Homework 3: Phys 7230 (Spring 2022)

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Problem 1 (Derivation of ensembles):
(a) Grand canonical ensemble
Start with the expression

$$W\left[\{n_q\}\right] = \frac{\mathcal{N}!}{\prod_q n_q!} \tag{1.1}$$

for the number of configurations in a grandcanonical ensemble consisting of $\mathcal{N}$ systems with a set $\{n_q\}$ describing the number of systems with energy E_q and number of particles N_q, discussed in lectures. Utilizing lowest order Stirling approximation, maximize $W\left[\{n_q\}\right]$ over n_q, subject to three constraints,

$$\sum_q n_q = \mathcal{N}, \qquad \sum_q n_q E_q = E\mathcal{N}, \qquad \sum_q n_q N_q = N\mathcal{N}, \tag{1.2}$$

imposed via Lagrange multiplier γ, β, α, with E and N the average energy and particle number in the ensemble, derive the most likely n_q^* and thereby obtain the grandcanonical probability distribution $P_q = n_q^*/\mathcal{N}$.

Hint: Maximizing $\ln W$ may be more convenient.

Solution.
First, using Stirling approximation, we write

$$\ln W = \mathcal{N} \ln \mathcal{N} - \mathcal{N} - \sum_q \left(n_q \ln n_q - n_q\right) = \mathcal{N} \ln \mathcal{N} - \sum_q n_q \ln n_q. \tag{1.3}$$

Extremizing this function, we calculate

$$\boldsymbol{\nabla}(\ln W) - \gamma \boldsymbol{\nabla}\left(\sum_q n_q - \mathcal{N}\right) - \beta \boldsymbol{\nabla}\left(\sum_q n_q E_q - E\mathcal{N}\right) - \alpha \boldsymbol{\nabla}\left(\sum_q n_q N_q - N\mathcal{N}\right)$$

$$= \left[\ln \mathcal{N} - 1 - \ln n_q + 1 + \beta(E - E_q) + \alpha(N - N_q)\right]\hat{e}_q = 0. \tag{1.4}$$

where $\boldsymbol{\nabla} = (\partial/\partial n_q)\hat{e}_q$ (Einstein summation used implicitly). Inverting each expression, we get

$$\frac{n_q}{\mathcal{N}} = e^{\beta(E-E_q)+\alpha(N-N_q)}. \tag{1.5}$$

By the normalization condition,

$$1 = \sum_q \frac{n_q}{\mathcal{N}} = e^{\beta E + \alpha N} \sum_q e^{-\beta E_q - \alpha N_q} = e^{\beta E + \alpha N} \mathcal{Z}. \tag{1.6}$$

where $\beta = 1/k_B T$ and $\alpha = -\mu\beta$. Then, letting $n_q = n_q^*$, the most probable state satisfying (1.5), we can write the probability distribution as

$$P_q = \frac{n_q^*}{\mathcal{N}} = \frac{e^{-\beta E_q - \alpha N_q}}{\mathcal{Z}}. \tag{1.7}$$

$\square$

(b) Derivation redux

Let us rederive all three ensembles distributions in a more streamlined way by focusing on P_q and noting that P_q can be determined by maximizing the (Shannon's) entropy $S = -k_B \sum_q P_q \ln P_q$ subject to the appropriate number of constraints for each ensemble. Thus, derive

(i) Microcanonical ensemble subject to its one constraint, showing that it is just given by a normalized *constant* $P_q = 1/\Omega$.

(ii) Canonical ensemble subject to its two constraints, showing that it is given by the Gibbs form.

(iii) Grandcanonical ensemble subject to its three constraints, showing that it is given by the Gibbs form.

Solution.

(i) The constraint for the microcanonical ensemble is the normalization condition

$$\sum_q P_q = 1. \tag{1.8}$$

Then, we differentiate to find P_q that extremizes S

$$\boldsymbol{\nabla}(S) - \lambda \boldsymbol{\nabla} \left(\sum_q P_q - 1 \right) = \left[-k_B \left(\ln P_q + 1 \right) - \lambda_1 \right] \hat{e}_q \Rightarrow P_q = e^{-1 - \lambda/k_B}. \tag{1.9}$$

Plugging this back into the normalization condition, we get

$$\sum_q P_q = e^{-1 - \lambda_1/k_B} \sum_q 1 = e^{-1 - \lambda_1/k_B} \Omega, \tag{1.10}$$

where $\Omega = \sum_{\{q_i\}} 1$ is the multiplicity of the system. Then we can rewrite the probability distribution function

$$P_q = \frac{1}{\Omega}, \tag{1.11}$$

which is a constant, indicating a uniform distribution. Also, we can invert to solve for λ_1

$$\lambda_1 = S_t - k_B, \tag{1.12}$$

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where $S_t = k_B \ln \Omega$ is the thermodynamic entropy.

    (ii) In addition to the normalization condition (1.8), we add a constraint

$$\sum_q E_q P_q = E, \tag{1.13}$$

where E is the average energy of the system. Then, the P_q that extremizes S satisfies

$$\left[-k_B\left(\ln P_q + 1\right) - \lambda_1 - \lambda_2 E_q\right]\hat{e}_q = 0 \Rightarrow P_q = e^{-1-\lambda_1/k_B - \lambda_2 E_q/k_B}. \tag{1.14}$$

Applying the normalization,

$$1 = \sum_q P_q = e^{-1-\lambda_1/k_B}\sum_q e^{-\lambda_2 E_q/k_B} = e^{-1-\lambda_1/k_B}\sum_q e^{-\beta E_q} \Rightarrow e^{-1-\lambda_1/k_B} = \frac{1}{Z}, \tag{1.15}$$

where we have let the constant $\lambda_2 = 1/T$, with T the equilibrium temperature, and Z is the partition function of the canonical ensemble. It then follows that the distribution function

$$P_q = \frac{e^{-\beta E_q}}{Z} \tag{1.16}$$

has the Gibbs form.

    (iii) The third constraint to add is

$$\sum_q N_q P_q = N, \tag{1.17}$$

where N is the average number of particles per partition. Then P_q extremizing S satisfies

$$-k_B\left(\ln P_q + 1\right) - \lambda_1 - \lambda_2 E_q - \lambda_3 N_q = -k_B \ln P_q - S_t - E_q/T - \lambda_3 N_q = 0, \tag{1.18}$$

where we have replaced the first two Lagrange multipliers with physical quantities derived in (i-ii). The probability distribution function is

$$P_q = e^{-S-\beta E_q - \lambda_3 N_q/k_B} = e^{-S-\beta E_q + \beta\mu N_q}, \tag{1.19}$$

where we have let the constant $\lambda_3 = -\mu/T$. Then, with the normalization condition,

$$1 = e^{-S}\sum_q e^{-\beta(E_q + \mu N_q)} = e^{-S}\mathcal{Z}, \tag{1.20}$$

and the probability distribution function can be written as

$$P_q = \frac{e^{-\beta(E_q + \mu N_q)}}{\mathcal{Z}}, \tag{1.21}$$

which has the Gibbs form. $\qquad\qquad\qquad\square$

(c) Recall the expression for $\Omega(E)$ for the microcanonical ensemble of a 3d ideal Boltzmann gas of N particles. Using it, calculate the probability P_ϵ of a *particular* particle to have energy in the neighborhood of $\epsilon \ll E$.

From your answer for P_ϵ and comparing it with the standard Boltzmann-Gibbs weight, read off the corresponding effective temperature of this single particle in terms of E and N.

Hint: (i) From above total $\Omega(E)$ first think about the number of states (sub-multiplicity) $\Omega_\epsilon(E)$ for one of the particle to have energy ϵ and the remaining $N-1$ sharing the remaining energy. (ii) Note that $P_\epsilon = \Omega_\epsilon/\Omega$. (iii) Use Stirling's approximation and $\epsilon \ll E$ to simplify your answer.

