

MATH THAT COMES IN HANDY

Taylor Expansion is often quite useful:

$$f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!} (x-a)^n$$

Stirling's Approximation is essential:

$$\ln(n!) \approx n \ln(n) - n + \ln(2\pi n)/2$$

$$\frac{d}{dn} \ln(n!) \approx \ln(n) + \frac{1}{2n}$$

Integration by Parts is foundational:

$$\int u dv = uv - \int v du$$

The Chain Rule is good to simplify:

$$\frac{\partial U}{\partial t} = \frac{\partial U}{\partial x_1} \frac{\partial x_1}{\partial t} + \frac{\partial U}{\partial x_2} \frac{\partial x_2}{\partial t} + \dots$$

Geometric Series helps now and then:

$$\sum_{n=0}^{\infty} ar^n = \frac{a}{1-r} \quad (r < 1)$$

Binomial Expansion helps sometimes:

$$(x+y)^N = \sum_{t=0}^N \frac{N!}{(N-t)!t!} x^{N-t} y^t$$

HYPERBOLIC IDENTITIES

Hyperbolic functions are defined by:

$$\cosh(x) = \frac{e^x + e^{-x}}{2}; \quad \sinh(x) = \frac{e^x - e^{-x}}{2}$$

These identities then follow naturally:

$$\sinh(2x) = 2 \sinh(x) \cosh(x)$$

$$\cosh(2x) = \cosh^2(x) + \sinh^2(x)$$

$$\cosh^2(x) = 1 + \sinh^2(x)$$

$$\tanh^2(x) = 1 - \operatorname{sech}^2(x)$$

$$\coth^2(x) = 1 + \operatorname{csch}^2(x)$$

INTEGRALS OF INTEREST

$$\int_0^{\infty} dx e^{-\alpha^2 x^2} = \frac{1}{\alpha} \frac{\sqrt{\pi}}{2}$$

$$\int_0^{\infty} dx x^2 \ln(1 - e^{-x}) = -\frac{\pi^4}{45}$$

$$\int_0^{\infty} dx \frac{x^2 e^x}{(e^x - 1)^2} = \frac{\pi^2}{3}$$

$$\int_0^{\infty} dx \frac{x}{e^x - 1} = \frac{\pi^2}{6}$$

$$\int_0^{\infty} dx \frac{x^2}{e^x - 1} = 2.404$$

$$\int_0^{\infty} dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$$

$$\int_0^{\infty} dx \frac{x^{1/2}}{e^x - 1} = 2.315$$

CONSTANTS

These constants are fundamental:

$$k_B = 1.380649 \times 10^{-23} \text{ J/K}$$

$$= 8.617330 \times 10^{-5} \text{ eV/K}$$

$$\hbar = 1.054572 \times 10^{-34} \text{ J} \cdot \text{s}$$

$$= 6.582120 \times 10^{-16} \text{ eV} \cdot \text{s}$$

$$c = 2.997925 \times 10^8 \text{ m/s}$$

PROBABILITY

For the multiplicity or accessible states $g(q)$ that realize value q , probability is:

$$P(q) \equiv \frac{g(q)}{\sum_i g(q_i)} \implies \sum_i P(q_i) = 1$$

The "expectation value" (average) is:

$$\langle q \rangle \equiv \sum_i q_i P(q_i)$$

USEFUL PHYSICAL TERMS

Entropy is defined as $\sigma \equiv \ln(g)$, and $S = k_B \sigma$. Meanwhile, temperature is:

$$\frac{1}{\tau} \equiv \frac{\partial \sigma}{\partial U}, \quad \text{and } \tau = k_B T$$

The inverse of temperature is "thermodynamic beta", $\beta = 1/\tau$. The number density is number per volume, or N/V .

