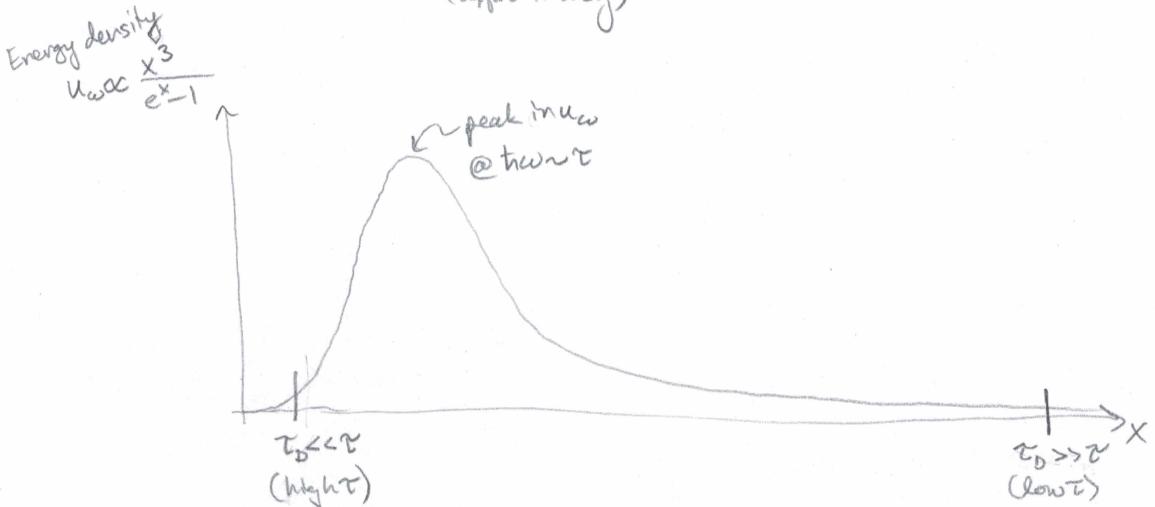


Last time, we derived an expression for vibrational energy of a solid

$$U = \frac{9N\tau^4}{T_D^3} \underbrace{\int_0^{x_D} dx}_{x} \cdot \frac{x^3}{e^x - 1} \quad \text{where } x_D = \frac{\tau}{T_D} \leftarrow T_D = \hbar \omega_D$$



Debye frequency ω_D set by shortest possible wavelength on discrete lattice.
(approximately)



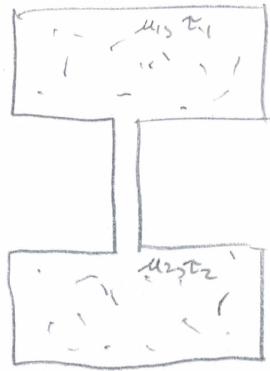
$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

- @ End of class, we were evaluating in limiting cases of high and low τ ...
.. finish this (Ex 7A, pg. 7, part h).

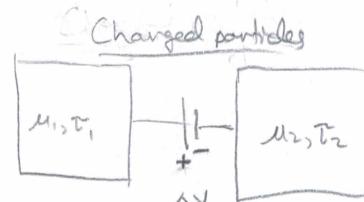
* Already discussed low- τ — analogous to radiation — high- ω cutoff is irrelevant

* High- T \Rightarrow Matches expectation from equipartition.

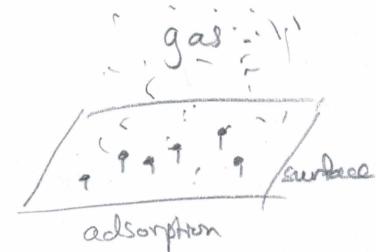
Chemical / Diffusive Equilibrium



↓ gravity



electrochemical potential
(e.g. batteries)

