



StatMech Basics II



Microcanonical Ensemble

- Calculate $\Omega(E, V, N)$
- $S(E, V, N) = k_B \ln \Omega$
- Can derive any thermodynamic potential with this
- Example: Equilibrium concentration of vacancies
- Example: Negative thermal expansion of polymers



Some Useful Formulae

- Several formulae come in handy when trying to count!
- For large N , $\ln(N!) = N \ln N - N \dots$ the Sterling approximation
- Another, useful formula $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$
- ..
- Don't bother if you don't follow all the mathematical details...just make sure that you follow the logic



Equilibrium Concentration of Vacancies

- It is well known that the equilibrium concentration of vacancies in a solid scales as $e^{-E_v/k_B T}$ where E_v is the vacancy formation energy...where does this come from?
- Logic:
 1. Compute entropy for a given concentration c of vacancies $S(c)$
 2. Compute Helmholtz free energy $A(T, c) = U - TS$
 3. Find the value of c that minimizes A , this gives the equilibrium concentration of c



Equilibrium Concentration of Vacancies

- Solid thought of a collection of N atomic sites
- Each site may or may not be occupied
- If a site is not occupied then the system has an additional energy...the vacancy formation energy E_v
- Assume now that N_o sites are occupied and N_v sites are vacant
- How many microstates Ω are possible?

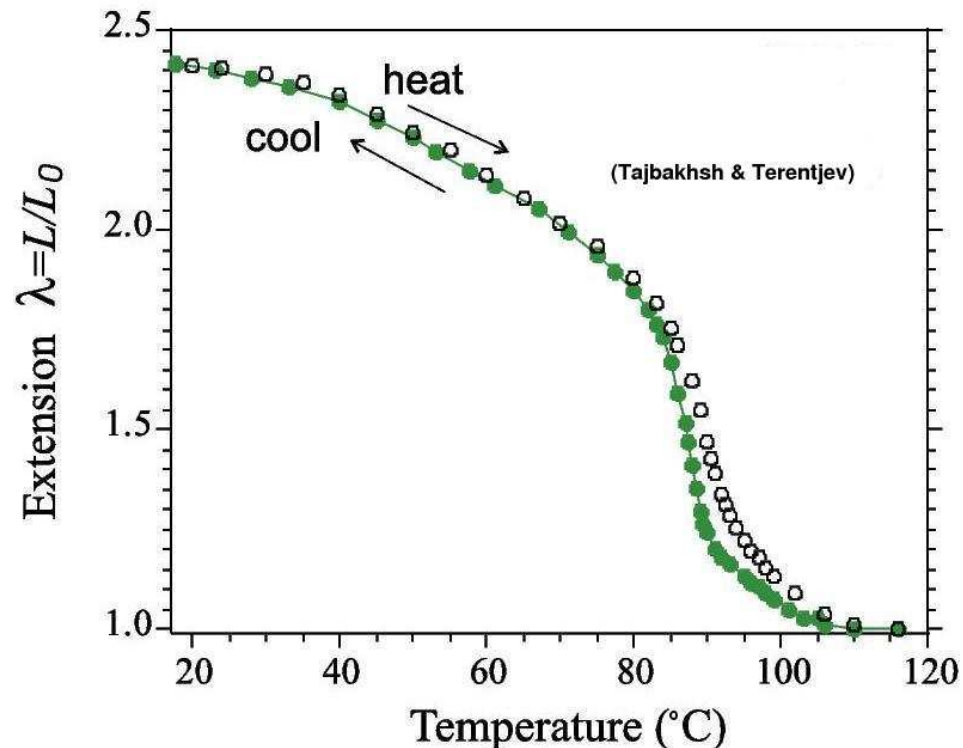


Equilibrium Concentration of Vacancies

- $\Omega = \frac{N!}{N_o!N_v!}$, thus, $S = k_B \ln \left(\frac{N!}{N_o!N_v!} \right)$
- **Taking $c = \frac{N_v}{N}$ and $\frac{N_o}{N} = (1 - c)$, we get**
$$S = -Nk_B (c \ln c + (1 - c) \ln (1 - c))$$
- **The internal energy of the system is $U = NcE_v$**
- **The Helmholtz free energy**
$$A(T, c) = U - TS = N(cE_v + k_B T (c \ln c + (1 - c) \ln (1 - c)))$$
- **Taking $c \ll 1$, $\frac{A(T, c)}{N} \approx cE_v + k_B T c \ln c$**
- **Equilibrium concentration $c \sim e^{-E_v/k_B T}$**

