

# Statistical Mechanics: Qual Review

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# 1 Thermodynamic Laws

## 0th law

- if 2 systems are in equilibrium with a 3rd, they are in equilibrium with each other

## 1st law

- Conservation of energy
  - assumes condition holds at the microscopic level

$$dU = dQ + dW \tag{1}$$

## 2nd law

- Entropy always increases

## 3rd law

- The entropy per particle goes to zero at absolute zero
  - follows the statistical definition of entropy:  $S(T = 0) = k_b \ln \Omega_0$

## 2 Thermodynamic Potentials

- [check section on partial derivative in the equation sheet](#)

- fundamental relation:

$$U = TS - PV + \mu N \quad (2)$$

- total energy of a system (microcanonical ensemble)
- you can multiply this by a factor:  $\lambda U = \lambda(TS - PV + \mu N)$
- the derivative is unaffected

- Gibbs-Duhem relation:  $d\mu = -sdT + \nu dP$ ,  $s = S/N$  &  $\nu = V/N$

### 2.1 Legendre Transforms & free energies

- Legendre transforms are used to change which variables a thermodynamic potential depends on

$$Y(p) = y - px, p = dy/dx$$

- Helmholtz Free Energy: represents the energy available to do useful work at constant temp & volume

$$F(T, V, N) = U - TS$$

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

- Enthalpy: changing the independent variable from V to P, constant P & entropy

$$H(S, P, N) = U + PV$$

$$dH = TdS + VdP + \mu dN$$

- Gibbs Free Energy: how much energy is available to do non-volume work at constant T & P

$$G(T, P, N) = F + PV = H - TS = U - TS + PV$$

$$dG = SdT + VdP + \mu dN$$

### 2.2 Maxwell Relations

- if the integral of dF along a path in x y space is independent of the path:

$$\frac{\partial f(x, y)}{\partial y} = \frac{\partial^2 F(x, y)}{\partial x \partial y} = \frac{\partial^2 F(x, y)}{\partial y \partial x} = \frac{\partial g(x, y)}{\partial x}$$

given  $dF = f(x, y)dx + g(x, y)dy$

- thus (setting  $dN = 0$ )

$$\text{Energy: } dU = TdS - PdV \rightarrow \frac{\partial T}{\partial V}|_{S,N} = -\frac{\partial P}{\partial S}|_{V,N}$$

$$\text{Helmholts Free Energy: } dF = -SdT - PdV \rightarrow \frac{\partial S}{\partial V}|_T = \frac{\partial P}{\partial T}|_V$$

$$\text{Enthalpy: } dH = TdS + VdP \rightarrow \frac{\partial T}{\partial P}|_S = \frac{\partial V}{\partial S}|_P$$

$$\text{Gibbs Free Energy: } dG = SdT + VdP \rightarrow \frac{\partial S}{\partial P}|_T = -\frac{\partial V}{\partial T}|_P$$

## 2.3 Partition Function

- the partition function is the summation over the Boltzmann factor for all states  $s$  of a system

$$Z(T) = \sum_s \exp\left(\frac{-E_s}{kT}\right) \quad (3)$$

$$P(E) = \frac{\exp\left(\frac{-E_s}{kT}\right)}{Z} \quad (4)$$

- note that  $\sum P(E_s) = Z/Z = 1$

### 3 Cyclic processes

Cyclic processes: thermodynamic process in which a system returns to its initial thermodynamic state (i.e same U, P, V, T) after a process.

- aka  $\Delta U = 0$
- We are reminded of the first law:  $\Delta U = \Delta Q - pdv$ 
  - meaning for a cyclic process  $\rightarrow \Delta U = 0 \rightarrow Q = W$
  - total heat added over the cycle = total work done by the system
- Most of this section referenced Chapter 8 (Heat & Work) from Kittel

#### 3.1 Energy & Entropy Transfer Definitions

- heat is the transfer of energy to a system by thermal contact with a reservoir
- work is the transfer of energy to a system by a change in the external parameters that describe the system
- entropy transfer in a reversible process is zero when only work is performed and no heat is transferred.
- we want to convert heat to work (steam engine, combustion engine)
- bringing 2 systems together, the total energy is conserved but not the entropy, may increase
- it is defined that  $dQ \equiv TdS$  which means  $dW = dU - dQ = dU - TdS$ 
  - $dS = 0 \rightarrow$  pure work
  - $dU = TdS \rightarrow$  pure heat