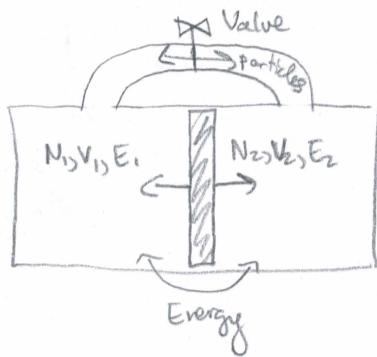


Define chemical potential by

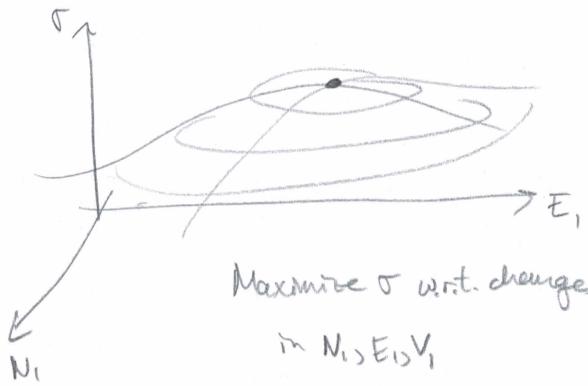
$$dE = \tau d\sigma - pdV + \mu dN$$

(Chemical work)

Condition for chemical equilibrium in terms of μ ?



General conditions for equilibrium?



③ Comment on ideal gas:

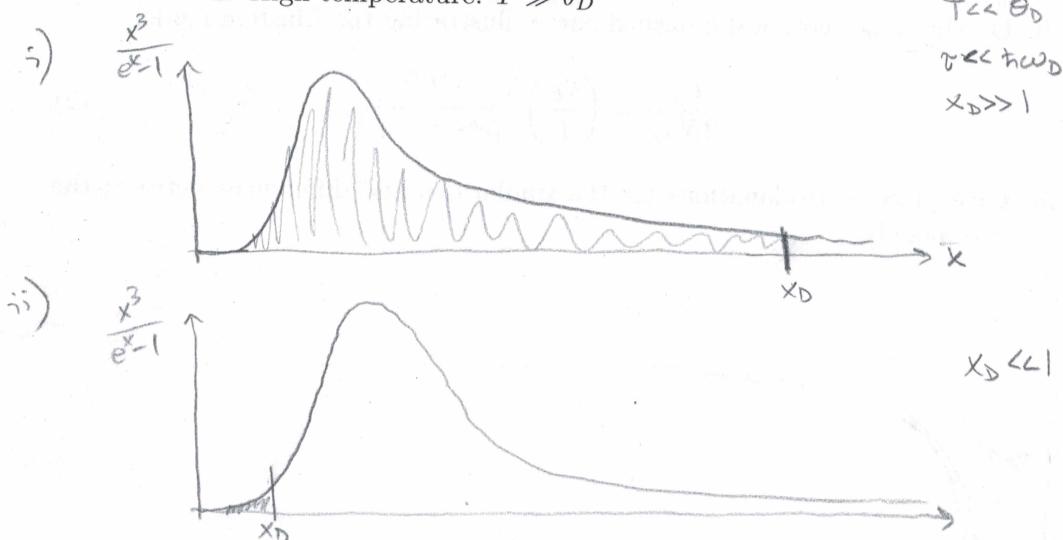
...to be discussed next week...

* Today: get an intuition for μ by quickly evaluating from $F(N, \tau, V)$

* Next week! See how we would arrive at μ and F starting from Z

— correct first-principles treatment of gas of identical particles.

- g. Sketch the integrand from d., shading in the region of integration, for two cases:
- Low temperature: $T \ll \theta_D$
 - High temperature: $T \gg \theta_D$



- h. Evaluate the integral \mathcal{I} and determine the heat capacity:

- ... in the low-temperature limit $T \ll \theta_D$
- ... in the high-temperature limit $T \gg \theta_D$

i) In low-T limits can approximate as

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

$$\rightarrow U = \frac{9N\tau^4}{\tau_D^3} \cdot \frac{\pi^4}{15} = \frac{3N\tau^4 \pi^4}{5\tau_D^3} \Rightarrow C_V = \left(\frac{dU}{d\tau} \right)_V = \frac{12\pi^4 N}{5} \left(\frac{\tau}{\tau_D} \right)^3$$

ii) High-T: $\mathcal{I} \approx \int_0^{x_D} \frac{x^3 dx}{x} \approx \int_0^{x_D} x^2 dx \approx \frac{1}{3} x_D^3$

$$\Rightarrow U = \frac{9N\tau^4}{\tau_D^3} \cdot \frac{1}{3} \left(\frac{\tau_D}{\tau} \right)^3 = 3N\tau \Rightarrow C_V = 3N$$

