Statistical Mechanics - Class Exercise 2

April 5, 2022

Free energy and entropy

The partition function

$$Z(\beta, X) = \sum_r e^{-\beta E_r}$$

We can define a function

$$Z(\beta, X) = e^{-\beta F(\beta, X)}$$

so

$$F(\beta, X) = -\frac{1}{\beta} \ln Z$$

We can define the entropy

$$S = -\sum_r p_r \ln p_r = -\sum_r p_r \left(-\beta E_r - \ln Z\right) = \beta \sum_r p_r E_r + \sum_r p_r \ln Z = \beta E + \ln Z$$

$$\rightarrow F = E - TS$$

Exercise 1817 - Adiabatic cooling of spins

Consider an ideal gas whose N atoms have mass m, spin 1/2 and a magnetic moment γ. The kinetic energy of a particle is $p^2/(2m)$ and the interaction with the magnetic field B is $\pm\gamma B$ for up/down spins.

1. Calculate the entropy as $S(T, B) = S_{kinetic} + S_{spin}$.
2. Consider an adiabatic process in which the magnetic field is varied from B to zero. Show that the initial and final temperatures T_i and T_f are related by the equation:

$$\ln \frac{T_f}{T_i} = \frac{2}{3N} [S_{spin}(T_i, B) - S_{spin}(T_f, 0)]$$

3. Find the solution for $\frac{T_f}{T_i}$ in the large B limit.
4. Extend (3) to the case of space dimensionality d and general spin S.

Answer

1. The Hamiltonian is

$$H = \sum_{n=1}^{N} \frac{p_n^2}{2m} + \sum_{n=1}^{N} \gamma B \sigma_z^n$$

We can define a thermal wavelength

$$\lambda_T = \sqrt{\frac{2\pi}{mT}}$$

$$\begin{aligned}
Z =& \sum_r e^{-\beta E_r} = \sum_r e^{-\beta \sum_{n=1}^{N} \frac{p_n^2}{2m}} e^{-\beta \sum_{n=1}^{N} \gamma B \sigma_z^n} \\
=& \left(\prod_{n=1}^{N} \int \int \frac{d\vec{x}_n d\vec{p}_n}{2\pi} e^{-\beta \frac{p_n^2}{2m}} \right) \left(\prod_{n=1}^{N} \left(e^{\beta\gamma B} + e^{-\beta\gamma B} \right) \right) = \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N 2^N \cosh^N (\beta\gamma B) \\
=& Z_{kinetic} Z_{spin}
\end{aligned}$$

We use Stirling's approximation

$$\ln N! \approx N \ln N - N$$

$$F = -\frac{1}{\beta} \ln Z = -NT \ln \left(\frac{V}{N\lambda_T^3} \right) - NT - NT \ln \left(2\cosh \left(\frac{\gamma B}{T} \right) \right) = F_{kinetic} + F_{spin}$$

$$S = -\frac{\partial F}{\partial T} = N \ln \left(\frac{V}{N\lambda_T^3} \right) + \frac{5}{2} N + N \ln 2\cosh \left(\frac{\gamma B}{T} \right) - \frac{N\gamma B}{T} \tanh \left(\frac{\gamma B}{T} \right)$$

$$S_{kinetic} = \frac{5}{2} N + N \ln \left(\frac{V}{N\lambda_T^3} \right)$$

$$S_{spin} = N \ln \left(2\cosh \left(\frac{\gamma B}{T} \right) \right) - \frac{N\gamma B}{T} \tanh \left(\frac{\gamma B}{T} \right)$$

2. For adiabatic process the entropy stay constant

$$S(T_i, B) = S_{kinetic}(T_i) + S_{spin}(T_i, B) = S_{kinetic}(T_f) + S_{spin}(T_f, 0) = S(T_f, 0)$$

$$S_{kinetic}(T_f) - S_{kinetic}(T_i) = \frac{5}{2} N + N \ln \left(\frac{V T_f^{\frac{3}{2}}}{N \left(\frac{2\pi}{m} \right)^{\frac{3}{2}}} \right) - \frac{5}{2} N - N \ln \left(\frac{V T_i^{\frac{3}{2}}}{N \left(\frac{2\pi}{m} \right)^{\frac{3}{2}}} \right) = \frac{3}{2} N \ln \frac{T_f}{T_i}$$