#### 3.2 Heat Engines: conversion of heat into work

##### 3.2.1 Carnot inequality

- all forms of work are freely convertible, they are thermodynamically equivalent to each other
- work can be completely converted to heat but the inverse is not true
  - entropy enters the system with the heat but does not leave the system with the work

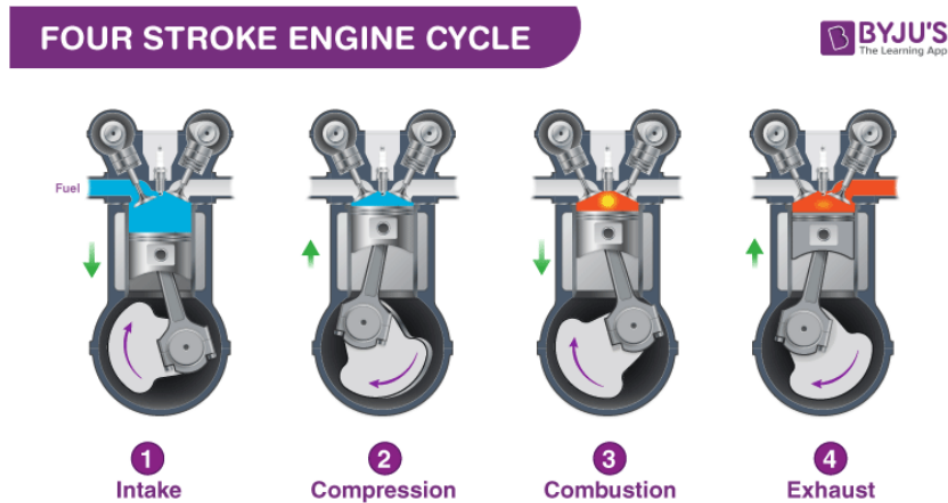


Figure 1: Entropy is at the min near the beginning of the intake stroke and max at the beginning of the exhaust stroke.

- "To prevent the accumulation of entropy [in a system] there must be some output heat; therefore it is impossible to convert all the input heat to work!"
- entropy must ultimately be removed
- heat engine: energy conversion device that operates in cycles
- work generated during 1 cycle of a reversible process:

$$W = Q_h - Q_l = (1 - T_l/T_h)Q_h = \frac{T_h - T_l}{T_l}Q_h \quad (5)$$

$$\text{Carnot efficiency } \eta_c \equiv \left(\frac{W}{Q_h}\right)_{\text{rev}} = \frac{T_h - T_l}{T_l} \quad (6)$$

where h is the input heat and l is the leaving heat,  
aka we can not convert all input heat into work

$$\text{Carnot inequality } \eta = W/Q \leq 1 - (T_l/T_h) \equiv \eta_c \quad (7)$$

- Carnot inequality is the basic limit for heat engines

### 3.2.2 Refrigerators

- refrigerators consume work to remove heat

$$\text{coefficient of refrigerator performance } \lambda \equiv Q_l/W \quad (8)$$

$\lambda$  can be greater or less than 1

$$\text{Carnot coefficient of refrigerator performance } \lambda_c = (Q_l/W)_{\text{rev}} = \frac{T_l}{T_h - T_l} \quad (9)$$

This is an upper limit to the actual coefficient of refrigerator

- air conditioners are refrigerators
- heat pumps are reverse connections of an air conditioner

### 3.2.3 Carnot Cycle

- gas is expanded & compressed in 4 stages (2 isothermal & 2 isentropic)
  1. gas has the temp  $T_{\text{high}}$  & entropy  $S_{\text{Low}}$ 
    - gas expands at constant T until the entropy increases to  $S_H$
  2. gas has the temp  $T_h$  & entropy  $S_H$ 
    - gas expands with constant S, until temp drops to  $T_l$
  3. gas has the temp  $T_l$  & entropy  $S_H$ 
    - gas is compressed isothermally
  4. gas has the temp  $T_l$  & entropy  $S_L$ 
    - compressed isentropically to original state
- work done by the system is the area of the rectangle (Carnot cycle)

$$W = (T_h - T_l)(S_H - S_L) \quad (10)$$

$$(11)$$

which comes from

$$\oint dU = 0 = \oint TdS - \oint pdV \rightarrow W = \oint TdS \quad (12)$$

### 3.2.4 Path Dependence of Heat & Work

- transfers of heat and work between state (a) and state (b) depend on the path taken between the two states **heat & work are not state functions**
- "Without the path dependence of heat and work there would not exist cyclical processes that permit the generation of work from heat."



