

Stat Mech Main Points

Qualifier

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1 Basic Thermo

Definitions:

- Adiabatic: No heat is exchanged in or out of system. $dQ = 0$
- Quasi-static: Uniform pressure throughout system
- Isoentropic: Adiabatic, quasi-static, and constant entropy
- Reversible: constant entropy

Equations:

- Most all basic thermo relations can be derived from these two equations/derivations:

$$F = E - TS \rightarrow dF = dE - TdS - SdT \quad (1)$$

$$dU = TdS - PdV + \sum \mu dN \quad (2)$$

- Internal energy:

$$\Delta U = Q - W \quad (3)$$

- Work done **by** the system is calculated as:

$$W = \int PdV \quad (4)$$

- Relationship between pressure, force and area:

$$P = \frac{F}{A} \quad (5)$$

- **Ideal Gases:**

- Ideal gas law equation: $PV = NkT = nRT$. $N = \#$ of particles, $n = \#$ of moles of particles
- Energy of an ideal gas = $\frac{N}{2}kT$, where N represents degrees of freedom.
Energy of a **monatomic** ideal gas = $\frac{3}{2}NkT$
Energy of a **diatomic** ideal gas = $\frac{5}{2}NkT$

- Clausius-Clapeyron Equation:

$$\frac{dP}{dT} = \frac{L}{T(V_G - V_L)} \quad (6)$$

- We can also see from the free energy equation that we can relate the pressure derivative to the entropy at equilibrium:

$$\frac{dP}{dT} = \frac{S_G - S_L}{V_G - V_L} \quad (7)$$

- Enthalpy:

$$H = E - pV \quad (8)$$

1.1 Extensivity

A thermo property such as entropy is properly **extensive** if: $S(\lambda N, \lambda E, \lambda V) = \lambda S$. Equations of state can be given as **intensive** instead. That means they are given as a per-particle measurement - such as:

$$e = \frac{E}{N} \quad v = \frac{V}{N} \quad s = \frac{S}{N} \quad (9)$$

All the same derivative relations still hold for these intensive properties.

1.2 Basic Temperature & Entropy Relationships

- Heat to raise/lower temp: $Q = C_p m \int dT$
- Heat to melt ice: $Q = mL$
- $\Delta S = \frac{Q}{T}$; plug in Q and then integrate (the integral in definition of Q)
- C_v and C_p for a liquid are basically the same
- At high temperatures, we expect the macrostate of a system to be in its most random state. That means that every microstate should have equal probability of occurring.

1.3 Maxwell Relations

Knowing the dU and dF equations listed previously, we can find additional physics by taking mixed partial derivatives. Since partial derivatives can switch order without changing the result, doing so can lead to additional physics relationships. For example:

$$\frac{\partial}{\partial E} \frac{\partial S}{\partial V} = \frac{\partial}{\partial V} \frac{\partial S}{\partial E} \rightarrow \frac{\partial}{\partial E} \frac{P}{T} = \frac{\partial}{\partial V} \frac{1}{T} \rightarrow P = \frac{\partial E}{\partial V} \quad (10)$$

1.4 Engines

- Work done by an engine is positive if the **area under the curve of a P-V diagram is positive**.
- A **Carnot cycle** consists of **two isotherms** and **two adiabats**.
- An adiabat line goes from a lower isotherm to a higher isotherm line (so an adiabat line is **steeper** than an isotherm line).
- Adiabat: $dQ = 0$; and since $dS = \frac{dQ}{T}$, we find that $dS = 0$.
Also for an adiabat:

$$PV^\gamma = \text{constant} \quad \& \quad TV^{\gamma-1} = \text{constant} \quad (11)$$

Where $\gamma = \frac{f+2}{f} = \frac{C_p}{C_v}$ and f represents the degrees of freedom (3 for monatomic ideal gas).

- Isotherm: $dT = 0$
- Isochore: $dV = 0$, and $Q = C_v m \Delta T$

Efficiency:

$$\eta = \frac{\text{benefit}}{\text{cost}} = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} \quad (12)$$

2 Classical Statistical Mechanics

Classical stat mech systems are usually **distinguishable** and energy levels can be **either discrete or continuous**. Usually the question must give information about the particles' energy levels and distinguishability.