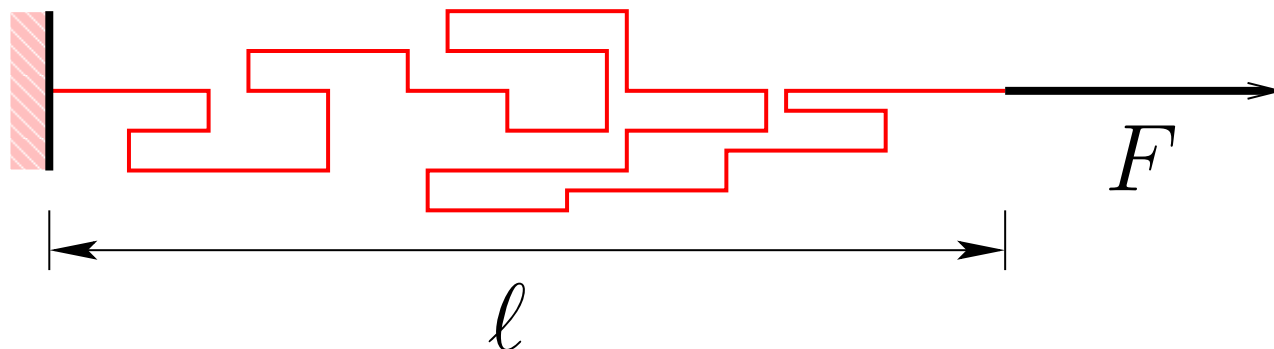
Thermal Expansion of Polymers

- Experiment: Take a piece of rubber band, and use it to hang a weight...gently heat the rubber band...you will see that the weight will be lifted up!
- Moral: “Soft” polymers contract on heating! (Why?)



Chain Model for Polymers

- Think of a polymer as a chain of N links each of length a , total length of chain $L = Na$ under the action of a dead load F
- The chain folds up such that the end-to-end distance is ℓ (no energy cost to bend bonds)



- Strategy: Calculate S , and from there G ...the Gibbs free energy (Recall, system kept at constant “pressure” (force) and temperature minimizes Gibbs free energy...



Chain Model for Polymers

- To calculate the entropy, we need to find the number of ways the chain of total length $L = Na$ can have end to end distance of $\ell = na$ (a “length of a unit polymer”)
- In a simple “1 – D thinking”, the chain is made of segments that are pointing from left to right, and those that are pointing from right to left
- Let $n_{\rightarrow} = \#$ segments from left to right, $n_{\leftarrow} = \#$ segments from right to left
- Also, $n_{\rightarrow} + n_{\leftarrow} = N$ and $n_{\rightarrow} - n_{\leftarrow} = n$, or $n_{\rightarrow} = \frac{N+n}{2}$ and $n_{\leftarrow} = \frac{N-n}{2}$
- $$\Omega = \frac{N!}{(n_{\rightarrow})!(n_{\leftarrow})!} = \frac{N!}{\left(\frac{N+n}{2}\right)!\left(\frac{N-n}{2}\right)!}$$



Chain Model for Polymers

- **With a little algebra**

$$S = k_B \ln \Omega = \frac{k_B}{2} \left[\left(1 - \frac{\ell}{L}\right) \ln \left(1 - \frac{\ell}{L}\right) + \frac{\ell}{L} \ln \left(\frac{\ell}{L}\right) \right]$$