### 3.2.5 Irreversible Work

- if newly created entropy arises by the conversion of work to heat, irreversible work has been performed
- pure heat transfer not involving any work done between 2 systems with different temperatures

## 3.3 Heat & Work at Constant Temp or Pressure

- Isobaric process: constant pressure
- the effective work  $dW \equiv dW + d(pV) = dU + d(pV) - dQ = dH - dQ$  where H is enthalpy ( $H = U + pV$ )
  - $dQ = dH$ : no effective work is done (heat liquid with no cap)
  - constant pressure and temp  $dQ = TdS = d(TS)$
- use enthalpy at constant pressure
- use gibbs free energy at constant P & T ( $G = F + pV = U + pV - TS$ )

### 3.3.1 Chemical Work

- Chemical work: work performed by the transfer of particles to a system (associated with chemical potential)

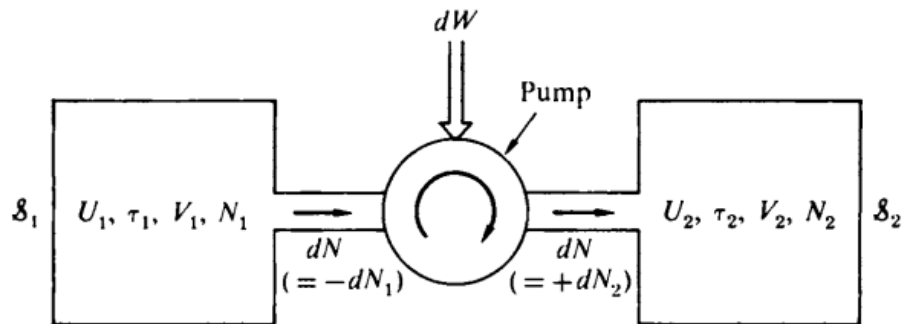
$$dW = \mu dN \quad (13)$$

- Chemical potential (reference figure 8.14)
  - is the work required to transfer 1 particle into the system
  - the difference in chemical potential between 2 systems is equal to the net work required to move a particle from 1 system to the other (if there is 0 volume work)
 
$$dW = \mu_a dN_a + \mu_b dN_b = (\mu_b - \mu_a) dN$$
  - if 2 systems are in diffuse equilibrium ( $\mu_a = \mu_b$ ), no work is required to move the particles

### 3.3.2 Heat Capacity

- the heat capacity is the amount of heat needed to raise its temperature per degree

$$C \equiv \frac{Q}{\Delta T} = \frac{\Delta U + p dv}{\Delta T} \quad (14)$$



**Figure 8.14** Chemical work is the work performed when particles are moved reversibly from one system to another, with the two systems having different chemical potentials. If the two volumes do not change, the work is pure chemical work; the amount per particle is the difference in chemical potentials.

- where the specific heat capacity is simply the heat capacity per unit of mass ( $c \equiv \frac{C}{m}$ )
- Where we can take a case of constant volume (no work is done) and use the thermodynamic identity to get

$$C_V = \frac{\Delta U + 0}{\Delta T}|_V = \frac{\partial U}{\partial T}|_V \quad (15)$$

which we can also substitute back  $dq$  as we know  $dq = TdS$ :

$$C_V = \frac{\partial U}{\partial T}|_V = T \frac{\partial S}{\partial T}|_V \quad (16)$$

- for the case where we have constant P we have

$$C_P = \frac{\Delta U + pdv}{\Delta T}|_P = \frac{\Delta U}{\Delta T}|_P + p \frac{\Delta V}{\Delta T}|_P \quad (17)$$