$$\to \ln \frac{T_f}{T_i} = \frac{2}{3N} [S_{spin}(T_i, B) - S_{spin}(T_f, 0)]$$

3. In the large B limit:

$$\lim_{B\to\infty} S_{spin}(T_i, B) = \lim_{B\to\infty} N \ln \left(e^{\frac{\gamma B}{T_i}} + e^{-\frac{\gamma B}{T_i}} \right) - \frac{N\gamma B}{T_i} \tanh \left(\frac{\gamma B}{T_i} \right) = \frac{N\gamma B}{T_i} - \frac{N\gamma B}{T_i} = 0$$

in the other hand

$$\lim_{B\to 0} S_{spin}(T, B) = \lim_{B\to 0} N \ln \left(2\cosh \left(\frac{\gamma B}{T} \right) \right) - \frac{N\gamma B}{T} \tanh \left(\frac{\gamma B}{T} \right) = N \ln 2$$

$$\rightarrow \ln\frac{T_f}{T_i} = \frac{2}{3N}\left[S_{spin}(T_i,B) - S_{spin}(T_f,0)\right] = -\frac{2}{3}\ln 2$$

$$\frac{T_f}{T_i} = 2^{-\frac{2}{3}}$$

4. For the case of space dimensionality d and general spin S:

$$Z_{kinetic} = \frac{1}{N!}\left(\frac{L}{\lambda_T}\right)^{dN}$$

$$\rightarrow S_{kinetic}(T_f) - S_{kinetic}(T_i) = \frac{d}{2}N\ln\frac{T_f}{T_i}$$

$$Z_{spin} = \left(e^{\beta\gamma BS} + e^{\beta\gamma B(S-1)}\cdots + e^{-\beta\gamma B(S-1)} + e^{-\beta\gamma BS}\right)^N$$

$$\rightarrow S_{spin} = \ln Z_{spin} + T\frac{\partial}{\partial T}\ln Z_{spin}$$

$$S_{spin} = N\ln\left(e^{\beta\gamma BS} + e^{\beta\gamma B(S-1)}\cdots + e^{-\beta\gamma BS}\right) - \frac{N\gamma B}{T}\frac{\left(Se^{\beta\gamma BS} + (S-1)e^{\beta\gamma B(S-1)}\cdots - Se^{-\beta\gamma BS}\right)}{\left(e^{\beta\gamma BS} + e^{\beta\gamma B(S-1)}\cdots + e^{-\beta\gamma BS}\right)}$$

$$\lim_{B\to\infty} S_{spin}(T_i,B) = \lim_{B\to\infty} N\ln\left[e^{\beta\gamma BS}\left(1 + e^{-\beta\gamma B}\cdots + e^{-2\beta\gamma BS}\right)\right] - \frac{N\gamma B}{T}\frac{\left(S + (S-1)e^{-\beta\gamma B}\cdots - Se^{-2\beta\gamma BS}\right)}{\left(1 + e^{-\beta\gamma B}\cdots + e^{-2\beta\gamma BS}\right)}$$

$$= \frac{N\gamma BS}{T} - \frac{N\gamma BS}{T} = 0$$

$$\lim_{B\to 0} S_{spin}(T,B) = N\ln(2S+1)$$

$$\rightarrow \frac{T_f}{T_i} = (2S+1)^{-\frac{2}{d}}$$

Exercise 2311 - Imperfect lattice with defects

A perfect lattice is composed of N atoms on N sites. If n of these atoms are shifted to interstitial sites (i.e. between regular positions) we have an imperfect lattice with n defects. The number of available interstitial sites is M and is of order N. Every atom can be shifted from lattice to any defect site. The energy needed to create a defect is ω. The temperature is T. Define $x \equiv e^{-\omega/T}$.

1. Write the expression for the partition function $Z(x)$ as a sum over n.
2. Using Stirling approximation (see note) determine what is the most probable n, and write for it the simplest approximation assuming $x \ll 1$.
3. Explain why your result for $\bar{n}$ merely reproduces the law of mass action.