Solution.

From Sackur-Tetrode, we can write the multiplicity as $\Omega = e^{S/k_B} = (V^N/N!)f(N, E)$ where

$$f(N, E) = e^{5N/2}\left(\frac{4\pi mE}{3Nh^2}\right)^{3N/2}. \tag{1.22}$$

Then, we note that there is only one way to distribute an energy of ϵ into a particular particle. Thus, the multiplicity for the entire system of one particle of energy ϵ and $N-1$ particles of energy $E-\epsilon$ is

$$
\begin{aligned}
\Omega_\epsilon &= \frac{V^{N-1}}{(N-1)!}f(N-1, E-\epsilon) \\
&= \frac{V^{N-1}}{(N-1)!}e^{5(N-1)/2}\left(\frac{4\pi m(E-\epsilon)}{3(N-1)h^2}\right)^{3(N-1)/2} \\
&\approx \frac{V^{N-1}}{(N-1)!}e^{5(N-1)/2}\left(\frac{4\pi m(E-\epsilon)}{3Nh^2}\right)^{3(N-1)/2}. \tag{1.23}
\end{aligned}
$$

The probability is thus

$$
\begin{aligned}
P_\epsilon &= \frac{\Omega_\epsilon}{\Omega} \\
&\approx \frac{N}{V}e^{-5/2}\left(\frac{4\pi mE}{3Nh^2}\right)^{-3/2}\left(1 - \frac{\epsilon}{E}\right)^{3(N-1)/2} \\
&\approx \frac{N}{V}e^{-5/2}\left(\frac{4\pi mE}{3Nh^2}\right)^{-3/2}e^{-3(N-1)\epsilon/2E}, \tag{1.24}
\end{aligned}
$$

which follows the Gibbs form if the effective temperature is defined as

$$k_B T_{\text{eff}} = \frac{2E}{3(N-1)}. \tag{1.25}$$

$\square$

(d) Variance (i.e., mean-squared fluctuations) in the number of particles N in the grand canonical ensemble is given by $\langle(\Delta N)^2\rangle$. Show that quite generally it is given by

$$N_{\text{rms}}^2 = \left\langle(\Delta N)^2\right\rangle = -\left.\frac{\partial\overline{N}}{\partial\alpha}\right|_{\beta,V} = \left.\frac{\partial^2(\ln\mathcal{Z})}{\partial\alpha^2}\right|_{\beta,V} \tag{1.26}$$

Solution.

First, from $\mathcal{Z}$, we can calculate

$$\frac{\partial \mathcal{Z}}{\partial \alpha} = \frac{\partial}{\partial \alpha} \sum_q e^{-\beta E_q - \alpha N_q} = -\sum_q N_q e^{-\beta E_q - \alpha N_q} = -\langle N \rangle \, \mathcal{Z}, \qquad (1.27)$$

and

$$\frac{\partial^2 \mathcal{Z}}{\partial \alpha^2} = \sum_q N_q^2 e^{-\beta E_q - \alpha N_q} = \langle N^2 \rangle \, \mathcal{Z}. \qquad (1.28)$$

Differentiating (1.27) again, we get

$$\langle N^2 \rangle \, \mathcal{Z} = -\frac{\partial \langle N \rangle}{\partial \alpha} \mathcal{Z} + \langle N \rangle^2 \, \mathcal{Z} \Rightarrow \langle (\Delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = -\frac{\partial \langle N \rangle}{\partial \alpha}. \qquad (1.29)$$

Also,

$$\frac{\partial (\ln \mathcal{Z})}{\partial \alpha} = -\langle N \rangle. \qquad (1.30)$$

So taking the differentation again leads us to the second equality

$$\frac{\partial^2 (\ln \mathcal{Z})}{\partial \alpha^2} = -\frac{\partial \langle N \rangle}{\partial \alpha}. \qquad (1.31)$$

$\square$

Problem 2 (Ultra-relativistic gas)**:** Consider a non-interacting 3d gas of identical ultra-relativistic particles (i.e., ignoring their mass), with a dispersion $\epsilon_i = p_i c$, at temperature T and chemical potential μ, where $p_i = |\mathbf{p}_i| = \sqrt{p_{xi}^2 + p_{yi}^2 + p_{zi}^2}$.

Following similar steps that we did in class for nonrelativistic Boltzmann gas, compute:

(a) Grandcanonical partition function, $\mathcal{Z}(\mu, T)$ by first computing the canonical one, $Z(N, T)$, introducing fugacity and then summing over N.

Hint: it is nice to do the integral in the spherical coordinate system.

Solution.

By definition, the canonical partition function is

$$
\begin{aligned}
Z(N, T) &= \frac{1}{N!} \prod_{i=1}^{N} \left[\int \frac{d^3\mathbf{r}_i d^3\mathbf{p}_i}{(2\pi\hbar)^3} \right] e^{-\beta \sum_{j=1}^{N} \epsilon_i} \\
&= \frac{V^N}{N!} \frac{1}{h^{3N}} \prod_{i=1}^{N} \left[\int d^3\mathbf{p}_i \exp\left(-\beta |\mathbf{p}_i| c\right) \right] \\
&= \frac{V^N}{N!} \frac{1}{h^{3N}} \left[\int_0^{4\pi} d\Omega \int_0^{\infty} dp\, p^2 e^{-\beta pc} \right]^N \\
&= \frac{V^N}{N!} \left[\frac{4\pi}{(\beta hc)^3} \right]^N \left[\int_0^{\infty} dx\, x^2 e^{-x} \right]^N \qquad (x = \beta pc) \\
&= \frac{1}{N!} \left[\frac{8\pi V}{(\beta hc)^3} \right]^N.
\end{aligned}
\tag{2.1}
$$

The grandcanonical partition function is then

$$
\mathcal{Z}(\alpha, \beta) = \sum_{N=0}^{\infty} z^N Z(N, T) = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\frac{8\pi z V}{(\beta hc)^3} \right]^N = \exp\left[\frac{8\pi z V}{(\beta hc)^3} \right] = \exp\left[\frac{8\pi V}{(\beta hc)^3} e^{-\alpha} \right], \tag{2.2}
$$

where $z = e^{-\alpha}$ is the fugacity. Unpacking these definitions, we get

$$
\mathcal{Z}(\mu, T) = \exp\left[8\pi V e^{\mu/k_B T} \left(\frac{k_B T}{hc} \right)^3 \right]. \tag{2.3}
$$

$\square$

(b) Grandcanonical free energy $\mathcal{F}(\mu, T)$.

Solution.

From (2.3), it is a straightforward calculation to get

$$
\mathcal{F}(\mu, T) = -k_B T \ln \mathcal{Z} = -8\pi V k_B T \left(\frac{k_B T}{hc} \right)^3 e^{\mu/k_B T}. \tag{2.4}
$$

$\square$

(c) Average energy $E(\mu, T)$.

Solution.

Using the expression of $\mathcal{Z}$ in terms of α and β (2.2), we can calculate

$$
\begin{aligned}
E(\mu, T) &= -\frac{\partial(\ln \mathcal{Z})}{\partial \beta} \\
&= -\frac{\partial}{\partial \beta}\left[\frac{8\pi V}{(\beta hc)^3} e^{-\alpha}\right] \\
&= \frac{1}{\beta}\frac{24\pi V}{(\beta hc)^3} e^{-\alpha} \\
&= 24\pi V k_B T\left(\frac{k_B T}{hc}\right)^3 e^{\mu/k_B T}.
\end{aligned}
\tag{2.5}
$$

$\square$

(d) Average particle number $N(\mu, T)$.

Solution.