Given an average measurement per time \bar{n}_s , we find the **variance** as:

$$\overline{(\Delta n_s)^2} = \langle (n_s - \langle n_s \rangle)^2 \rangle = \langle n_s^2 \rangle - \bar{n}_s^2 \quad (13)$$

2.1 Ensembles

2.1.1 Microcanonical Ensemble (E, N, V fixed)

Entropy:

$$S = k \ln \Omega \quad (14)$$

Where Ω represents multiplicity, which is the number of possible states present.

Partition function is $\frac{1}{\Omega}$

Binomial distribution:

$$\binom{N}{n} = \frac{N!}{n!(N-n)!} \quad (15)$$

If asked to calculate the multiplicity Ω or other derivations in the MCE for a more complicated system, such as a classical harmonic oscillator ($H = \frac{p^2}{2m} + \frac{m}{2}\omega^2 x^2$), remember that Ω represents the total number of states present - so integrate with a step function in order to include all energies up to the given energy:

$$\Omega = \left[\int \frac{d^3x d^3p}{h^3} \Theta \left(E - \sum_i \left(\frac{p_i^2}{2m} + \frac{m}{2}\omega^2 x^2 \right) \right) \right]^N \quad (16)$$

We can write this as a 6-dimensional sphere of radius \sqrt{E} in phase space. (Probably won't encounter it.)

2.1.2 Canonical Ensemble (N, V, T fixed)

The canonical ensemble represents a system in equilibrium with a reservoir.

Use this partition function for a single particle:

$$z = \sum_{n=0}^{\infty} e^{-\beta n} \quad (17)$$

and for N particles (add an $\frac{1}{N!}$ if indistinguishable):

$$Z = z^N \quad (18)$$

Along with the relations derived from the dF and dU equations, we also have:

$$E = -\frac{\partial}{\partial \beta} \ln Z \quad F = -\frac{1}{\beta} \ln Z \quad C_V = \frac{\partial E}{\partial T} \quad (19)$$

More CE details:

- If given energy in term of p or k (in CE or GCE), as long as it is not bosons or fermions, integrate over all phase space to find the partition function. This means the partition function in 3D looks like:

$$z = \frac{1}{h^3} \int e^{-\beta E(x,p)} d^3x d^3p \quad (20)$$

Remember that if integrating over momentum space, p , divide by a factor of h for each dimension in the integration. If integrating over k space instead, only divide by a factor of 2π for each dimension.

- If a system has multiple sources of energy, the partition function is the multiplicative combination of each energy source. For example, for a system of indistinguishable particles with internal energy as well as translational energy (if they are point particles):

$$Z = Z_{trans} Z_{internal} = \frac{1}{N!} (z_{trans} z_{internal})^N \quad (21)$$

These z 's can be calculated independently. For example, if given point particles with two internal energy states, 0 and Δ :

$$Z = \frac{1}{N!} [e^0 + e^{-\beta \Delta}]^N \left[\int \frac{d^3x d^3p}{h^3} e^{-\beta p^2/2m} \right]^N \quad (22)$$

- Similarly, if we have a gas made up of two or more particles, the combined partition function is the multiplicative combination of each kind of particle. For example, the partition function for a gas made up of two particles, A and B , looks like:

$$Z = Z_A Z_B \quad (23)$$

- If two or more gases/liquids are in equilibrium in the same volume, their chemical potentials must be equal.
- If asked for less traditional calculations (such as the average height of atoms in a gravitational field), look at the partition function and see what derivative to take to bring that quantity down from the exponent (and divide by any extraneous terms that would come down). For example, for the average height of atoms in a gravitational field:

$$Z = \frac{1}{N!} \left(\int \frac{d^3x d^3p}{h^3} e^{-\beta(p^2/2m - mgz)} \right)^N \quad (24)$$

$$\langle z \rangle = -\frac{1}{N\beta m} \frac{\partial}{\partial g} \ln Z \quad (25)$$

2.1.3 Grand Canonical Ensemble (V, T, μ fixed)

Along with the dU and dF equations, use the grand potential \mathcal{G} to derive relations for the GCE:

$$\mathcal{G} = F - \mu N = E - TS - \mu N = -pV = -kT \ln Q = -\frac{1}{\beta} \ln Q \quad (26)$$