4. Evaluate $Z(x)$ using a Gaussian integral.

5. Derive the expressions for the entropy and for the specific heat.

6. What would be the result if instead of Gaussian integration one were taking only the largest term in the sum?

Note: Regarding n as a continuous variable the derivative of $\ln(n!)$ is approximately $\ln(n)$.

Answer

1. If n is the number of the atoms that shifted the energy is $E = n\omega$, for the degeneracy we known that from N site and M interstitial sites we have $N - n$ occupied sites and n unoccupied sites and n occupied interstitial sites and $M - n$ unoccupied interstitial sites:

$$Z(x) = \sum_{n=0}^{N} \frac{M!}{n!\,(M-n)!} \frac{N!}{n!\,(N-n)!} x^n = \sum_{n=0}^{N} Z_n(x)$$

   where $Z_n(x)$ is the partition function for n shifted atoms

2. The probability of n shifted atoms is $p_n = \frac{Z_n(x)}{Z(x)} = \frac{e^{-\beta F_n(x)}}{Z(x)}$, so if we want to find the most probable n we need to derivative $F_n(x)$ for n and found the minima of $F_n(x)$

$$F_n(x) = -\frac{1}{\beta} \ln Z_n(x) = -\frac{1}{\beta} \left(\ln M! + \ln N! - 2\ln n! - \ln (N-n)! - \ln (M-n)! + \ln x^n\right)$$

   from the Stirling approximation we get

$$F_n(x) \approx -\frac{1}{\beta} \left(M \ln M + N \ln N - 2n \ln n - (N-n)\ln(N-n) - (M-n)\ln(M-n) + n \ln x\right)$$

$$\frac{\partial}{\partial n} F_n(x) = -\frac{1}{\beta} \left(-2\ln n + \ln(N-n) + \ln(M-n) + \ln x\right) = 0$$

$$\frac{n^2}{(N-n)(M-n)} = x$$

   in the limit $x \ll 1$ and when N, M are the same order we get that $n \ll N, M$ so we can neglect n in the denominator and get

$$\bar{n} = \sqrt{NMx} = \sqrt{NM} e^{-\frac{\omega}{2T}}$$

3. We can look on the system like four type of particles, full site, empty site, full shifted site and empty shifted site. In this view our result is exactly the law of mass action

4. In our case the most probable state is for $n = \bar{n}$, where $F_n'(x)|_{n=\bar{n}} = 0$, so we can develop $F_n(x)$ around $\bar{n}$

$$F_n(x) = F_n(\bar{n}) + \frac{F_n''(\bar{n})}{2} (n - \bar{n})^2$$

$$Z(x) = \sum_{n=0}^{N} e^{-\beta F_n(x)}$$

$$\sum_{n=0}^{N} \to \int_0^\infty = \frac{1}{2}\int_{-\infty}^\infty$$

$$Z(x) \approx \frac{1}{2}e^{-\beta F_n(\bar{n})}\int_{-\infty}^\infty e^{-\frac{\beta F_n''(\bar{n})}{2}(n-\bar{n})^2} = \sqrt{\frac{\pi}{2\beta F_n''(\bar{n})}}e^{-\beta F_n(\bar{n})}$$

$$\begin{aligned} e^{-\beta F_n(\bar{n})} &= e^{\left(M\ln M + N\ln N - 2\bar{n}\ln\bar{n} - (N-\bar{n})\ln(N-\bar{n}) - (M-\bar{n})\ln(M-\bar{n}) + \bar{n}\ln\left(\frac{\bar{n}^2}{NM}\right)\right)} \\ &= e^{-\left((N-\bar{n})\ln\left(1-\frac{\bar{n}}{N}\right) + (M-\bar{n})\ln\left(1-\frac{\bar{n}}{M}\right)\right)} \approx e^{2\bar{n}} \end{aligned}$$

$$F_n''(x) = \frac{1}{\beta}\left(\frac{2}{n} + \frac{1}{(N-n)} + \frac{1}{(M-n)}\right) \approx \frac{2}{\beta n}$$

$$Z(x) = \sqrt{\frac{\pi\bar{n}}{4}}e^{2\bar{n}} = \sqrt{\frac{\pi\sqrt{MN}}{4}}e^{2\bar{n}}e^{-\frac{\omega}{4T}}$$