Recall that $z = e^\alpha$, we can calculate

$$
N(\mu, T) = -\frac{\partial}{\partial \alpha}\left[\frac{8\pi V}{(\beta hc)^3} e^{-\alpha}\right] = 8\pi V\left(\frac{k_B T}{hc}\right)^3 e^{\mu/k_B T} = \frac{E}{3k_B T}.
\tag{2.6}
$$

$\square$

(e) Pressure $P(\mu, T)$. Find the relation between P and E.

Solution.

By definition, we write

$$
P(\mu, T) = \frac{1}{\beta}\frac{\partial(\ln \mathcal{Z})}{\partial V} = 8\pi k_B T\left(\frac{k_B T}{hc}\right)^3 e^{\mu/k_B T} = \frac{N k_B T}{V}.
\tag{2.7}
$$

Together with (2.5), we can write

$$
E = 3PV.
\tag{2.8}
$$

$\square$

(f) Heat capacities C_v and C_p and find the ratio $\gamma = C_p/C_v$.

Hint: While in thermodynamics observables are obtained by appropriate derivative of the free energy $\mathcal{F}$, in statistical mechanics, it is often mathematically more convenient (but equivalent) to instead differentiate $q = \ln \mathcal{Z}$.

Solution.

By definition,

$$
C_v = \frac{\partial E}{\partial T} = 3Nk_B, \qquad \text{and} \qquad C_p = C_v + P\frac{\partial V}{\partial T} = 3Nk_B + Nk_B = 4Nk_B.
\tag{2.9}
$$

Thus, $\gamma = C_p/C_v = 4/3$.

$\square$

Problem 3 (Boltzmann diatomic gas): Consider a noninteracting 3d gas of N nonrelativistic *diatomic* molecules, e.g., O_2, at temperature T, in a box of volume V, as dicussed in lecture and described by a Hamiltonian,

$$\mathcal{H} = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + U\big(|\mathbf{r}_1 - \mathbf{r}_2|\big), \tag{3.1}$$

where the potential has a minimum at a nonzero value of the average bond length l, with

$$U(|\mathbf{r}|) = \frac{1}{2}m\omega_0^2(r - l)^2 = \frac{1}{2}m\omega_0^2\Big(\sqrt{x^2 + y^2 + z^2} - l\Big)^2. \tag{3.2}$$

Let's calculate the thermodynamics of this gas by computing the canonical partition function,

$$Z(T, V, N) = \frac{1}{N!} \prod_i^N \left[\int \frac{d^3\mathbf{r}_{1i}d^3\mathbf{p}_{1i}d^3\mathbf{r}_{2i}d^3\mathbf{p}_{2i}}{(2\pi\hbar)^6} \right] e^{-\beta\mathcal{H}\left[\{\mathbf{p}_{1i}, \mathbf{p}_{2i}, \mathbf{r}_{1i}, \mathbf{r}_{2i}\}\right]}, \tag{3.3}$$

where $\mathbf{r}_{1i}, \mathbf{r}_{2i}$, and $\mathbf{p}_{1i}, \mathbf{p}_{2i}$ are position and momentum of, respectively, atom 1 and 2 in a molecule i.

Although this looks complicated by now, we know that for noninteracting molecules we have a simplification with partition function reducing to that of a single molecule according to $Z(T, V, N) = Z(T, V, 1)^N/N!$. So let's focus on the computation of $Z(T, V, 1)$.

(a) Compute $Z(T, V, 1)$ and obtain from it (i) free energy $F(T, V, 1)$, and (ii) heat capacity $c_v(T)$ per molecule, and plot the latter as a function of T.

Hint: (i) As discussed in class the center of mass momentum $\mathbf{P}$ and position $\mathbf{R}$ will decouple giving their own multipicative contribution to $Z(T, V, 1)$. (ii) The relative momentum $\mathbf{p}$ will also decouple, so the nontrivial part of the problem reduces to the trace over the relative coordinate $\mathbf{r}$, i.e., to a *three*-dimensional integral $\int d^3\mathbf{r}$. Note however, that given the form of $U(|\mathbf{r}|)$ above, this last integral is not a standard Gaussian. To solve the problem express the above physical observables $F(T, V, 1)$ and $c_v(T)$ in terms of this last integral over $\mathbf{r}$ (that can still be simplified to a single one-dimensional integral, utilizing rotational invariance). Then compute the final integral numerically for a given value of bond length l and plot the corresponding $c_v(T)$. Make sure to demonstrate, not just accept all of the above "hint" steps.

Solution.

See part (b). $\qquad\square$

(b) Identify the low and high temperature asymptotic number of degrees of freedom, n_{dof} per molecule, appearing through the heat capacity plot vs. T, and thereby confirming our in class discussion.

Solution.

By definition, the canonical partition function for a single molecule is

$$Z_1 = \frac{1}{(2\pi\hbar)^6} \int d^3\mathbf{r}_1 d^3\mathbf{p}_1 d^3\mathbf{r}_2 d^3\mathbf{p}_2 \exp\left[-\frac{1}{2}\frac{\beta}{m}(\mathbf{p}_1^2 + \mathbf{p}_2^2) - \beta U(r)\right]$$

$$= \frac{1}{(2\pi\hbar)^6} \left(\int_{-\infty}^{\infty} dp\, e^{-\beta p^2/2m}\right)^6 \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 e^{-\beta U(r)}$$

$$= \frac{1}{(2\pi)^3 \hbar^6} \left(\frac{m}{\beta}\right)^3 \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 e^{-\beta U(r)}. \tag{3.4}$$

Now, we define the transformation $T : \mathbb{R}^6 \mapsto \mathbb{R}^6$ as follows

$$T(\mathbf{r}_1, \mathbf{r}_2) = \left[\mathbf{r}_1 - \mathbf{r}_2 \quad (1/2)(\mathbf{r}_1 + \mathbf{r}_2)\right]^T. \tag{3.5}$$

The Jacobian of T is

$$\|\boldsymbol{\nabla} T\| = \det \begin{pmatrix} \mathbb{1}_3 & (1/2)\mathbb{1}_3 \\ -\mathbb{1}_3 & (1/2)\mathbb{1}_3 \end{pmatrix} = 1, \tag{3.6}$$

where $\mathbb{1}_3$ is the 3x3 identity matrix. Thus, the integration in (3.4) becomes

$$\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 e^{-\beta U(r)} = \int d^3\mathbf{r} d^3\mathbf{R} \|\boldsymbol{\nabla} T\| e^{-\beta U(r)} = 4\pi V_R \int_0^{\infty} dr\, r^2 \exp\left[-\frac{1}{2}\beta m \omega_0^2 (r - l)^2\right] \tag{3.7}$$

where we have let $V_R = \int d^3\mathbf{R}$, which blows up. However, since the free energy is $F \sim \ln Z_1 \sim \ln V_R +$ other terms, we can later redefine the ground energy at $F_0 \approx \ln V_R$ to get out of this situation, which is physically valid. Now, set $\beta_* = 1/m\omega_0^2 l^2 = 1/k_B T_*$ and $u = (r/l)\sqrt{\beta/\beta_*}$, we can rewrite the integral (3.7) as

$$4\pi V_R l^3 \left(\frac{\beta_*}{\beta}\right)^{3/2} I_1(x),$$

where we have defined

$$I_1(x) \equiv \int_0^{\infty} du\, u^2 e^{-(u - \sqrt{x})^2/2}. \tag{3.8}$$

The partition function is now

$$Z_1 = \frac{1}{2\pi^2} \frac{V_R}{l^3} \frac{1}{(\hbar\omega_0)^6} \frac{1}{\beta_*^{3/2} \beta^{9/2}} I_1(\beta/\beta_*). \tag{3.9}$$