- **Since, bond-bending costs no energy, $U = 0$**

- $G = U - TS - F\ell =$
 $\frac{k_B T}{2} \left[\left(1 - \frac{\ell}{L}\right) \ln \left(1 - \frac{\ell}{L}\right) + \frac{\ell}{L} \ln \left(\frac{\ell}{L}\right) \right] - F\ell$

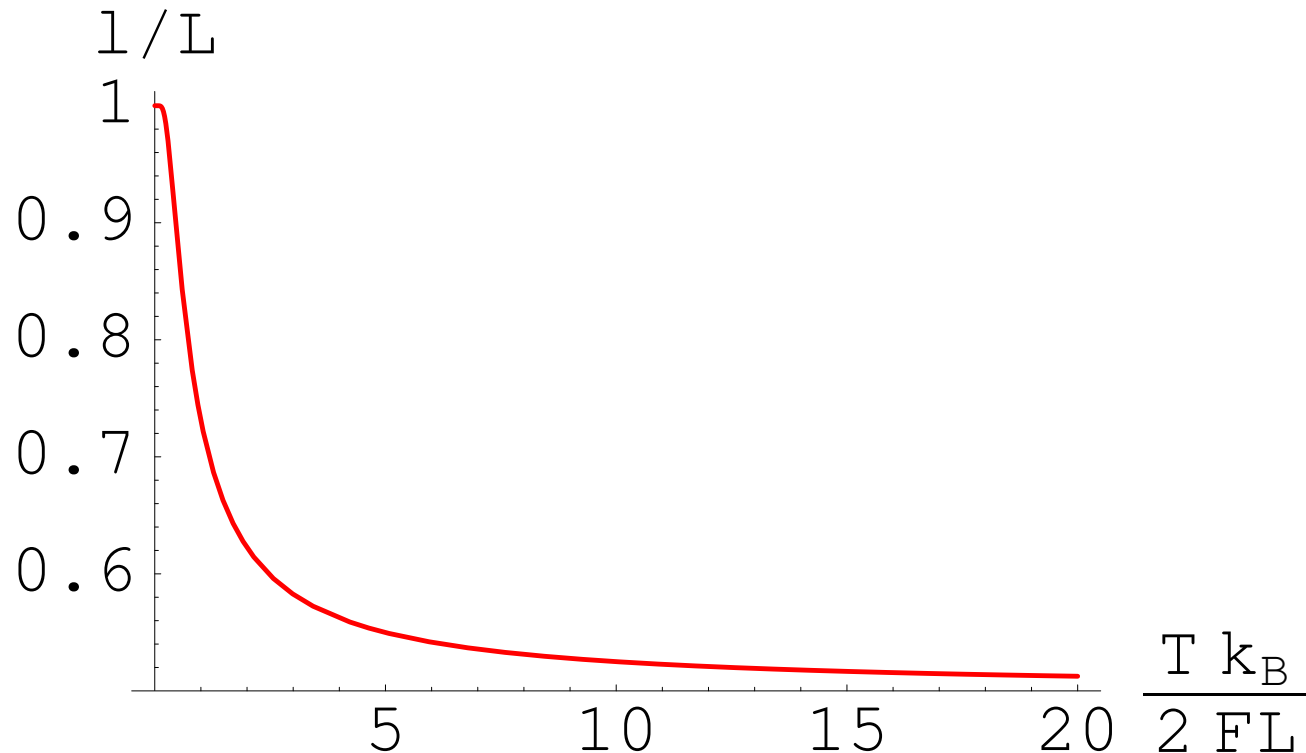
- **At a given temperature T and force F , the equilibrium value of ℓ is found to be (by $\partial G / \partial \ell = 0$ as**

$$\frac{\ell}{L} = \frac{e^{\frac{2FL}{k_B T}}}{1 + e^{\frac{2FL}{k_B T}}}$$

- **Check limits, $T \rightarrow 0$ and $T \rightarrow \infty$!**



Chain Model for Polymers



- There is amazingly good qualitative agreement!
- Note that this effect is entirely due to entropy!