Use the grand partition function with this ensemble:

$$Q = \sum e^{\beta\mu N} \sum e^{-\beta E_n} \quad (27)$$

Another entity used in GCE is the **grand canonical potential**, ψ (is actually derivable from $d\mathcal{G}$ as $\psi = \frac{PV}{kT}$):

$$\psi = \ln Q \quad (28)$$

As with CE, if given a composite substance (such as electrons and positrons), it's easiest to write the partition function as a product of the two partition functions:

$$Q_{tot} = Q_+ Q_- \quad (29)$$

This also works if given an energy that varies based on spin, such as $H = \frac{\hbar^2 k^2}{2m} + m_z B$, where $m_z = \pm 1$:

$$Q_{tot} = Q(m_z = 1) \times Q(m_z = -1) \quad (30)$$

3 Quantum Statistical Mechanics

Quantum statistical mechanics particles usually have **discrete energy levels** and are usually **indistinguishable**, but in the case of *bosons* or *fermions*, we take care of indistinguishability when we calculate the partition function according to **distribution functions** rather than just using the $\frac{1}{N!}$ that we used for classical particles.

Usually we use the Grand Canonical Ensemble to analyze quantum systems, but we can no longer sum over N in the partition function (Z), since we need to sum over *states* rather than *particles*.

For example, for a Fermi gas with a particular defined energy:

$$Q = \sum_{N=0}^{\infty} \sum_{\{\sigma\}} e^{\beta\mu N} e^{-\beta E_{\sigma}} \quad (31)$$

We must convert our sum over N to a sum over states, so $N = \sum_{i=0}^{\infty} n_i$:

$$Q = \sum_{n_i=0}^{\infty} e^{\sum_i n_i \beta(\mu - E_i)} = \prod_i \left(\sum_{n_i=0}^{\infty} e^{-n_i \beta(E_i - \mu)} \right) \quad (32)$$

It's easiest to calculate this for spin zero particles, in which case $n_i = 0, 1$:

$$Q = \prod_i \left(1 + e^{-\beta(E_i - \mu)} \right) \quad (33)$$

For nonzero spin, the n_i should be multiplied by a factor of $2S + 1$. So for example, for a particle with spin $\frac{5}{2}$, $2S + 1 = 6$ and the grand partition function becomes:

$$Q = \prod_i \left(1 + e^{-\beta(E_i - \mu)} \right)^6 \quad (34)$$

As a general rule, quantum effects should dominate at low temperatures; classical effects should dominate at high temperatures.

3.1 Photons

Remember that **N is not conserved for photons**, and likewise, $\mu = 0$.

3.2 Condensates

How to tell if we have a condensate:

Set $\mu = 0$ and $T = 0$. If $N \rightarrow \infty$, no condensate. If $N \rightarrow 0$ or $N \rightarrow$ a number, condensate.

Or, solve for μ , set $T = 0$ and see if we have any restrictions on N to make μ equal the ground state energy. No restrictions on $N =$ no condensate. Essentially if you can even find μ by itself, there's no condensate.

How to find critical temperature:

Set $\mu = 0$ and solve for T as a function of N . This is the critical temperature.

3.3 Distribution Functions

We can use the probability distribution $f(\epsilon_i)$ for bosons and fermions to calculate various useful things. (We can derive these distribution functions from the canonical ensemble, where Z has an added $\frac{1}{N!}$ for bosons.) In these formulas:

- The distribution function $f(\epsilon_i)$ represents the **number of particles with energy** ϵ_i . When called a “probability function”, it does not include g_s in the numerator; when used to calculate “population”, it does. Be careful with wording and note which case you are assuming.
- Spin degeneracy g_s represents the **spin degeneracy of state i** being calculated. This is $2S + 1$ except in the case of massless particles, which have spin degeneracy $2S$. If the energy ϵ_i depends on the spin, this is just 1.
- ϵ_i represents an **energy** that the state can have.
- $g(k)$ and $g(\epsilon)$ represent the **density of states**. These must be calculated depending on the energy and dimensions of the question. The easiest way to do that is:

$$g(\epsilon) = \int \left(\frac{L}{2\pi} \right)^n d\vec{k} \delta(\epsilon - \epsilon_k) \quad (35)$$

In this definition for density of states, $d\vec{k}$ should be written according to the number of dimensions, and ϵ_k is the reference energy relating ϵ and k (for example, $\epsilon_k = pc = \hbar kc$). Write $d\vec{k}$ in terms of

energy and the integral becomes trivial.

Remember this definition does not include **spin degeneracy** g_s , which some people do include in their definition of density of states.

The following calculations assume that g_s is **not** included in the distribution function $f(\epsilon)$ or the density of states $g(\epsilon)$.