It then follows that (i) the free energy is

$$F = -k_B T \ln Z_1 = -k_B T \ln\left[\frac{V_R/l^3}{2\pi^2(\beta_* \hbar\omega_0)^6}\right] - k_B T \ln\left[\left(\frac{\beta_*}{\beta}\right)^{9/2} I_1(\beta/\beta_*)\right], \tag{3.10}$$

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where the first term may be set to be the temperature-dependent ground energy. The heat capacity is

$$
\begin{aligned}
c_v &= \frac{\partial E}{\partial T} \\
&= k_B \beta^2 \frac{\partial^2 (\ln Z_1)}{\partial \beta^2} \\
&= \frac{9}{2} k_B + k_B \beta^2 \frac{I_1(x) I_1''(x) - \left[I_1'(x)\right]^2}{\left[I_1(x)\right]^2} \\
&= \frac{9}{2} k_B + k_B \frac{I_1(x) I_3(x) - I_2(x)}{\left[I_1(x)\right]^2},
\end{aligned}
\tag{3.11}
$$

where the argument of the I_i functions are $x = \beta/\beta_* = T_*/T$, and we have used Mathematica to solve the integrals I_1, I_2, I_3 numerically as follows

$$
I_1(x) = -2I_3(x) + \sqrt{\frac{\pi}{2}}(1+x)\left[1 + \mathrm{erf}\left(\sqrt{\frac{x}{2}}\right)\right]
\tag{3.12a}
$$

$$
I_2(x) = \frac{\partial I_1(x)}{\partial \beta} = \left\{-2I_3(x) + \sqrt{\frac{\pi}{2}}x\left[1 + \mathrm{erf}\left(\sqrt{\frac{x}{2}}\right)\right]\right\}^2
\tag{3.12b}
$$

$$
I_3(x) = \frac{\partial^2 I_1(x)}{\partial \beta^2} = -\frac{1}{2}\sqrt{x}e^{-x/2},
\tag{3.12c}
$$

where $\mathrm{erf}(x)$ is the well-known error function. A plot of (3.11) is given in Fig. 1 with the crossover temperature $T_* = 1/k_B \beta_* = m\omega_0^2 l^2/k_B$. We observe that at the high temperature limit, $n_{\mathrm{dof}} = 2c_v/k_B \to 9$ degrees of freedom, while $n_{\mathrm{dof}} \to 7$ as $T \to 0$, in agreement with the in-class discussion.
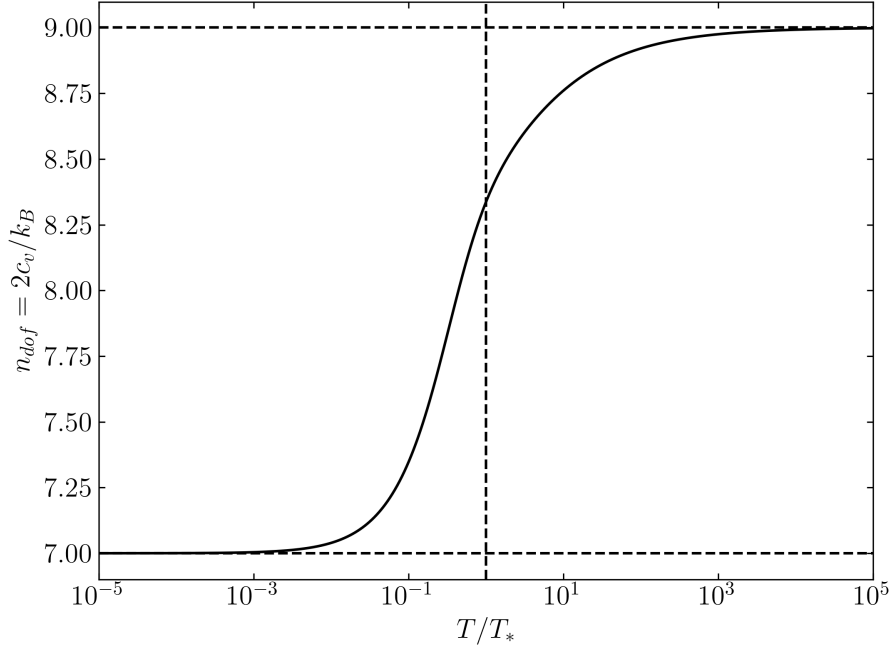
Figure 1: Number of degrees of freedom per molecule in terms of temperature in a Boltzmann diatomic gas.

$\square$

(c) By examining your analytical expression (before doing the final numerical integral over r above), give a dimensionless parameter in terms of $l, T, \ldots$ that determines T_* and controls whether one is in low $T \ll T_*$ or high $T \gg T_*$ limits of $c_v(T)$. What is T_*?

Solution.
First, note that $I_3 \to 0$ at both limits (low temperature $- x \to \infty$, and high temperature $- x \to 0$). Thus, the heat capacity at the extremes is

$$\frac{c_v}{k_B} \approx \frac{9}{2} - \frac{I_2(x)}{\left[I_1(x)\right]^2}. \tag{3.13}$$

Now, at high temperature ($T \gg T_*$ and $x \to 0$), the error function vanishes. Thus, $I_1 \to \sqrt{\pi/2}$, while $I_2 \to 0$. So the heat capacity is $c_v \approx (9/2)k_B$, as expected from Fig. 1.

At low temperature ($x \to \infty$), the error function approaches unity. So I_2 grows as $2\pi x^2$, while I_1^2 grows as $2\pi(1+x)^2$. Both of them grows at the same rate (quadratically), thus, by L'Hôpital's Rule,

$$\frac{c_v}{k_B} = \frac{9}{2} - \lim_{x \to \infty} \frac{x^2}{(1+x)^2} = \frac{9}{2} - 1 = \frac{7}{2}, \tag{3.14}$$

as expected! $\square$

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(d) Now go back to the original Hamiltonian and in particular to the nontrivial "difficult" part involving the potential $U(|\mathbf{r}|)$ and neglect the bond length l, setting it to 0. Using this simplification, recompute $Z(T, V, 1)$ (now best done in Cartesian coordinates using Gaussian integrals calculus) and the corresponding heat capacity $c_v(T)$ per particle and compare it with your above result for nonzero l, particularly with the high T limit of the plot.

Solution.

For $l = 0$, the canonical partition function is now

$$Z = \frac{1}{N!h^{6N}} \prod_{i=1}^{N} \left[\int d^3\mathbf{r}_{1i} d^3\mathbf{p}_{1i} d^3\mathbf{r}_{2i} d^3\mathbf{p}_{2i} \exp\left[-\frac{1}{2}\frac{\beta}{m}\left(\mathbf{p}_{1i}^2 + \mathbf{p}_{2i}^2\right) - \frac{1}{2}\beta m\omega_0^2 r^2 \right] \right]$$

$$= \frac{1}{N!h^{6N}} \left[\int_{-\infty}^{\infty} dp\, e^{-(1/2)(\beta/m)p^2} \right]^{6N} \left[\int_{-\infty}^{\infty} dx\, e^{-(1/2)\beta m\omega_0^2 x^2} \right]^{3N}$$

$$= \frac{1}{N!} \left(\frac{1}{h^2}\frac{2\pi m}{\beta} \sqrt{\frac{2\pi}{\beta m\omega_0^2}} \right)^{3N}$$

$$= \frac{1}{N!}\frac{1}{\hbar^{6N}} \left(\frac{m}{2\pi\beta^3\omega_0^2} \right)^{3N/2}. \tag{3.15}$$

Then, the free energy is

$$F = -k_B T \ln Z = -k_B T \ln\left[\frac{1}{N!}\frac{1}{\hbar^{6N}}\left(\frac{m}{2\pi\omega_0^2}\right)^{3N/2} \right] + \frac{9N}{2}k_B T \ln\beta. \tag{3.16}$$

The first term grows linearly with T, so it vanishes under second-order differentiation. Thus, the heat capacity is

$$C_v = -T\frac{\partial^2 F}{\partial T^2} = -\frac{9N}{2}T\frac{\partial^2}{\partial T^2}(k_B T \ln\beta) = \frac{9N k_B}{2}. \tag{3.17}$$

So the heat capacity per molecule is $c_v = C_V/N = 9k_B/2$, which indicates 9 degrees of freedom, in congruence with the high T behavior in Fig. 1. $\square$

Problem 4 (Classical oscillator):

(a) As a warm up consider N 1d classical *harmonic* oscillator.

