# Statistical Mechanics - Class Exercise 2.5

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## Gibbs Hamiltonian

For the Hamiltonian

$$H\left(\cdots,x\right)$$

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

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

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

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

## 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

$$H_G^1 = E_x + fx$$

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

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

2. We define

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

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

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

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 $L = na + (N-n)b \to \frac{L-Nb}{a-b} = n$

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

By definition

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

And by definition

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

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.

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

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

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

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

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

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

## The basic integrals for ideal gas

$$N = \sum_r f(\epsilon_r - \mu) = \int_0^\infty g(\epsilon) f(\epsilon - \mu) d\epsilon$$

$$E = \sum_r \epsilon_r f(\epsilon_r - \mu) = \int_0^\infty g(\epsilon)\epsilon f(\epsilon - \mu) d\epsilon$$

$$\boldsymbol{Z}=\prod_{r}\mathcal{Z}^{(r)},\quad \mathcal{Z}^{(r)}=\sum_{n}e^{-\beta(\epsilon_{r}-\mu)n_{r}}=\left(1\pm e^{-\beta(\epsilon_{r}-\mu)}\right)^{\pm1}$$

$$\ln\left(\boldsymbol{Z}\right)=\pm\sum_{r}\ln\left(1\pm e^{-\beta(\epsilon_{r}-\mu)}\right)=\{\text{Integration by parts}\}=\beta\int_{0}^{\infty}\mathcal{N}\left(\epsilon\right)f\left(\epsilon-\mu\right)d\epsilon$$

$$P=\frac{1}{\beta}\frac{\partial\ln\left(\boldsymbol{Z}\right)}{\partial V}=\frac{1}{\beta}\frac{\ln\left(\boldsymbol{Z}\right)}{V}=\frac{1}{V}\int_{0}^{\infty}\mathcal{N}\left(\epsilon\right)f\left(\epsilon-\mu\right)d\epsilon$$

## Exercise 3745 - Fermions in a uniform gravitational field

Consider fermions of mass $M$ and spin 1/2 in a gravitational field with constant acceleration $g$ and at uniform temperature $T$. The density of the Fermions at zero height is $n(0)=n_0$. In item (3) assume that at zero height the fermions form a degenerate gas with Fermi energy $\epsilon_F^0$ that is much larger compared with $T$.

1. Assume that the fermions behave as classical particles and find their density $n(h)$ as function of the height.
2. Assume $T=0$. Find the local Fermi momentum $p_F(h)$ and the density $n(h)$ as function of the height.
3. Assume low temperatures. Estimate the height $h_c$ such that for $h\gg h_c$ the fermions are non-degenerate.
4. In the latter case find $n(h)$ for $h\gg h_c$, given as before $n_0$ at zero height.

## Answer

1. We look on a layer of gas in the high $z\in[h,h+\delta h]$ in a virtual box with size $L\times L\times\delta h$.
The partition function for one classical particles

$$\mathcal{Z}_{1}\left(\beta,h\right)=\underbrace{2}_{spin}\int_{0}^{L}\int_{0}^{L}\int_{h}^{h+\delta h}e^{-\beta\left(\frac{p^{2}}{2m}+mgz\right)}\frac{dxdydzd^{3}p}{\left(2\pi\right)^{3}}=\frac{2L^{2}}{\beta mg\lambda_{T}^{3}}\left(e^{-\beta mgh}-e^{-\beta mg(h+\delta h)}\right)$$

$$=\frac{2L^{2}}{\beta mg\lambda_{T}^{3}}e^{-\beta mgh}\left(1-e^{-\beta mg\delta h}\right)\approx\frac{2L^{2}\delta h}{\lambda_{T}^{3}}e^{-\beta mgh}$$

The partition function with $L^2\delta h=V$:

$$\mathcal{Z}_{N}\left(\beta,h\right)=\frac{1}{N\left(h\right)!}\left(\frac{2V}{\lambda_{T}^{3}}e^{-\beta mgh}\right)^{N(h)}$$

The Free energy:

$$F\left(\beta,h\right)=-T\ln\mathcal{Z}_{N}=T\ln\left(N\left(h\right)!\right)-TN\left(h\right)\ln\left(\frac{2V}{\lambda_{T}^{3}}\right)+N\left(h\right)mgh$$

with Stirling's approximation

$$F\left(\beta,h\right)\approx-TN\left(h\right)-TN\left(h\right)\ln\left(\frac{2V}{N\left(h\right)\lambda_{T}^{3}}\right)+N\left(h\right)mgh$$