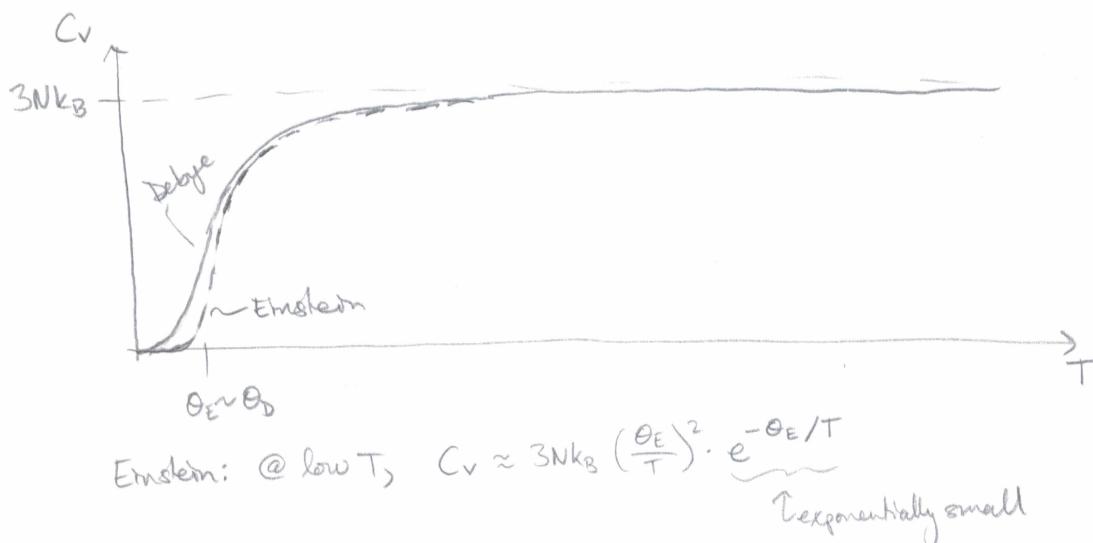
consistent w/
classical limit.

- i. Sketch the dependence of the heat capacity on temperature T (interpolating between the high- and low-temperature results.

- Draw a solid curve showing the Debye model
- On the same plot, add a dashed curve illustrating the Einstein model

$$\frac{C_V}{3Nk_B} = \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}. \quad (2)$$

- Give physical explanations for the similarities and differences between the two models.



- iii) High- T : both approach classical result from equipartition

Low- T : both have $C_V \rightarrow 0$ as $T \rightarrow 0$

Einstein — no accessible excitations for $\tau < \hbar\omega \Rightarrow$ exponential suppression of C_V

Debye — density of states $\propto \omega^2$, so # of accessible modes
for excitation vanishes as $\tau \rightarrow 0$... but at arbitrarily
low τ there are $\sim \tau^3$ modes accessible $\Rightarrow C_V \propto \tau^3$

- j. What other degrees of freedom, not considered above, might modify the heat capacity of a real solid?

Spin or electron orbital degrees of freedom.

↳ We will come back to this soon w/ proper treatment
of identical fermions.

Need new concept: chemical potential. \rightarrow Ex. 7B

EXERCISE 7B: DIFFUSIVE EQUILIBRIUM AND CHEMICAL POTENTIAL*Objectives:*

- Define the **chemical potential**, and chemical or diffusive equilibrium
- Determine the relative probabilities of microstates in the **grand canonical ensemble**
- Calculate and interpret the chemical potential of an ideal gas