(i) For one oscillator, compute its average kinetic energy $K = \langle p^2/2m \rangle$ and potential energy $U = \langle (1/2)m\omega_0^2 x^2 \rangle$, and thereby verify the equipartition theorem and compute the ratio K/U.

(ii) For N oscillators, calculate the energy standard deviation E_{rms}, defined by

$$E_{\text{rms}}^2 = \left\langle (\Delta E)^2 \right\rangle = \left\langle \left(\mathcal{H} - \langle \mathcal{H} \rangle \right)^2 \right\rangle = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2, \tag{4.1}$$

confirm that $E_{\text{rms}}^2 = k_B T^2 C_v$ and that indeed $E_{\text{rms}}/E \to 0$ in the thermodynamic limit with $N \to \infty$.

Hint: You will find Gaussian calculus useful.

Solution.

(i) Recall from the lecture notes that the partition function of a classical 1d harmonic oscillator is $Z = 1/\beta\hbar\omega_0$. Then, by definition,

$$
\begin{aligned}
K &= \left\langle \frac{p^2}{2m} \right\rangle \\
&= \beta\hbar\omega_0 \int \frac{dxdp}{2\pi\hbar} \frac{p^2}{2m} \exp\left(-\frac{1}{2}\frac{\beta}{m}p^2 - \frac{1}{2}\beta m\omega_0^2 x^2 \right) \\
&= \frac{\beta\omega_0}{4\pi m} \sqrt{\frac{2\pi}{\beta m\omega_0^2}} \frac{m}{\beta} \sqrt{\frac{2\pi m}{\beta}} \\
&= \frac{1}{2\beta} \\
&= \frac{1}{2}k_B T,
\end{aligned} \tag{4.2}
$$

as expected from equipartition theorem. Similarly,

$$
\begin{aligned}
U &= \left\langle \frac{1}{2}m\omega_0^2 x^2 \right\rangle \\
&= \beta\hbar\omega_0 \int \frac{dxdp}{2\pi\hbar} \frac{1}{2}m\omega_0^2 x^2 \exp\left(-\frac{1}{2}\frac{\beta}{m}p^2 - \frac{1}{2}\beta m\omega_0^2 x^2 \right) \\
&= \frac{\beta m\omega_0^3}{4\pi} \sqrt{\frac{2\pi}{\beta/m}} \frac{1}{\beta m\omega_0^2} \sqrt{\frac{2\pi}{\beta m\omega_0^2}} \\
&= \frac{1}{2\beta} \\
&= \frac{1}{2}k_B T.
\end{aligned} \tag{4.3}
$$

Thus, $K/U = 1$, meaning total energy is equally partitioned into the potential and kinetic energy.

(ii) Given the previous result, we can easily calculate

$$\langle \mathcal{H} \rangle = \sum_{i=1}^{N} \langle \mathcal{H}_i \rangle = \sum_{i=1}^{N} \left(\left\langle \frac{p_i^2}{2m} \right\rangle + \left\langle \frac{1}{2}m\omega_0^2 x_i^2 \right\rangle \right) = Nk_B T. \tag{4.4}$$

Now, note that we can write

$$\mathcal{H}^2 = \left(\sum_{i=1}^{N} \mathcal{H}_i \right)^2 = \sum_{i=1}^{N} \mathcal{H}_i^2 + 2\sum_{j \neq k} \mathcal{H}_j \mathcal{H}_k. \tag{4.5}$$

By combinatorics, there are $\binom{N}{2}$ terms in the mixed summation, since there are that many ways to choose groups of 2 out of N objects. We can thus calculate

$$
\begin{aligned}
\langle \mathcal{H}^2 \rangle &= \sum_{i=1}^{N} \langle \mathcal{H}_i^2 \rangle + 2\sum_{j \neq k} \langle \mathcal{H}_j \rangle \langle \mathcal{H}_k \rangle \\
&= N \langle \mathcal{H}_1^2 \rangle + \frac{N!}{(N-2)!}(k_B T)^2 \\
&= N \langle \mathcal{H}_1^2 \rangle + N(N-1)k_B^2 T^2 \\
&= N\beta\hbar\omega_0 \int \frac{dx\,dp}{2\pi\hbar} \left(\frac{p^4}{4m^2} + \frac{1}{4}m^2\omega_0^4 x^4 + \frac{1}{2}\omega_0^2 p^2 x^2 \right) \exp\left(-\frac{1}{2}\frac{\beta}{m}p^2 - \frac{1}{2}\beta m\omega_0^2 x^2 \right) \\
&\quad + (N^2 - N)k_B^2 T^2 \\
&= (N^2 + N)k_B^2 T^2. \tag{4.6}
\end{aligned}
$$

Finally, the energy variance is $E_{\text{rms}}^2 = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H}^2 \rangle = Nk_B^2 T^2 = k_B T^2 C_v$, where $C_v = Nk_B$. We can also show that $E_{\text{rms}}/E = 1/\sqrt{N} \to 0$ at the thermodynamic limit ($N \to \infty$). $\quad\square$

(b) *Nonlinear* 1d oscillator

Consider a nonlinear classical oscillator with a quartic potential, described by a Hamiltonian,

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 + gx^4, \tag{4.7}$$

with $g > 0$.

(i) For one such nonlinear oscillator with $\omega_0 = 0$, compute its average kinetic energy $K = \langle p^2/2m \rangle$ and potential energy $U = \langle gx^4 \rangle$, showing the expected non-adherence to the equipartition theorem and computing the ratio K/U.
Hint: You will find Gamma functions useful.

(ii) Now for nonzero ω_0, but in the limit of a small coupling g, calculate the variance x_{rms}^2 to a lowest nonzero order in perturbation theory in g.

(iii) For the above problem with nonzero ω_0, calculate the heat capacity to lowest nonzero roder in g and note how it differs from the equipartition $g = 0$ case. *Hint*: You will find Gaussian calculus useful.

Solution.

(i) First, we need to calculate the partition function

$$Z = \int \frac{dxdp}{2\pi\hbar} \exp\left(-\frac{1}{2}\frac{\beta}{m}p^2 - \beta g x^4\right) = \frac{1}{\pi\hbar}\sqrt{\frac{2\pi m}{\beta}}\frac{\Gamma(5/4)}{(\beta g)^{1/4}}. \tag{4.8}$$

Then, it follows that

$$\begin{aligned}
K = \left\langle \frac{p^2}{2m} \right\rangle &= \frac{1}{Z}\int \frac{dxdp}{2\pi\hbar}\frac{p^2}{2m}\exp\left(-\frac{1}{2}\frac{\beta}{m}p^2 - \beta g x^4\right) \\
&= \frac{1}{Z}\frac{1}{4\pi\hbar m}\frac{m}{\beta}\sqrt{\frac{2\pi m}{\beta}}\frac{2\Gamma(5/4)}{(\beta g)^{1/4}} \\
&= \frac{1}{2\beta} \\
&= \frac{1}{2}k_B T,
\end{aligned} \tag{4.9}$$

as expected of a quadratic degree of freedom. The average potential is

$$\begin{aligned}
U = \langle g x^4 \rangle &= \frac{1}{Z}\int \frac{dxdp}{2\pi\hbar}g x^4 \exp\left(-\frac{1}{2}\frac{\beta}{m}p^2 - \beta g x^4\right) \\
&= \frac{1}{Z}\frac{g}{2\pi\hbar}\sqrt{\frac{2\pi m}{\beta}}\frac{\Gamma(5/4)}{2(\beta g)^{5/4}} \\
&= \frac{1}{4\beta} \\
&= \frac{1}{4}k_B T,
\end{aligned} \tag{4.10}$$

which is not expected by equipartition theorem. Then $K/U = 2$.