Bosons:

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} - 1} \quad (36)$$

Fermions:

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \quad (37)$$

Boltzmann Distribution:

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}} \quad (38)$$

The following are particularly helpful for quantum systems:

Average internal energy:

$$U = \int \epsilon g_s g(\epsilon) f(\epsilon) d\epsilon \quad (39)$$

Number of particles:

$$N = \int g_s g(\epsilon) f(\epsilon) d\epsilon \quad (40)$$

Specific heat capacity:

$$C = \frac{\partial}{\partial T} \int \epsilon g_s g(\epsilon) f(\epsilon) d\epsilon \quad (41)$$

The average of any random quantity n , if we know that quantity in terms of ϵ , $n(\epsilon)$:

$$\langle n \rangle = \int n(\epsilon) f(\epsilon) g(\epsilon) d\epsilon \quad (42)$$

We can also find the average of a quantity by integrating over phase space:

$$\langle \epsilon \rangle = \int \epsilon_k f(k) g(k) d^3k d^3x \quad (43)$$

At $T = 0K$, we can find a few more properties:

$$N = \int_0^{\epsilon_f} g(\epsilon) d\epsilon \quad (44)$$

$$\mu = \epsilon_f \text{ at } T = 0K \quad (45)$$

4 Phase Transitions & Mean Field Theory

Magnetization:

$$M = -\frac{\partial F}{\partial B} = \mu_0 (N_+ - N_-) \quad (46)$$

Magnetic Susceptibility :

$$\chi = \frac{\partial M}{\partial B} \quad (47)$$

Evidence of Phase Transition:

- Divergence of E or M (or divergence of their derivatives)
- Multiple states for a fixed temperature (example, high and low density states simultaneously present)

To find the solution(s) of a transcendental equation, set the *slope* of each side equal to each other.

For example, when looking for spontaneous magnetization, remember that the slope of $\tanh(\alpha x)$ at $x = 0$ is α (or just take the derivative of the function to get the slope! evaluate result at $M=0$ for most linear case). So, to find solutions for $\beta x = \tanh(\alpha x)$, set the slopes equal: $\beta = \alpha$ in this case.

5 Helpful Maths

Taylor expansion:

$$F(x_0 + dx) = F(x_0) + dx \frac{dF}{dx} \Big|_{x=x_0} + dx^2 \frac{d^2F}{dx^2} \Big|_{x=x_0} + \dots \quad (48)$$

Don't forget the chain rule for derivatives:

$$\frac{dT}{dz} = \frac{\partial T}{\partial P} \frac{\partial P}{\partial z} \quad (49)$$

Stirling's approximation:

$$\ln N! = N \ln N - N \quad (50)$$

To take the derivative of a function that has multiple variables, such as $S(T, N, V)$:

$$dS(T, N, V) = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial N} dN + \frac{\partial S}{\partial V} dV \quad (51)$$

We can think of this from taking the whole time derivative and "canceling out" the dt from each term:

$$\frac{d}{dt} S(T, N, V) = \frac{\partial S}{\partial T} \frac{dT}{dt} + \frac{\partial S}{\partial N} \frac{dN}{dt} + \frac{\partial S}{\partial V} \frac{dV}{dt} \quad (52)$$

Expansions for small x (useful for temperature limits!):

$$(1 + x)^n \simeq 1 + nx \quad (53)$$

$$e^x \simeq 1 + x + \dots \quad (54)$$

Helpful summation tricks

$$\sum_{N=0}^{\infty} a^N = \frac{1}{1-a} \quad a \ll 1 \quad (55)$$

$$\sum_{N=0}^{\infty} \frac{1}{N!} x^N = e^x \quad (56)$$

Sometimes a partition function (grand partition functions especially) cannot be easily calculated. Then it helps to look at the high and low temperature limits. For example:

$$Z \sim \sum e^{-\beta E n^2} \quad (57)$$

For $T \rightarrow \infty$, $\beta \rightarrow 0$, so exponent gets small. **Integrate.**

For $T \rightarrow 0$, $\beta \rightarrow \infty$, so $e^{-\beta E}$ gets small. **Sum**, keeping only the first couple terms.

Remember this integral for help solving N in grand canonical ensemble problems:

$$\int_0^\infty \frac{x^{n-1}}{z^{-1}e^x - 1} = \Gamma(n)g_n(z) \quad (58)$$

Standard deviation:

$$\Delta n^2 = \langle n^2 \rangle - \langle n \rangle^2 \quad (59)$$

Gamma function:

$$\Gamma(n+1) = n\Gamma(n) \quad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \quad (60)$$