The chemical potential:

$$\mu\left(\beta,h\right)=\frac{\partial F\left(\beta,h\right)}{\partial N\left(h\right)}=-T\ln\left(\frac{2V}{N\left(h\right)\lambda_{T}^{3}}\right)+mgh=-T\ln\left(\frac{2}{n\left(h\right)\lambda_{T}^{3}}\right)+mgh$$

at zero height

$$\mu(0) = -T\ln\left(\frac{2}{n(0)\lambda_T^3}\right)$$

From chemical equilibrium $\mu(h) = \mu(0)$

$$-T\ln\left(\frac{2}{n(h)\lambda_T^3}\right) + mgh = -T\ln\left(\frac{2}{n_0\lambda_T^3}\right)$$

$$\beta mgh = \ln\left(\frac{n_0}{n(h)}\right)$$

$$n(h) = n_0 e^{-\beta mgh}$$

2. At $T = 0$ we have a degenerate gas when all the energy state up to $\epsilon_F$ are occupied. For fermions of mass $m$ and spin 1/2 the number of the states is

$$\mathcal{N}(\epsilon) = 2\int_{p=\sqrt{2m\epsilon}} \frac{d^3x d^3p}{(2\pi)^3} = \frac{2V}{(2\pi)^3}\frac{4\pi p^3}{3} = \frac{4V(2m\epsilon)^{\frac{3}{2}}}{3(2\pi)^2}$$

and the density of states is

$$g(\epsilon) = \frac{\partial\mathcal{N}(\epsilon)}{\partial\epsilon} = 2\frac{V(2m)^{\frac{3}{2}}}{(2\pi)^2}\epsilon^{\frac{1}{2}}$$

The number of the occupied states:

$$N(\beta, h, \mu) = \int_0^\infty g(\epsilon_p) f(\epsilon_p + mgh - \mu)\, d\epsilon_p$$

In $T = 0$ the occupation function is a step function with $\mu'(h) = \epsilon_F - mgh$ , so we get

$$n(h) = \frac{(2m)^{\frac{3}{2}}}{3\pi^2}(\epsilon_F - mgh)^{\frac{3}{2}}$$

At zero hight

$$n(0) = n_0 = \frac{(2m)^{\frac{3}{2}}}{3\pi^2}(\epsilon_F)^{\frac{3}{2}}$$

$$\epsilon_F = \frac{\left(3\pi^2 n_0\right)^{\frac{2}{3}}}{2m}$$

$$\to n(h) = \frac{(2m)^{\frac{3}{2}}}{3\pi^2}\left(\frac{\left(3\pi^2 n_0\right)^{\frac{2}{3}}}{2m} - mgh\right)^{\frac{3}{2}}$$

For the Fermi momentum

$$\epsilon_F = \frac{p_F^2(h)}{2m} + mgh$$

$$\to p_F(h) = \sqrt{2m\epsilon_F - 2m^2gh} = \sqrt{\left(3\pi^2 n_0\right)^{\frac{2}{3}} - 2m^2gh}$$

3. We assume that at zero height the fermions form a degenerate gas with Fermi energy $\epsilon_F^0$, for $h > 0$ the energy form the momentum is

$$\epsilon_p = \epsilon_F^0 - mgh$$

The limit for non-degenerate fermions is $\epsilon_p \left(h_c\right) = T$

$$\epsilon_F^0 - mgh_c = T$$

$$\rightarrow h_c = \frac{\epsilon_F^0 - T}{mg} \approx \frac{\epsilon_F^0}{mg}$$

4. For $h \gg h_c$ the gas behave as classical gas, we have the same chemical equilibrium $\mu\left(h\right) = \mu\left(0\right)$, but now $\mu\left(0\right) = \epsilon_F^0 \approx mgh_c$

$$-T \ln\left(\frac{2}{n\left(h\right)\lambda_T^3}\right) + mgh = mgh_c$$

$$n\left(h\right) = \frac{2}{\lambda_T^3} e^{-\beta mg\left(h - h_c\right)}$$

For $h = 0$

$$n\left(0\right) = \frac{2}{\lambda_T^3} e^{\beta mgh_c}$$

$$\rightarrow n\left(h\right) = n_0 e^{-\beta mgh}$$