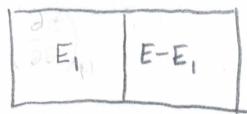
References: Kittel & Kroemer, Ch. 5

1. *General conditions for equilibrium.* Consider two systems \mathcal{A}_1 and \mathcal{A}_2 that are allowed to exchange particles. We would like a way of quantifying which way particles must flow to establish **diffusive** or **chemical equilibrium**, just as their temperatures indicate which way heat must flow to establish thermal equilibrium. To this end, we define the chemical potential μ so that

$$dE = \tau d\sigma - pdV + \mu dN. \quad (1)$$

Let σ denote the entropy of the composite system $\mathcal{A}_1 + \mathcal{A}_2$, with fixed total energy $E = E_1 + E_2$, volume $V = V_1 + V_2$, and number of particles $N = N_1 + N_2$. Based on Eq. 1, derive a set of conditions for systems \mathcal{A}_1 and \mathcal{A}_2 to be in equilibrium.

- a. Derive a condition for **thermal equilibrium** by maximizing σ with respect to exchange of energy between subsystems.



$$\frac{\partial}{\partial E_1} (\sigma_1 + \sigma_2) \Big|_{\substack{N_1, N_2 \\ V_1, V_2}} = \frac{\partial \sigma_1}{\partial E_1} \Big|_{N_1, V_1} + \frac{\partial \sigma_2}{\partial E_1} \Big|_{N_2, V_2}$$

$$\Rightarrow 0 = \frac{\partial \sigma_1}{\partial E_1} \Big|_{N_1, V_1} - \frac{\partial \sigma_2}{\partial E_1} \Big|_{N_2, V_2} = \frac{1}{\tau_1} - \frac{1}{\tau_2}$$

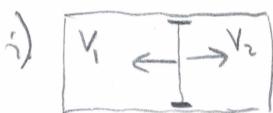
$$\Rightarrow \boxed{\tau_1 = \tau_2} \equiv \tau$$

- b. What additional conditions must hold for the system to be in...

i. ... **mechanical equilibrium?**

ii. ... **chemical equilibrium?**

Next page. →



$$\frac{\partial \sigma_1}{\partial V_1} \Big|_{N_1, E_1} = \frac{\partial \sigma_2}{\partial V_2} \Big|_{N_2, E_2} \Rightarrow \frac{P_1}{\tau} = \frac{P_2}{\tau} \Rightarrow \boxed{P_1 = P_2}$$

Const N, E : $\tau d\sigma_i = P_i dV_i$



$$\frac{\partial \sigma_1}{\partial N_1} \Big|_{V, E} = \frac{\partial \sigma_2}{\partial N_2} \Big|_{V, E} \Rightarrow \frac{\mu_1}{\tau} = \frac{\mu_2}{\tau} \Rightarrow \boxed{\mu_1 = \mu_2}$$

Const V, E : $\tau d\sigma = \mu dN$

ii. Chemical equilibrium
 (see previous page)

c. Find expressions for the chemical potential μ in terms of ...

- i. ... the entropy σ and temperature τ
- ii. ... the Helmholtz free energy F

$$\text{i) } dE = \tau d\sigma - p dV + \mu dN \Rightarrow -\tau d\sigma = \mu dN \text{ @ const } E, V$$

$$\Rightarrow \boxed{\mu = -\tau \left(\frac{\partial \sigma}{\partial N} \right)_{E,V}}$$

This expression is of limited utility b/c in practice either τ or E is fixed, not both...

$$\text{ii) } dF = -\sigma d\tau - p dV + \mu dN \Rightarrow \boxed{\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}}$$

d. *Sign check.* Suppose two systems A_1 and A_2 that initially had different chemical potentials $\mu_2 > \mu_1$ are allowed to equilibrate at constant temperature τ . Which way do the particles tend to flow?

$$\frac{\partial(F_1 + F_2)}{\partial N_1} = \Delta \frac{\partial F_1}{\partial N_1} - \frac{\partial F_2}{\partial N_2} = \mu_1 - \mu_2 < 0$$

N_1 must increase to decrease $F \Rightarrow$ particles flow from A_2 to A_1 , i.e., from high to low chemical potential.