Stock Taking..

- **Microcanonical Ensemble: Count states, Find Entropy, Get Any Thermodynamic Potential**
- **This is possible only in simple cases, since determination of Ω can be nontrivial**
- **Further, we always work at constant (T, V, N) or (T, P, N) and therefore look to determine A or $G...$**
- **Is there a direct way to get there rather than go through S ?**
- **Yes! The Canonical Ensemble...system kept at constant (T, V, N) ! But, first some thermodynamics...**



Helmholtz Free Energy

- A system kept at constant (T, V, N) will go to a state of minimum Helmholtz free energy $A = U - TS$
- $dA = dU - TdS - SdT = -SdT - PdV + \mu dN$
- Thus,

$$\left. \frac{\partial A}{\partial T} \right|_{V,N} = -S, \quad \left. \frac{\partial A}{\partial V} \right|_{T,N} = -P, \quad \left. \frac{\partial A}{\partial N} \right|_{T,V} = \mu$$

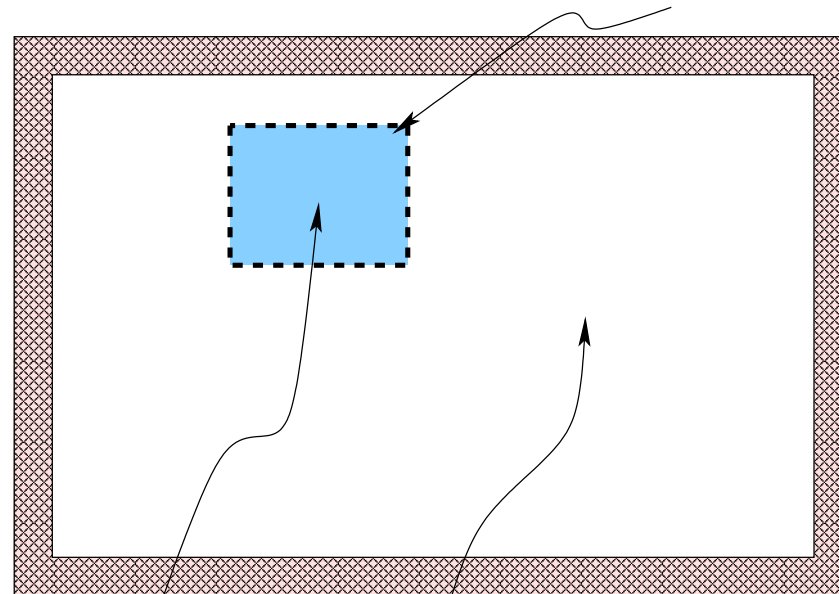
- Also,

$$C_V = -T \frac{\partial^2 A}{\partial T^2}$$

Canonical Ensemble

- Consists of a “System” + a “Reservoir” that make up the “Universe”

Energy Permeable Membrane



$$E + E_R = E_U$$

$$V + V_R = V_U$$

$$N + N_R = N_U$$

System + Reservoir = Universe
 “System $\ll$ Reservoir”

- The “Universe” is microcanonical...thus system and

reservoir are at the same temperature T



Canonical Ensemble

- What is the probability that the system has energy E ?

- EAPP...** $P(E) = \frac{\Omega(E, V, N) \Omega_R(E_U - E, V_R, N_R)}{\Omega_U(E_U, N_U, V_U)}$

- Look at Ω_R closely..** $\Omega_R = e^{\frac{S_R(E_U - E, V_R, N_R)}{k_B}}$

- $S_R(E_U - E, V_R, N_R) \approx \underbrace{S_R(E_U, V_R, N_R)}_{S_R^0} - \underbrace{\left(\frac{\partial S}{\partial E}\right)}_{1/T} E =$

$$S_R^0 - \frac{E}{T}, \text{ Thus, } \Omega_R \approx e^{\frac{S_R}{k}} e^{-\frac{E}{k_B T}}$$