The energy is the expectation value:

$$U \equiv \langle \epsilon \rangle$$

From energy, the heat capacity is:

$$C \equiv \tau \frac{\partial \sigma}{\partial \tau} \equiv \frac{\partial U}{\partial \tau}$$

Pressure is defined by the expansion:

$$\epsilon(V - \Delta V) = \epsilon(V) - \frac{d\epsilon}{dV} \Delta V + \dots$$

With rearrangement, this yields:

$$p = -\frac{\partial U}{\partial V} = \tau \left(\frac{\partial \sigma}{\partial V} \right)$$

Work is defined along a path:

$$W = \int_{V_1}^{V_2} p dV$$

PARTITION FUNCTION

The partition function summarizes the thermodynamic state of a system when paired with temperature:

$$Z = \sum_s \exp\left(-\frac{\epsilon_s}{\tau}\right)$$

Probabilities are given by the relation:

$$P(\epsilon_s) = \frac{\exp(-\frac{\epsilon_s}{\tau})}{Z}$$

APPLYING Z TO ENERGY

From algebra, the energy is found as:

$$U = \tau^2 \frac{\partial \ln(Z)}{\partial \tau} = \tau^2 \frac{1}{Z} \frac{\partial Z}{\partial \tau}$$

Recalling thermodynamic beta, find:

$$\frac{\partial}{\partial \tau} = -\beta^2 \frac{\partial}{\partial \beta}, \quad U = -\frac{\partial \ln(Z)}{\partial \beta}$$

From which the heat capacity follows:

$$C_V = \left(\frac{\partial U}{\partial \tau} \right)_V = \beta^2 \frac{\partial^2}{\partial \beta^2} \ln(Z)$$

HELMHOLTZ FREE ENERGY

One thermodynamic generating function is the Helmholtz Free Energy:

$$F \equiv U - \tau \sigma = -\tau \ln(Z)$$

Entropy and pressure are its partials:

$$\sigma = -\frac{\partial F}{\partial \tau}, \quad p = -\frac{\partial F}{\partial V}$$

CHEMICAL POTENTIAL

Chemical potential describes the tendency of a system to transport particles. Its many definitions include:

$$\mu \equiv \left(\frac{\partial F}{\partial N} \right)_{\tau, V} \equiv \left(\frac{\partial F}{\partial U} \right)_{\tau, V} - \tau \left(\frac{\partial \sigma}{\partial N} \right)_{\tau, V}$$

$$= \left(\frac{\partial U}{\partial N} \right)_{\sigma, V} = -\tau \left(\frac{\partial \sigma}{\partial N} \right)_{U, V}$$

With an external potential, μ becomes:

$$\mu = \mu_{\text{int}} + \mu_{\text{ext}}$$

μ provides a way to quantify effective concentration, or activity of species i :

$$\lambda_i \equiv \exp(\mu_i/\tau)$$

EQUILIBRIUM

At equilibrium, σ is maximized, F is minimized, and thermodynamic quantities are uniform, $\tau_1 = \tau_2$, and $\mu_1 = \mu_2$. Relations like this are satisfied:

$$\left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} = \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau}$$

THERMODYNAMIC IDENTITIES

$$dF = \frac{\partial F}{\partial \tau} d\tau + \frac{\partial F}{\partial V} dV + \frac{\partial F}{\partial N} dN$$

$$\implies dF = -\sigma d\tau - p dV + \mu dN$$

$$d\sigma = \frac{\partial \sigma}{\partial U} dU + \frac{\partial \sigma}{\partial V} dV + \frac{\partial \sigma}{\partial N} dN$$

$$\implies dU = +\tau d\sigma - p dV + \mu dN$$

GIBBS SUM

The Gibbs Sum, or Grand Canonical Ensemble, is an extension of the partition function, or Canonical Ensemble, by the inclusion of terms such as the chemical potential.

$$z = \sum \exp((N\mu - \epsilon_s)/\tau)$$

BOLTZMANN & GIBBS FACTOR

Boltzmann factor between two states:

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{\exp(-\epsilon_1/\tau)}{\exp(-\epsilon_2/\tau)}$$

Gibbs factor between two states:

$$\frac{P(N, \epsilon_1)}{P(N, \epsilon_2)} = \frac{\exp((N\mu - \epsilon_1)/\tau)}{\exp((N\mu - \epsilon_2)/\tau)}$$

DISTRIBUTION FUNCTIONS

Define the distribution function as:

$$f(\epsilon, \mu, \tau) \equiv \langle N(\epsilon, \mu, \tau) \rangle$$

Fermi-Dirac distribution function:

$$f(\epsilon, \mu, \tau) = \frac{1}{\exp((\epsilon - \mu)/\tau) + 1}$$

Bose-Einstein distribution function:

$$f(\epsilon, \mu, \tau) = \frac{1}{\exp((\epsilon - \mu)/\tau) - 1}$$

Classical distribution function:

$$f(\epsilon, \mu, \tau) = \frac{1}{\exp((\epsilon - \mu)/\tau)}$$

EXPECTATION VALUES

Expectation values can be found from the density of states and dist. function:

$$\begin{aligned} \langle q \rangle &= \sum_i f(\epsilon_i, \tau, \mu) q_i \\ &= \int d\epsilon D(\epsilon) f(\epsilon, \tau, \mu) q(\epsilon) \end{aligned}$$