5. For the entropy

$$S = -\frac{\partial F}{\partial T} = \frac{\partial}{\partial T}(T\ln Z) = \frac{\partial}{\partial T}T\left(\frac{1}{2}\ln\frac{\pi}{4} + \frac{1}{2}\ln\bar{n} + 2\bar{n}\right) = \left(\frac{1}{2}\ln\frac{\pi}{4} + \frac{1}{2}\ln\bar{n} + \frac{T}{2\bar{n}}\frac{\partial\bar{n}}{\partial T} + 2\bar{n} + T2\frac{\partial\bar{n}}{\partial T}\right) =$$

$$= \left(\frac{1}{2}\ln\frac{\pi}{4} + \frac{1}{2}\ln\sqrt{NM} - \frac{\omega}{4T} + \frac{\omega}{4T} + 2\bar{n} + \frac{\omega\bar{n}}{T}\right) = \frac{1}{2}\ln\left(\frac{\pi\sqrt{MN}}{4}\right) + \left(2 + \frac{\omega}{T}\right)\bar{n}$$

When we use

$$\frac{\partial\bar{n}}{\partial T} = \frac{\omega}{2T^2}\sqrt{NM}e^{-\frac{\omega}{2T}} = \frac{\omega\bar{n}}{2T^2}$$

and for the specific heat.

$$C = T\frac{\partial S}{\partial T} = T\left[-\frac{\omega}{T^2}\bar{n} + \left(2 + \frac{\omega}{T}\right)\frac{\omega}{2T^2}\bar{n}\right] = \frac{\bar{n}}{2}\left(\frac{\omega}{T}\right)^2$$

6. If instead of Gaussian integration one were taking only the largest term in the sum

$$Z(x) \approx e^{-\beta F_n(\bar{n})}$$

we will get the same equation without a prefactor, so

$$S = \left(2 + \frac{\omega}{T}\right)\bar{n}$$

$$C = \frac{\bar{n}}{2}\left(\frac{\omega}{T}\right)^2$$

Gibbs Hamiltonian

For the Hamiltonian

$$H(\cdots, x)$$

where x is parameter of the system, we can apply force f and change x to be a dynamical variable ,the new Hamiltonian

$$H_G(\cdots, f) = H(\cdots, x) + fx$$

The partition function of H_G is a Laplace transform of the partition function of H

$$Z_G(\beta, f) = \sum_{r,x} e^{-\beta(E_{r,x}+fx)} = \sum_x \sum_r e^{-\beta E_{r,x}} e^{-\beta f x} = \sum_x Z(\beta, x) e^{-\beta f x}$$

Exercise 2351 - Tension of a rubber band

The elasticity of a rubber band can be described by a one dimensional model of a polymer. The polymer consists of N monomers that are arranged along a straight line, hence forming a chain. Each unit can be either in a state of length a with energy E_a, or in a state of length b with energy E_b. We define f as the tension, i.e. the force that is applied while holding the polymer in equilibrium.

1. Write expressions for the partition function $Z_G(\beta, f)$.
2. For very high temperatures $F_G(T, f) \approx F_G^{(\infty)}(T, f)$, where $F_G^{(\infty)}(T, f)$ is a linear function of T. Write the explicit expression for $F_G^{(\infty)}(T, f)$.
3. Write the expression for $F_G(T, f) - F_G^{(\infty)}(T, f)$. Hint: this expression is quite simple - within this expression f should appear only once in a linear combination with other parameters.
4. Derive an expression for the length L of the polymer at thermal equilibrium, given the tension f. Write two separate expressions: one for the infinite temperature result $L(\infty, f)$ and one for the difference $L(T, f) - L(\infty, f)$.
5. Assuming $E_a = E_b$, write a linear approximation for the function $L(T, f)$ in the limit of weak tension.
6. Treating L as a continuous variable, find the probability distribution $P(L)$, assuming $E_a = E_b$ and $f = 0$.
7. Write an expression that relates the function $f(L)$ to the probability distribution $P(L)$. Write also the result that you get from this expression.
8. Find what would be the results for $Z_G(\beta, f)$ if the monomer could have any length $\in [a, b]$. Assume that the energy of the monomer is independent of its length.
9. Find what would be the results for $L(T, f)$ in the latter case.