- Since,** $\frac{e^{\frac{S_R}{k}}}{\Omega_U} = \text{const}, P(E) \sim \Omega(E, V, N) e^{-\beta E}, \quad \beta = \frac{1}{k_B T}$

- This is it!**



Canonical Ensemble

- The probability of a microstate with energy E of the system is proportional to $e^{-\beta E}$
- We can fix the constant of proportionality... $Z = \int_0^\infty \Omega(E, V, N) e^{-\beta E} dE = \int_{\mathcal{C}} e^{-\beta E(\mathcal{C})} d\mathcal{C}$...note that we can convert the integral over energy to integral over all configurations (all phase space in classical mechanics) and thus avoid counting of states!
- $Z = \int_{\mathcal{C}} e^{-\beta E(\mathcal{C})} d\mathcal{C}$ is called the Partition Function and has all thermodynamics information!
- $P(\mathcal{C}) = \frac{e^{-\beta E(\mathcal{C})}}{Z}$
- How does Z give thermodynamics?

Canonical Ensemble

- Energy of our system “fluctuates”, but the mean energy $\overline{E}$ is the internal energy U ...That is
$$U = \overline{E} = \frac{1}{Z} \int_{\mathcal{C}} E e^{-\beta E(\mathcal{C})} d\mathcal{C}$$
- A bit of algebra get: $U = -\frac{\partial \ln Z}{\partial \beta}$
- Note now that $\frac{\partial U}{\partial T} = -T \frac{\partial^2 F}{\partial T^2}$, a bit more algebra later :
$$A = -k_B T \ln Z$$
...THIS IS THE FORMULA OF STATMECH
- Calculate partition function Z and...you are home!
- “Canonical” advantage: Don’t have to count states...every state $\mathcal{C}$ is possible with probability
$$\sim e^{-\beta E(\mathcal{C})}$$



StatMech So Far

- **Microcanonical Logic:** Count states, Calculate entropy, Thermodynamic functions
- **Canonical (T, V, N) logic:** Any microstate in this ensemble has probability proportional to $e^{-\beta E}$... Calculate the partition function Z and $A = -k_B T \ln Z$... everything else follows
- **Canonical Ensemble Example:** Ideal Gas
- **Canonical Ensemble Example:** Harmonic Oscillator
- **Canonical Ensemble Example:** “Classical” Solid



Ideal Gas

- N non-interacting atoms occupying a region of volume V at temperature T (Recall, satisfies $PV = Nk_B T$...where does this come from?)
- Main idea...in canonical ensemble any microstate $\mathcal{C}$ is possible with probability $e^{-\beta E(\mathcal{C})}$
- Microstate is $(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N \dots$ the energy associated is $\sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m}$
- Partition function
- Simplifies to

$$Z = \frac{1}{h^{3N} N!} \int_V d\mathbf{r}_1 \dots \int_V d\mathbf{r}_N \int d\mathbf{p}_1 \dots \int d\mathbf{p}_N e^{-\beta \left(\sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} \right)}$$
$$Z = \frac{V^N}{h^{3N} N!} \left(\int_{-\infty}^{\infty} e^{-\frac{\beta \mathbf{p}^2}{2m}} d\mathbf{p} \right)^N = \frac{V^N}{h^{3N} N!} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

Ideal Gas

- **Internal energy** $U = \overline{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}Nk_B T!$
- **Now, with**
 $A = -k_B T \left(N \ln V - N \ln N + N + \frac{3N}{2} \ln \left(\frac{2\pi m}{\hbar^2 \beta} \right) \right)$, and
 $P = -\frac{\partial A}{\partial V}$, **we get** $P = \frac{Nk_B T}{V}$...**Shri. Bolye “rises” from microscopics!**
- **The mean energy is U ...but what about standard deviation? This is**
 $\Delta U^2 = \overline{(E - \overline{E})^2} = \frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{3}{2}Nk_B^2 T^2$...**thus**
 $\frac{\Delta U}{U} \sim \frac{1}{\sqrt{N}} \longrightarrow 0$ **as** $N \longrightarrow \infty!$ **Thermodynamic limit,**
and why we see very reproducible things in experiments with no affect of particular microstates etc...think of the copper puzzle...it is resolved!