(ii) First, we calculate the partition function

$$\begin{aligned}
Z &= \int \frac{dxdp}{2\pi\hbar}(1 - \beta g x^4)\exp\left(-\frac{1}{2}\frac{\beta}{m}p^2 - \frac{1}{2}\beta m\omega_0^2 x^2\right) \\
&= \frac{1}{2\pi\hbar}\sqrt{\frac{2\pi m}{\beta}}\left[\int_{-\infty}^{\infty} dx \exp\left(-\frac{1}{2}\beta m\omega_0^2 x^2\right) - \beta g\int_{-\infty}^{\infty} dx x^4 \exp\left(-\frac{1}{2}\beta m\omega_0^2 x^2\right)\right] \\
&= \frac{1}{\beta\hbar\omega_0}\left[1 - \frac{3\beta}{(\beta m\omega_0^2)^2}g\right].
\end{aligned} \tag{4.11}$$

Then, we need only calculate $\langle x^2 \rangle$ since $\langle x \rangle = 0$ due to parity.

$$x_{\text{rms}}^2 = \langle x^2 \rangle = \frac{1}{Z} \frac{1}{2\pi\hbar} \sqrt{\frac{2\pi m}{\beta}} \int \frac{dxdp}{2\pi\hbar} \left[\int_{-\infty}^{\infty} dx x^2 \exp\left(-\frac{1}{2}\beta m\omega_0^2 x^2 \right) \right.$$

$$\left. - \beta g \int_{-\infty}^{\infty} dx x^6 \exp\left(-\frac{1}{2}\beta m\omega_0^2 x^2 \right) \right]$$

$$= \frac{1}{\beta m\omega_0^2} \frac{1 - (15\beta/(\beta m\omega_0^2)^2)g}{1 - (3\beta/(\beta m\omega_0^2)^2)g}$$

$$= \frac{1}{\beta m\omega_0^2} \left[1 - \frac{12\beta}{(\beta m\omega_0^2)^2} g \right] \tag{4.12}$$

(iii) Now, we calculate

$$\langle x^4 \rangle = \frac{1}{Z} \frac{1}{2\pi\hbar} \sqrt{\frac{2\pi m}{\beta}} \left[\int_{-\infty}^{\infty} dx x^4 \exp\left(-\frac{1}{2}\beta m\omega_0^2 x^2 \right) - \beta g \int_{-\infty}^{\infty} dx x^8 \exp\left(-\frac{1}{2}\beta m\omega_0^2 x^2 \right) \right]$$

$$= \frac{3}{Z\beta\hbar\omega_0} \frac{1}{(\beta m\omega_0^2)^2} \left[1 - \frac{35\beta}{(\beta m\omega_0^2)^2} g \right]$$

$$\approx \frac{3}{(\beta m\omega_0^2)^2} \left[-\frac{32\beta}{(\beta m\omega_0^2)^2} g \right]. \tag{4.13}$$

Then it follows that

$$E = \langle \mathcal{H} \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \frac{1}{2}m\omega_0^2 \langle x^2 \rangle + g \langle x^4 \rangle$$

$$\approx \frac{1}{2\beta} + \frac{1}{2\beta} \left[1 - \frac{12\beta}{(\beta m\omega_0^2)^2} g \right] + \frac{3g}{(\beta m\omega_0^2)^2}$$

$$= \frac{1}{\beta} - \frac{3g}{(\beta m\omega_0^2)^2}$$

$$= k_B T - \frac{3g}{(m\omega_0^2)^2} k_B^2 T^2. \tag{4.14}$$

Thus, the heat capacity is

$$C_v = \frac{\partial E}{\partial T} = k_B - \frac{6k_B^2 g}{(m\omega_0^2)^2} T. \tag{4.15}$$

For $g = 0$, this agrees with that of the 1d linear classical harmonic oscillator. □

(c) We can also attack this nonlinear oscillator problem with $\omega_0 \neq 0, g > 0$ using the variational theory described in lecture, where the upper bound for the free energy, F, is computed using a minimized variational free energy, F_{var} computed with a trial Hamiltonian, $\mathcal{H}_{\text{tr}}$.

Recall that the variational free energy is given by

$$F_{\text{var}} = F_{\text{tr}} + \langle \mathcal{H} - \mathcal{H}_{\text{tr}} \rangle_{\text{tr}} \geq F, \tag{4.16}$$

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and provides the upper bound for the actual free energy and $\mathcal{H}$ is the nonlinear oscillator Hamiltonian of interest above.

Taking the trial Hamiltonian $\mathcal{H}_{\mathrm{tr}} = (1/2)kx^2$, with k as the variational parameter to optimize over, compute the variational free energy $F_{\mathrm{var}}(k)$ and minimize it over k, finding its optimum value k_m. Using the resulting optimum $F_{\mathrm{var}}(k_m)$ compute the corresponding heat capacity c_v.

(i) I suggest that as a warm up you first do the $\omega = 0$ case.

(ii) Then repeat the calculation for $\omega > 0$, computing again c_v and compare your answer with that found in (b)iii through the lowest order perturbation theory in g. Check that your answers agree with expectations in the trivial limit of $g \to 0$.

Solution.

(i) First, with $\mathcal{H}_{\mathrm{tr}} = (1/2)kx^2 + p^2/2m$, we calculate

$$Z_{\mathrm{tr}} = \int \frac{dxdp}{2\pi\hbar} \exp\left(-\frac{1}{2}\beta kx^2 - \frac{1}{2}\frac{\beta}{m}p^2\right) = \frac{1}{\hbar\beta}\sqrt{\frac{m}{k}}. \tag{4.17}$$

Then the free energy for the trial Hamiltonian is

$$F_{\mathrm{tr}} = -k_BT \ln Z_{\mathrm{tr}} = k_BT \ln\left(\frac{\hbar}{k_BT}\sqrt{\frac{k}{m}}\right). \tag{4.18}$$

Also,

$$\langle \mathcal{H} - \mathcal{H}_{\mathrm{tr}}\rangle_{\mathrm{tr}} = \frac{1}{Z_{\mathrm{tr}}}\int \frac{dxdp}{2\pi\hbar}\left(gx^4 - \frac{1}{2}kx^2\right)\exp\left(-\frac{1}{2}\beta kx^2 - \frac{1}{2}\frac{\beta}{m}p^2\right)$$

$$= k_BT\left(\frac{3g}{k^2}k_BT - \frac{1}{2}\right). \tag{4.19}$$

Then the variational free energy is

$$F_{\mathrm{var}} = F_{\mathrm{tr}} + \langle \mathcal{H} - \mathcal{H}_{\mathrm{tr}}\rangle_{\mathrm{tr}} = k_BT\left[\frac{3g}{k^2}k_BT - \frac{1}{2} + \ln\left(\frac{\hbar}{k_BT}\sqrt{\frac{k}{m}}\right)\right]. \tag{4.20}$$

Using Mathematica, we can find the k_m satisfying $\partial F_{\mathrm{var}}/\partial k = 0$ as $k_m = 2\sqrt{3gk_BT}$. Then,

$$F_{\mathrm{var}}(k_m) = \frac{1}{4}k_BT\left[4\ln\left(\frac{\hbar}{k_BT}\sqrt{\frac{\sqrt{gk_BT}}{m}}\right) + \ln 12 - 1\right], \tag{4.21}$$

and we can calculate the heat capacity as follows

$$C_v = -T\frac{\partial^2 F_{\mathrm{var}}}{\partial T^2} = \frac{3}{4}k_B, \tag{4.22}$$

which agrees with (4.9) and (4.9) since the total energy there is $E = K + U = (3/4)k_BT$.