- molar heat capacity, simply the heat capacity per mole of atoms

$$c_m = \frac{C}{n} \quad (18)$$

- thermal expansion coefficient: materials expand when they are heated, this coefficient is the fractional increase in volume per unit change in temperature

$$\beta \equiv \frac{\Delta V/V}{\Delta T} \quad (19)$$

- linear thermal expansion coefficient:

$$\alpha \equiv \frac{\Delta L/L}{\Delta T} \quad (20)$$

- isothermal compressibility

$$\kappa_T \equiv -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T \quad (21)$$

### 3.4 Latent Heat

- how much heat is required to melt or boil a substance, the amount divided by the mass of the substance

$$L \equiv \frac{Q}{m} \quad (22)$$

### 3.5 Some Discussion Notes

- reversible process
  - to begin this system has no change in energy as well as entropy (like wut???)
  - since there is no change in entropy, it stands that there is no change in temp as:

$$\Delta S_{\text{tot}} = \frac{-Q}{T_A} + \frac{Q}{T_B} \quad (23)$$

which means that there is no heat exchange

- since  $\Delta U = 0$  &  $\Delta Q = 0$  it stands that  $\Delta W = 0$  ( $\Delta U = \Delta Q - \Delta W$ ), aka no work is done!!
- this system is also quassi static which means it's always in equilibrium

### 3.6 Example Problems to try:

- 2024 Qual: #1, #3, #4

## 4 Equilibrium Ensembles I.

### 4.1 Micro-canonical

### 4.2 Canonical

### 4.3 Grand-canonical

## 5 Equilibrium Ensembles II.

### 5.1 Classical Cases

### 5.2 Quantum Cases

## 6 Ideal Quantum Gases & Applications

## 7 Equation Sheet

### Forms of Entropy:

$$S(N, U) = k \log \Omega \quad (24)$$

### Partial derivatives:

$$\text{Entropy: } S(U, N, V) = \begin{cases} \frac{\partial S}{\partial U} = \frac{1}{T} \\ \frac{\partial S}{\partial V} = \frac{P}{T} \\ \frac{\partial S}{\partial N} = -\frac{\mu}{T} \end{cases} \quad (25)$$

### Maxwell's Relation:

$$\text{Energy: } U(S, V, N) = TS - PV + \mu N \begin{cases} \frac{\partial U}{\partial S} = T \\ \frac{\partial U}{\partial V} = -P \\ \frac{\partial U}{\partial N} = \mu \end{cases} \quad (26)$$

$$\text{Helmholts Free Energy: } F(T, N, V) = U - TS(U, N, V) \begin{cases} \frac{\partial F}{\partial T} = -S \\ \frac{\partial F}{\partial N} = \mu \\ \frac{\partial F}{\partial V} = -P \end{cases} \quad (27)$$

$$F = -kT \ln(z) \rightarrow P = kT \frac{\partial \ln(z)}{\partial V} \quad (28)$$

$$F = -kT \ln(z) \rightarrow S = -k \frac{\partial T \ln(z)}{\partial T} \quad (29)$$

$$\text{Gibbs Free Energy: } G(N, T, P) = F(N, T, V) + PV \begin{cases} \frac{\partial G}{\partial T} = -S \\ \frac{\partial G}{\partial P} = V \\ \frac{\partial G}{\partial N} = \mu \end{cases} \quad (30)$$

$$(31)$$

**Other Partial Derivatives:**

$$\text{Enthalpy: } H(S, P, N) = U + PV \begin{cases} \frac{\partial H}{\partial S} = T \\ \frac{\partial H}{\partial P} = V \\ \frac{\partial H}{\partial N} = \mu \end{cases} \quad (32)$$

$$\text{Grand Potential: } \Phi(T, \mu, V) = \mu N - F(T, N, V) \begin{cases} \frac{\partial \Phi}{\partial T} = S \\ \frac{\partial \Phi}{\partial \mu} = N \\ \frac{\partial \Phi}{\partial V} = P \end{cases} \quad (33)$$

**Ideal Gas:**

$$PV = NKT = nRT \quad (34)$$

$$U = \frac{f}{2}KT, \text{ where } f \text{ is the degrees of freedom} \quad (35)$$