Note: Above a "linear function" means $y = Ax + B$.
Please express all results using $(N, a, b, E_a, E_b, f, T, L)$.

Answer

1. For the partition function $Z_G(\beta, f)$.

$$H = nE_a + (N-n)\,E_b$$

$$H_G = nE_a + (N-n)\,E_b + f\,(na + (N-n)\,b)$$

$$\begin{aligned} Z_G\,(\beta, f) &= \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!} e^{-\beta[nE_a + (N-n)E_b + f(na + (N-n)b)]} \\ &= \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!} e^{-\beta n(E_a + fa)} e^{-\beta(N-n)(E_b + fb)} \end{aligned}$$

from the binomial theorem $(a+b)^N = \sum_{n=0}^{N} \frac{N!}{(N-n)!n!} a^n b^{N-n}$ we get

$$Z_G\,(\beta, f) = \left(e^{-\beta(E_a + fa)} + e^{-\beta(E_b + fb)}\right)^N$$

Another way

$$H^1 = E_x + fx$$

$$Z^1 = \sum_{x=a,b} e^{-\beta(E_x + fx)} = e^{-\beta(E_a + fa)} + e^{-\beta(E_b + fb)}$$

$$Z_G = \left(Z^1\right)^N = \left(e^{-\beta(E_a + fa)} + e^{-\beta(E_b + fb)}\right)^N$$

2. We define

$$\begin{aligned} \frac{F_G(T, f)}{N} &= -\frac{T}{N} \ln\left(Z_G\right) = -T \ln\left(e^{-\frac{1}{T}(E_a + fa)} + e^{-\frac{1}{T}(E_b + fb)}\right) \\ &= -T \ln\left(e^{-\frac{1}{2T}(E_a + E_b + fa + fb)}\left(e^{\frac{1}{2T}(E_b - E_a - fa + fb)} + e^{-\frac{1}{2T}(E_b - E_a - fa + fb)}\right)\right) \\ &= \frac{E_a + E_b}{2} + \frac{b+a}{2} f - T \ln\left(2\cosh\left(\frac{1}{T}\left(\frac{E_a - E_b}{2} + f\frac{a-b}{2}\right)\right)\right) \end{aligned}$$

For $T \to \infty$

$$\frac{F_G(\infty, f)}{N} \approx \frac{E_a + E_b}{2} + \frac{b+a}{2} f - T \ln(2)$$

3. We get

$$\begin{aligned} \frac{F_G(T, f) - F_G^{(\infty)}(T, f)}{N} &= \left(\frac{E_a + E_b}{2} + f\frac{b+a}{2}\right) - T \ln\left(2\cosh\left(\frac{1}{T}\left(\frac{E_a - E_b}{2} + f\frac{a-b}{2}\right)\right)\right) + T\ln(2) - \left(\frac{E_a + E_b}{2} + f\frac{b+a}{2}\right) \\ &= -T \ln\left(\cosh\left(\frac{1}{T}\left(\frac{E_a - E_b}{2} + f\frac{a-b}{2}\right)\right)\right) \end{aligned}$$

4. For the infinite temperature result $L(\infty, f)$

$$\frac{L(\infty, f)}{N} = \frac{1}{N}\frac{\partial F_G(\infty, f)}{\partial f} = \frac{b+a}{2}$$

$$\frac{L(T,f)-L(\infty,f)}{N}=\frac{\partial}{\partial f}\left(\frac{F_G(T,f)-F_G^{(\infty)}(T,f)}{N}\right)=-\frac{a-b}{2}\tanh\left(\frac{1}{T}\left(\frac{E_a-E_b}{2}+f\frac{a-b}{2}\right)\right)$$

5. For $E_a=E_b$

$$\frac{L(T,f)-L(\infty,f)}{N}=-\frac{a-b}{2}\tanh\left(\frac{f}{T}\frac{a-b}{2}\right)$$