(ii) Keeping the same trial Hamiltonian, the trial free energy remains. Then $\mathcal{H} - \mathcal{H}_{\mathrm{tr}} = p^2/2m + gx^4 + (1/2)(m\omega_0^2 - k)x^2$, and we can write

$$
\begin{aligned}
\langle \mathcal{H} - \mathcal{H}_{\mathrm{tr}} \rangle_{\mathrm{tr}} &= k_B T \left(\frac{3g}{k^2} k_B T - \frac{1}{2} \right) + \frac{1}{2} \left(m\omega_0^2 - k \right) \langle x^2 \rangle_{\mathrm{tr}} \\
&= k_B T \left(\frac{3g}{k^2} k_B T + \frac{m\omega_0^2}{2k} - 1 \right).
\end{aligned}
\tag{4.23}
$$

Then the variational free energy is

$$
F_{\mathrm{var}} = k_B T \left[\frac{3g}{k^2} k_B T + \frac{m\omega_0^2}{2k} - 1 + \ln \left(\frac{\hbar}{k_B T} \sqrt{\frac{k}{m}} \right) \right].
\tag{4.24}
$$

Similar to before, we use Mathematica to find that

$$
k_m = \frac{1}{2} m\omega_0^2 \left(1 + \sqrt{1 + 48 \frac{k_B T g}{m\omega_0^2}} \right).
\tag{4.25}
$$

The minimized variational free energy is then

$$
F_{\mathrm{var}}(k_m) = k_B T \left[-\frac{36x + (1 + \sqrt{1 + 48x})}{(1 + \sqrt{1 + 48x})^2} + \ln \left(\frac{\hbar \omega_0}{k_B T} \sqrt{\frac{1}{2} + \frac{1}{2}\sqrt{1 + 48x}} \right) \right],
\tag{4.26}
$$

where $x = k_B T g / m^2 \omega_0^4$. Then we can calculate the heat capacity and expand to first order in g,

$$
C_v = -T \frac{\partial^2 F_{\mathrm{var}}(k_m)}{\partial T^2} = k_B - \frac{6 k_B^2 T}{m^2 \omega_0^4} g,
\tag{4.27}
$$

which agrees with (4.15). □

Problem 5 (Lattice gas): Here we will explore in more detail the lattice gas problem in the lecture. We consider N_0 noninteracting absorption sites in the presence of a noninteracting Boltzmann gas, with 2d schematic illustrated in Fig. 2.
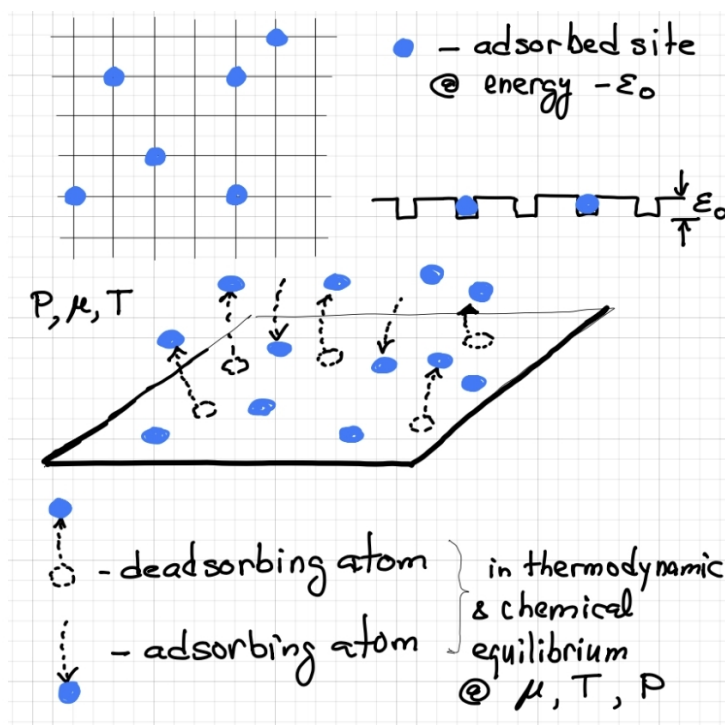

Figure 2: An illustration of a lattice gas with N atoms occupying N_0 absorption sites at temperature T.

(a) "Fermionic" lattice gas

We first focus on the simplest case of only single maximum occupancy per site in a single state of attractive energy $-\epsilon_0$. Thus, there are two states at each site 0 (unoccupied) and $-\epsilon_0$ (occupied by one atom), as illutrated in Fig. 2.

   (i) Compute the canonical partition function $Z(T, N)$, the corresponding free energy $F(T, N)$, and calculate the corresponding chemical potential $\bar{\mu}(T, N)$ as a function of prescribed fixed coverage $N = \sum_{i=1}^{N_0} n_i$.

   (A) using $Z(T, N)$ from above, and

   (B) directly without going through $Z(T, N)$

   Solution.

   (A) First, note that with N atoms to occupy N_0 sites, there are $\binom{N_0}{N}$ microstates with equal energy $\mathcal{H} = -N\epsilon_0$. So the canonical partition function is

   $$Z(T, N) = \binom{N_0}{N} \exp\left(-\beta\mathcal{H}\right) = \frac{N_0!}{N!(N_0 - N)!} e^{N\epsilon_0/k_B T}. \tag{5.1}$$

The free energy is thus

$$F(T, N) = -k_B T \ln Z$$
$$= -k_B T \left[\frac{N\epsilon_0}{k_B T} + N_0 \ln N_0 - N \ln N - (N_0 - N) \ln(N_0 - N) \right]. \quad (5.2)$$

Then it follows that the chemical potential is

$$\bar{\mu}(T, N) = \frac{\partial F}{\partial N} = -\epsilon_0 + k_B T \ln \left(\frac{N}{N_0 - N} \right). \quad (5.3)$$

(B) By definition, the grandcanonical partition function is

$$\mathcal{Z} = \left[1 + e^{\beta(\epsilon_0 + \mu)} \right]^{N_0}. \quad (5.4)$$

So the free energy is

$$\mathcal{F} = -N_0 k_B T \ln \left[1 + e^{\beta(\epsilon_0 + \mu)} \right], \quad (5.5)$$

and the coverage is

$$\overline{N} = -\frac{\partial \mathcal{F}}{\partial \mu} = \frac{N_0}{1 + e^{-\beta(\epsilon_0 + \mu)}}. \quad (5.6)$$

Inverting this expression, we get

$$e^{-\beta(\epsilon_0 + \mu)} = \frac{N_0 - N}{N} \Rightarrow \mu = -\epsilon_0 + \ln \left(\frac{N}{N_0 - N} \right), \quad (5.7)$$

which agrees with result for $\bar{\mu}$ in part (A).

$\square$

(ii) Using $\mathcal{Z}(T, \mu)$ or $\mathcal{F}(T, \mu)$ from either method above, compute the (1) entropy $S(T, \mu)$ and most importantly (2) the coverage – the average number of particles $\overline{N}(T, \mu)$ and demonstrate that it agrees with the $\mu(T, N)$ expression obtained from the canonical ensemble.