A Single Classical Harmonic Oscillator

- What is internal energy and specific heat? (Note,

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2)$$

- Microstate (x, p) is possible with probability $e^{-\beta E}$

- Partition function $Z =$

$$\frac{1}{h} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp e^{-\beta \left(\frac{p^2}{2m} + \frac{m\omega^2}{2} x^2 \right)} = \frac{1}{h} \sqrt{\frac{2\pi}{m\omega^2\beta}} \sqrt{\frac{2m\pi}{\beta}} = \frac{2\pi}{\beta h\omega}$$

- $U = \overline{E} = -\frac{\partial \ln Z}{\partial \beta} = k_B T!$ **Looks familiar!**

- Specific heat $C = k_B \dots$ also familiar!



A Single Classical Harmonic Oscillator (3D)

- What is internal energy and specific heat? (Note,
$$H = \frac{\mathbf{p} \cdot \mathbf{p}}{2m} + \frac{m\omega^2}{2} \mathbf{r} \cdot \mathbf{r}$$
)
- Microstate $(\mathbf{r}, \mathbf{p})$ is possible with probability $e^{-\beta E}$
- Partition function $Z = \frac{1}{h^3} \int d\mathbf{r} d\mathbf{p} e^{-\beta \left(\frac{\mathbf{p} \cdot \mathbf{p}}{2m} + \frac{m\omega^2}{2} \mathbf{r} \cdot \mathbf{r} \right)} =$
$$\frac{1}{h^3} \left(\sqrt{\frac{2\pi}{m\omega^2\beta}} \right)^3 \left(\sqrt{\frac{2m\pi}{\beta}} \right)^3 = \left(\frac{2\pi}{\beta \hbar \omega} \right)^3$$
- $U = \overline{E} = -\frac{\partial \ln Z}{\partial \beta} = 3k_B T!$ **Looks familiar!**
- Specific heat $C = 3k_B$...also familiar!

“Classical” Solid

- The solid (N) atoms may be thought of as a collection of $3N$ oscillators (phonons) with Hamiltonian (roughly)

$$H(\mathbf{A}_1, \dots, \mathbf{A}_N, \mathbf{P}_1, \dots, \mathbf{P}_N) = \sum_k \left(\frac{\mathbf{P}_k \cdot \mathbf{P}_k}{2m} + \frac{m\omega_k^2}{2} \mathbf{A}_k \cdot \mathbf{A}_k \right),$$

where k (total of N) is the wavevector of the phonon

- Since these are independent oscillators, we have

$$Z = \prod_k \left(\frac{2\pi}{\beta \hbar \omega_k} \right)^3$$

- $U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \left(\sum_k 3 \ln \left(\frac{2\pi}{\beta \hbar \omega_k} \right) \right) = \sum_k 3k_B T = 3Nk_B T$

- $C = 3Nk_B$, but hey, thats Dulong-Petit!



Just one more thing!

- How do we get specific heat C_V ? Well, $C_V = \frac{\partial U}{\partial T}$
- $C_V = \frac{\partial U}{\partial T} = -k_B \beta^2 \frac{\partial U}{\partial \beta} = k_B \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2}$
- But, $\frac{\partial^2 \ln Z}{\partial \beta^2} = \Delta U^2$, or $C_V = \frac{1}{k_B T^2} \Delta U^2$!
- Turns out that this is a key physical result...fluctuations at equilibrium are a measure of how system “resists” change of equilibrium! Related to the more general “Fluctuation-Dissipation Theorem”



Summary

- **Canonical Logic:** Calculate partition function...obtain free energy...go home!
- We have seen how StatMech helps understand material properties...from equilibrium concentration of vacancies, to polymers, to ideal gases etc!
- Next we shall look at “Quantum Statistical Mechanics” ...essentially same ideas, but counting will be different respecting type of particles...Bosons or fermions