For $f\to 0$

$$\frac{L(T,f)-L(\infty,f)}{N}\approx-\frac{(a-b)^2}{4T}f$$

We get Hook's law

$$f=-\frac{4T}{N(a-b)^2}\left(L-\langle L\rangle\right)$$

6. For $E_a=E_b$ the probability for configuration of a single monomer is $\frac{1}{2}$

$$\langle L\rangle=\sum_i\langle x_i\rangle=N\langle x_i\rangle=N\left(\frac{a+b}{2}\right)$$

$$\sigma^2=\left\langle L^2\right\rangle-\langle L\rangle^2=N\left[\left(\frac{a^2+b^2}{2}\right)-\left(\frac{a+b}{2}\right)^2\right]=N\left(\frac{a-b}{2}\right)^2$$

For a long monomer ($N\gg 1$) we can now use the central limit theorem, (Gaussian disterbution)

$$P(L)=\frac{1}{\sqrt{2\pi\sigma}}e^{-\frac{1}{2}\left(\frac{L-\langle L\rangle}{\sigma}\right)^2}$$

7. We can define $L=na+(N-n)b\to\frac{L-Nb}{a-b}=n$

$$\begin{aligned}Z_G(\beta,f)&=\sum_{n=0}^{N}\frac{N!}{n!(N-n)!}e^{-\beta[nE_a+(N-n)E_b+f(na+(N-n)b)]}\\&=\sum_L\frac{N!}{\left(\frac{L-Nb}{a-b}\right)!\left(\frac{L-Na}{b-a}\right)!}e^{-\beta\left[\frac{L(E_a-E_b)-N(bE_a-aE_b)}{a-b}+fL\right]}=\sum_L Z(L)\end{aligned}$$

By definition

$$P(L)=\frac{Z(L)}{Z}$$

And by definition

$$f(L)=\frac{\partial F}{\partial L}=\frac{1}{\beta}\frac{\partial\ln(Z(L))}{\partial L}=\frac{1}{\beta}\frac{\partial\ln(P(L))}{\partial L}=-T\left(\frac{L-\langle L\rangle}{\sigma^2}\right)=-\frac{4T}{N(a-b)^2}\left(L-\langle L\rangle\right)$$

8. For $E_x=E$ and $x\in[a,b]$

$$H^1=E+fx$$

$$Z^1=\int_a^b dxe^{-\beta(E+fx)}=e^{-\beta E}\int_a^b dxe^{-\beta fx}=\frac{1}{\beta f}\left(e^{-\beta(E+fa)}-e^{-\beta(E+fb)}\right)$$

$$Z_G = \left(Z^1\right)^N = \left[\frac{1}{\beta f}\left(e^{-\beta(E+fa)} - e^{-\beta(E+fb)}\right)\right]^N$$

We can take $E = 0$

$$Z_G = \left(Z^1\right)^N = \left[\frac{1}{\beta f}\left(e^{-\beta fa} - e^{-\beta fb}\right)\right]^N$$

9.

$$\begin{aligned}\frac{F_G(T,f)}{N} &= -\frac{T}{N}\ln\left(Z_G\right) = T\ln\left(\frac{f}{T}\right) - T\ln\left(e^{-\beta f\left(\frac{a+b}{2}\right)} 2\sinh\left(\beta f\left(\frac{a-b}{2}\right)\right)\right) \\ &= T\ln\left(\frac{f}{T}\right) + f\left(\frac{a+b}{2}\right) - T\ln\left(2\sinh\left(\frac{f}{T}\left(\frac{a-b}{2}\right)\right)\right)\end{aligned}$$

$$L = \frac{\partial F_G}{\partial f}$$

$$\frac{L(T,f)}{N} = \frac{T}{f} + \left(\frac{a+b}{2}\right) - \left(\frac{a-b}{2}\right)\coth\left(\frac{f}{T}\left(\frac{a-b}{2}\right)\right)$$

Thw expention of $\coth(x) \approx \frac{1}{x} + \frac{x}{3}$, so for $f \to 0$

$$\to \frac{L(T,f) - L(\infty,f)}{N} = \frac{T}{f} + \left(\frac{a+b}{2}\right) - \left[\frac{T}{f} + \frac{\frac{f}{T}\left(\frac{a-b}{2}\right)^2}{3}\right] - \left(\frac{a+b}{2}\right) = -\frac{(a-b)^2}{12T} f$$

$$f = -\frac{12T}{N\left(a-b\right)^2}\left(L - \langle L\rangle\right)$$