FERMI ENERGY

By the exclusion principle, fermions always have a finite chemical potential:

$$\mu(\tau = 0) = \epsilon_F$$

From the energy, a velocity is defined:

$$\epsilon_F = mv_F^2/2$$

For spin-half particles, this energy is:

$$\epsilon_F = \frac{\hbar^2}{2M} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \equiv \tau_F$$

For a spherical Fermi surface, find that:

$$N = 2 \cdot \frac{1}{8} \cdot \frac{4\pi}{3} \cdot n_F^3 = \frac{\pi}{3} n_F^3 \Rightarrow n_F = \left(\frac{3N}{\pi} \right)^{1/3}$$

Where the internal energy is found as:

$$U_0 = 2 \cdot \frac{1}{8} \cdot 4\pi \int_0^{n_F} dn n^2 \epsilon_n = \frac{3}{5} N \epsilon_F$$

QUANTUM CONCENTRATION

Above the quantum concentration, n_Q , quantum effects become significant:

$$n_Q = \left(\frac{M\tau}{2\pi\hbar^2} \right)^{3/2} \Rightarrow \tau_0 = \frac{2\pi\hbar^2}{M} n^{2/3}$$

For an ideal gas, μ_{int} becomes:

$$\mu_{\text{int}} = \tau \ln(n/n_Q)$$

EX. BAROMETRIC PRESSURE

In a gravitational potential, we have:

$$\mu = \tau \ln(n/n_Q) + Mgh$$

Equating at two different altitudes:

$$\tau \ln(n(h)/n_Q) + Mgh = \tau \ln(n(0)/n_Q)$$

So we find a relation for concentrations:

$$n(h) = n(0) \exp(-Mgh/\tau)$$

IDEAL GAS

For indistinguishable particles F is:

$$F = N\tau \left[\ln \left(\frac{N}{Vn_Q} \right) - 1 \right]$$

Ideal gas law in thermodynamic and molar units, derived by $P = -\partial F/\partial V$:

$$pV = N\tau \iff PV = nRT$$

The equipartition of energy follows:

$$U = \frac{\text{d.o.f.}}{2} N \cdot \tau$$

Heat capacities for monatomic gasses:

$$C_V = \frac{3}{2}N, \quad C_P = \frac{5}{2}N$$

BOSE GAS AND CONDENSATE

The density of states for a Bose Gas:

$$D(\epsilon) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}$$

In the low temperature limit find that:

$$N = \frac{1}{\exp(-\mu/\tau) - 1} \approx -\frac{\tau}{\mu}$$

The activity is then to first order:

$$\lambda \equiv \exp(\mu/\tau) \approx 1 - \frac{1}{N}$$

The total particle number is given by:

$$N = N_{\text{ground}}(\tau) + N_{\text{excited}}(\tau)$$

These numbers are calculated by:

$$N_g(\tau) = \frac{1}{\lambda^{-1} - 1}; \quad N_e(\tau) = 2.612 \frac{n_Q}{V}$$

Einstein temperature is $N_e(\tau) = N$:

$$\tau_E = \frac{2\pi\hbar^2}{M} \left(\frac{N}{2.612V} \right)^{2/3}$$

With some algebra it is shown that:

$$N_e \approx N \left(\frac{\tau}{\tau_E} \right)^{3/2}$$

FERMI GAS

The density of states for a Fermi Gas:

$$D(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}$$

Number is defined as usual:

$$N = \int_0^\infty d\epsilon D(\epsilon) f(\epsilon, \tau, \mu)$$

Energy is defined as usual:

$$U = \int_0^\infty d\epsilon \epsilon D(\epsilon) f(\epsilon, \tau, \mu)$$

At low temperature find that:

$$N = \int_0^{\epsilon_F} d\epsilon D(\epsilon); \quad U_0 = \int_0^{\epsilon_F} d\epsilon \epsilon D(\epsilon)$$

