m_e is the electron mass and e is the electron charge.

The partition function is straightforwardly written as the sum of all possible Boltzmann factors

$$Z_1 = \sum_{m_s=-J}^{m_s=J} (e^{-\gamma B / KT})^{m_s} = \frac{1 - e^{-q(J+1)}}{1 - e^{-q}} + \frac{1 - e^{q(J+1)}}{1 - e^q} - 1 ,$$

where the substitution $q = \gamma B / KT$ has been made and the geometric series identity

$$1 + q + q^2 + q^3 + \dots + q^{n-1} = \frac{1 - q^n}{1 - q}$$

has been used. Thus Z_1 simplifies 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. This can only be accomplished by setting $J \rightarrow \infty$. In this case, the Brillouin function reduces, as expected, to the Langevin function.

3.10 Problems

Entropic Rubber Band

Zipper Problem