**Partition Function:**

$$\text{Normal: } z = \sum e^{E_i/kT}, \text{ where } E = \frac{p^2}{2m} \quad (36)$$

$$\text{One: } z_1 = \frac{1}{h^3} \int d^3x d^3p e^{-E/kT}, \text{ where } d^3p = p^2 \sin \theta dp d\theta d\phi \quad (37)$$

$$\text{indistinguishable particles: } z_N = \frac{1}{N!} z_1^N \quad (38)$$

$$\text{identical particles: } z_N = \frac{1}{N!} (n_Q V)^N, \text{ where } n_Q = (MkT/2\pi\hbar^2)^{3/2} \quad (39)$$

$$\text{Grand: } \Xi = \sum_{N=0}^{\infty} z_N e^{\mu N/kT} = \sum_{N=0}^{\infty} \frac{1}{N!} \left( \sum_a e^{E_a/kT} \right)^N e^{\mu N/kT} \quad (40)$$

**Energy Forms:**

$$F = -KT \ln(z) \quad (41)$$

$$U = kT^2 \frac{\partial \ln(z_N)}{\partial T} \quad (42)$$

**Heat**

$$dS = \frac{dQ}{T} \quad (43)$$

$$S = \frac{Q}{T} \quad (44)$$



## In a Carnot Cycle

$$\oint dU = 0 = \oint TdS - \oint pdV \rightarrow W = (T_h - T_l)(S_H - S_L) \quad (45)$$

## A Thermodynamic Identity

$$dU = TdS - pdV \rightarrow TdS = dU + pdV \quad (46)$$

## Magnetism

$$\text{Energy (E)} = -\vec{\mu} \cdot \vec{B}, \text{ where } \mu \text{ is the magnetic moment} \quad (47)$$

## To cover all bases equations:

$$\text{Pressure } P = \rho gh \quad (48)$$

$$\text{Force } F = P * A = \rho gV \quad (49)$$

$$\text{Carnot efficiency } \eta_c \equiv \left(\frac{W}{Q_h}\right)_{\text{rev}} = \frac{T_h - T_l}{T_l} \quad (50)$$

$$\cosh(x) = \frac{e^x + e^{-x}}{2} \quad (51)$$

$$\sinh(x) = \frac{e^x - e^{-x}}{2} \quad (52)$$

$$(53)$$

## Approximations

- Stirling Approximation (large limits of n ignore the high order terms)

$$\ln(n!) = n \ln(n) - n + O(\ln(n))$$

$$\ln(n!) \approx n \ln(n) - n$$

## Dumb Abbreviations

$$kT = \tau = \beta^{-1}$$

$$\sigma = \log g$$

$$S = k\sigma$$

## 8 Extra

Things that have come up in Qualls / were an important topic in the Stat Mech course.

### 8.1 Equipotential Theorem

As mentioned in the stat mech course there is a crude and precise definition:

- Crude:  $\langle E / \text{particle} \rangle = \# \text{ of degrees of freedom} * \frac{1}{2} kT$
- Precise:  $\langle E / \text{particle} \rangle = \# \text{ of quadratic terms in the Hamiltonian} * \frac{1}{2} kT$ 
  - Notes: The Hamiltonian is the energy of the system, KE + PE, and if there is only momentum space there is no potential energy
  - Reminder: We can find the internal energy from the

### 8.2 Magnetization

- Magnetic Moment ( $\vec{\mu}$ ): measurement of the torque a system experiences in a  $\vec{B}$ 
  - From past qualls it seems the magnetic moment is given
  - Ampèrian loop:  $\vec{\mu} = I\vec{A}$ , I is the current & A is the area
  - Solenoid:  $\vec{\mu} = NI\vec{A}$ , where N is the turns
  - For spin particles:  $\vec{\mu} = -g\mu_B\vec{S}/\hbar$
- Energy in a  $\vec{B}$

$$E = -\vec{\mu} \cdot \vec{B} \quad (54)$$

- Adiabatic Demagnetization: process used to cool systems to very low temps
  - Apply strong  $\vec{B}$  (this aligns the spins thus reducing the entropy)
  - Thermally isolate the system
  - Reduce the  $\vec{B}$  but total entropy remains constant and temp drops
- Bohr Magneton ( $\mu_B$ ): the magnetic moment of an electron due to its spin

### 8.3 Density of State