Which lead to the expressions:

$$C_V = \frac{\pi^2}{3} D(\epsilon_F) \tau; \quad p = \frac{2N\epsilon_F}{5V}$$

EX. HEAT CAPACITY OF A FREE ELECTRON GAS

The heat capacity of an electron gas is:

$$C_{\text{el}} = \frac{dU}{d\tau} = \int_0^\infty d\epsilon (\epsilon - \epsilon_F) \frac{df}{d\tau} D(\epsilon)$$

Which becomes, with $x \equiv (\epsilon - \epsilon_F)/\tau$:

$$C_{\text{el}} = \tau D(\epsilon_F) \int_0^\infty dx x^2 \frac{e^x}{(e^x + 1)^2}$$

Which is, and has a density of states:

$$C_{\text{el}} = \frac{\pi^2}{3} D(\epsilon_F) \tau, \quad D(\epsilon_F) = \frac{3N}{2\tau_F}$$

Combining these, one finds that:

$$C_{\text{el}} = \frac{\pi^2 N \tau}{2\tau_F}$$

EX. DEBYE MODEL

Define the Debye Temperature as the highest temperature a crystal can reach during a normal mode of vibration:

$$T_D \equiv \frac{\hbar v}{k_B} \left(\frac{6\pi^2 N}{V} \right)^{1/3}$$

Integrating over temperatures to T_D , with the dimensionless $x \equiv \pi\hbar v/L\tau$:

$$\begin{aligned} U &= \sum_n \langle \epsilon_n \rangle \\ &= \frac{3\pi^2 \hbar v}{2L} \left(\frac{\tau L}{\pi \hbar v} \right)^4 \int_0^{x_D} dx \frac{x^3}{e^x - 1} \end{aligned}$$

Which gives the Debye T^3 law at low T :

$$C_V = \frac{12\pi^4 N}{5} \left(\frac{\tau}{k_B T_D} \right)^3$$

EX. PLANK LAW AND
STEFAN-BOLTZMANN LAW

Plank distribution for particles in box with quanta s such that $\epsilon = \langle s \rangle \hbar \omega$:

$$\langle s \rangle = \frac{1}{\exp(\hbar \omega / \tau) - 1}$$

The spectral density at ω is therefore:

$$u(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp(\hbar \omega / \tau) - 1}$$

Energy per area, or radiant flux density:

$$J = \frac{\pi^2}{60 \hbar^3 c^2} \tau^4 = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} T^4$$

EX. BINARY SPIN SYSTEM

A spin system with $N_\uparrow + N_\downarrow = N$ has:

$$g(N) = 2^N, \quad U(s) = -2smB$$

For a given total spin s , the number of accessible states is given by:

$$\begin{aligned} g(N, s) &= \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \\ &= \frac{N!}{(\frac{1}{2}N + s)! (\frac{1}{2}N - s)!} \\ &\approx \sqrt{\frac{2}{\pi N}} 2^N \exp\left(-\frac{2s^2}{N}\right) \end{aligned}$$

INTENTIONALLY LEFT BLANK

INTENTIONALLY LEFT BLANK

EX. DISRUPTED SPIN SYSTEM

It is illustrative to consider the entropy of a disrupted spin system. Viz, how sharply entropy peaks about $\delta = 0$:

$$\begin{aligned} &\frac{g_1(N_1, \hat{s}_1 + \delta) g_2(N_2, \hat{s}_2 - \delta)}{\max(g_1 g_2)} \\ &= \exp\left(-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}\right) \end{aligned}$$

EX. COMBINED SPIN SYSTEM

The entropy of a composite system made of two subsystems is the product. Note that thermodynamic variables are split between the two subsystems:

$$\begin{aligned} g(N, S) &= \sum_{s_1, s_2} g_1(N_1, s_1) g_2(N_2, s_2) \\ &= \sum_{U_1} g_1(N_1, U_1) g_2(N_2, U - U_1) \end{aligned}$$

EX. SPIN ENTROPY

Spin entropy in zero magnetic field is:

$$Z_{\text{int}} = (2I + 1) \implies \sigma_{\text{int}} = \ln(2I + 1)$$

The corresponding chemical potential:

$$\mu = \tau (\ln(n/n_Q) - \ln(2I + 1))$$