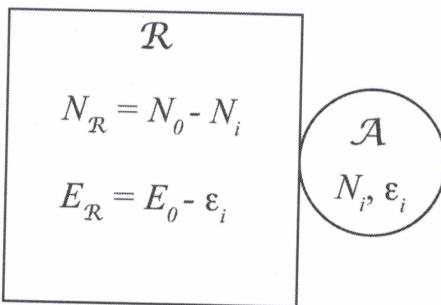


FIG. 1. A system \mathcal{A} in thermal and diffusive contact with a reservoir \mathcal{R} . In microstate i , the system contains N_i particles and has energy ε_i .

2. *Grand canonical ensemble.* Consider a system \mathcal{A} in thermal and diffusive contact with a reservoir \mathcal{R} at temperature τ and chemical potential μ , as illustrated in Figure 1.
- Determine the equilibrium ratio P_1/P_2 of probabilities for finding the system in microstates 1 and 2, where the i^{th} microstate has N_i particles and energy ε_i .

$$dE = T d\tau - \mu dN + \nu dV \Rightarrow \mu = -T \left(\frac{\partial \sigma}{\partial N} \right)_{E,V} \Rightarrow \frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial E} \right)_{V,N}$$

$$\frac{P_1}{P_2} = \frac{g_R(N_0 - N_1, E_0 - \varepsilon_1)}{g_R(N_0 - N_2, E_0 - \varepsilon_2)}$$

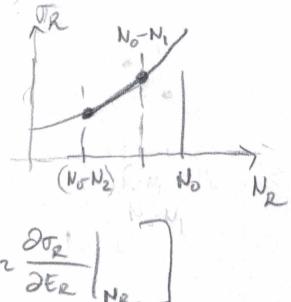
$$\ln \left(\frac{P_1}{P_2} \right) = \sigma_R(N_0 - N_1, E_0 - \varepsilon_1) - \sigma_R(N_0 - N_2, E_0 - \varepsilon_2)$$

$$\approx \sigma_R(N_0, E_0) - N_1 \left. \frac{\partial \sigma_R}{\partial N_R} \right|_{E_2} - \varepsilon_1 \left. \frac{\partial \sigma_R}{\partial E_R} \right|_{N_R} - \left[\sigma_R(N_0, E_0) - N_2 \left. \frac{\partial \sigma_R}{\partial N_R} \right|_{E_R} - \varepsilon_2 \left. \frac{\partial \sigma_R}{\partial E_R} \right|_{N_R} \right]$$

$$= + \frac{N_1 \mu}{\tau} - \frac{N_2 \mu}{\tau} - \frac{\varepsilon_1}{\tau} + \frac{\varepsilon_2}{\tau}$$

$$= \beta [(N_1 - N_2) \mu - (\varepsilon_1 - \varepsilon_2)]$$

$$\Rightarrow \boxed{\frac{P_1}{P_2} = \frac{e^{\beta(N_1 \mu - \varepsilon_1)}}{e^{\beta(N_2 \mu - \varepsilon_2)}}}$$



- b. Determine the probability P_i of finding the system in the i^{th} microstate.

$$P_i = \frac{e^{\beta(N_i; \mu - E_i)}}{\sum_i e^{\beta(N_i; \mu - E_i)}}$$

Microstate i specified by
of particles in \mathcal{A} and energy in \mathcal{A}

- c. Propose a definition for the **grand canonical partition function** (or **Gibbs sum**) \mathcal{Z} , and reexpress your result for P_i in terms of \mathcal{Z} .

$$\mathcal{Z} = \sum_i e^{\beta(N_i; \mu - E_i)}$$

(sum of Gibbs factors over all states
in Grand Canonical Ensemble.)

- d. Find an expression for the mean number of particles $\langle N \rangle$ in the system \mathcal{A} in terms of \mathcal{Z} .

$$\langle N \rangle = \frac{1}{\mathcal{Z}} \sum_i N_i e^{\beta(N_i; \mu - E_i)}$$

We have $\frac{\partial \mathcal{Z}}{\partial \mu} = \sum_i \beta N_i e^{\beta(N_i; \mu - E_i)} \rightarrow \text{so}$

$$\boxed{\langle N \rangle = \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}}$$

* C.F. calculating $\langle E \rangle$ in canonical ensemble

* We will see how this is useful on HW and next week...

Rest of this worksheet: a little more intuition for meaning of chemical potential.