Solution.
In part (i-B), we have already calculated (2) the coverage and check the agreement with $\bar{\mu}$ in (i-A). So now, using Mathematica, we calculate (1)
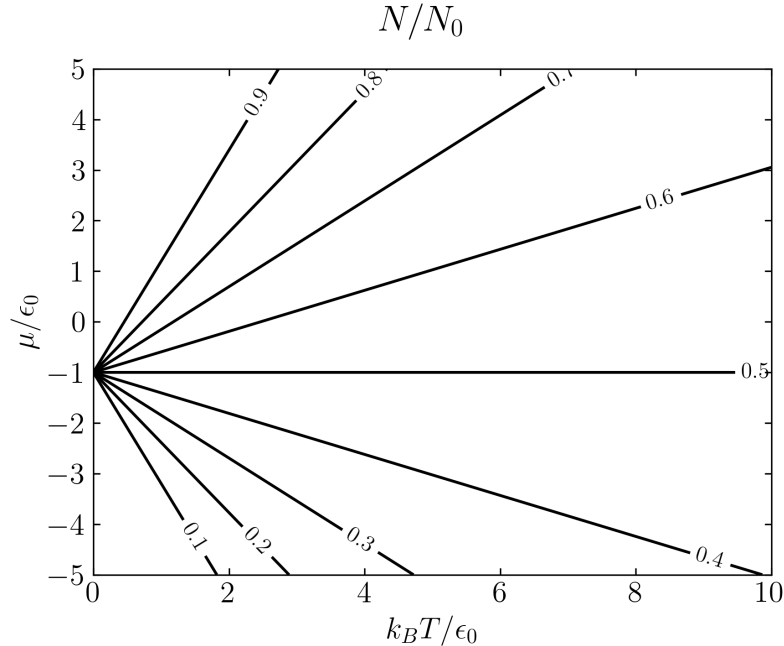
$$S(T, \mu) = -\frac{\partial \mathcal{F}}{\partial T}$$
$$= N_0 k_B \frac{\partial}{\partial T} \left\{ T \ln \left[1 + \exp \left(\frac{\epsilon_0 + \mu}{k_B T} \right) \right] \right\}$$
$$= N_0 k_B \left\{ \ln \left[1 + e^{(\epsilon_0 + \mu)/k_B T} \right] - \frac{\epsilon_0 + \mu}{k_B T} \frac{1}{1 + e^{-(\epsilon_0 + \mu)/k_B T}} \right\}. \quad (5.8)$$

$\square$

(iii) Sketch $\overline{N}(T, \mu)$, discussing its low and high T limits, and positive and negative μ limits. What is the characteristic value of the chemical potential μ at which the coverage changes at low T?

Solution.

A contour plot is given below.

$$N/N_0$$

At low T and negative μ, there is almost no coverage as $N/N_0 \to 0$. At low T and positive μ, $N/N_0 \to 1$ and the change occurs at $\mu/\epsilon_0 = -1$. At high T, the coverage changes less drastically for negative and positive μ. $\qquad \square$

(iv) As discussed in class, the adsorbed atoms are in thermal and chemical equilibrium with the Boltzmann vapor above it, with a common temperature T and chemical potential μ. Use this observation and your previous homework computation for the chemical potential of the Boltzmann gas to express your above result for coverage $\overline{N}(T, P)$ as a function of the pressure of the *gas*.

Solution.

Because they are in chemical equilibrium, we can write the chemical potential μ as

$$\mu = k_B T \ln \left(n \lambda_{dB}^3 \right) = k_B T \ln \left(\frac{P}{k_B T} \lambda_{dB}^3 \right), \tag{5.9}$$

where λ_{dB} is the deBroglie wavelength and we have made use of the fact that a Boltzmann gas is ideal. Then, plugging this into the expression for the coverage, we can write

$$\overline{N}(T, P) = \frac{N_0}{1 + (k_B T / P \lambda_{dB}^3) e^{-\epsilon_0 / k_B T}}. \tag{5.10}$$

$\square$

(b) "Bosonic" lattice gas

Now let's repeat the above analysis, but now allowing an arbitrary occupation of sites, $n_i \in \{0, 1, 2, 3, \ldots\}$, and ignoring particle interactions, i.e., still having energy $-\epsilon_0$ per occupied particle.

(i) Calculate the grandcanonical partition function $\mathcal{Z}(T, \mu)$ and the corresponding free energy $\mathcal{F}(T, \mu)$ for prescribed chemical potential μ, directly, without going through $Z(T, N)$.

(ii) Using $\mathcal{Z}(T, \mu)$ or $\mathcal{F}(T, \mu)$ compute the (1) pressure $P(T, \mu)$, (2) entropy $S(T, \mu)$ and most importantly (3) the coverage – the average number of particles $\overline{N}(T, \mu)$.

(iii) Sketch $\overline{N}(T, \mu)$, discussing its low and high T limits, and positive and negative μ. Indicate unphysical regime of μ and speculate what actually happens in a physical system, namely what is the model missing to give physical answers.

Solution.

(i) By definition and using the well-known geometric series $\sum_{n \in \mathbb{N}} x^n = 1/(1-x)$, we can calculate

$$\mathcal{Z} = \left[\sum_{n_i=0}^{\infty} e^{\beta(\epsilon_0 + \mu)n_i} \right]^{N_0} = \left[1 - \exp\left(\frac{\epsilon_0 + \mu}{k_B T} \right) \right]^{-N_0}. \tag{5.11}$$

Then the free energy is

$$\mathcal{F} = -k_B T \ln \mathcal{Z} = N_0 k_B T \ln \left[1 - \exp\left(\frac{\epsilon_0 + \mu}{k_B T} \right) \right]. \tag{5.12}$$

(ii) Then it folows that (1) the pressure is

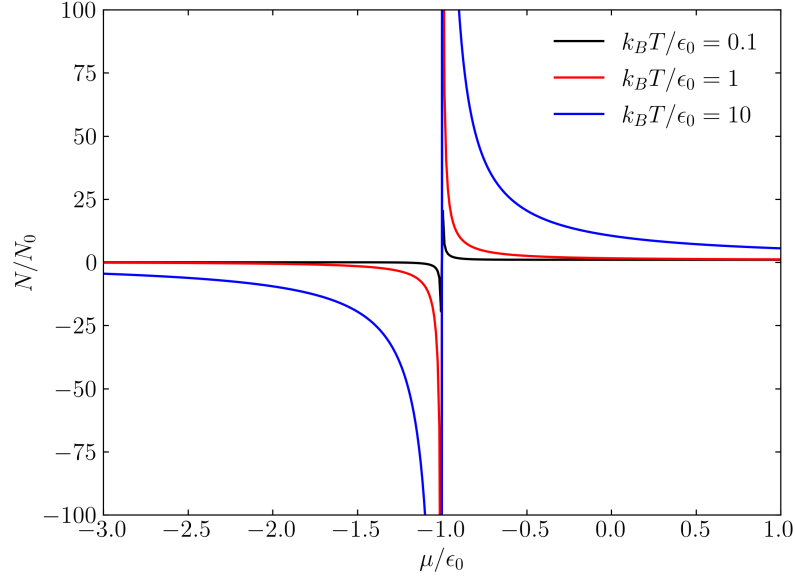$$P(T, \mu) = -\frac{\partial \mathcal{F}}{\partial V} = 0, \tag{5.13}$$

(2) the entropy is

$$S(T, \mu) = -\frac{\partial \mathcal{F}}{\partial T} = N_0 k_B \left[\frac{\epsilon_0 + \mu}{k_B T} \frac{1}{1 - \exp\left[-(\epsilon_0 + \mu)/k_B T \right]} - \ln\left[1 - e^{(\epsilon_0 + \mu)/k_B T} \right] \right], \tag{5.14}$$

(3) the coverage is

$$\overline{N} = -\frac{\partial \mathcal{F}}{\partial \mu} = \frac{N_0}{1 - \exp\left[-(\epsilon_0 + \mu)/k_B T \right]}. \tag{5.15}$$

(iii) A plot of $\overline{N}$ is included below.

The behavior is very different from the Fermionic case. Both at low and high T, the coverage vanishes everywhere except for when $\mu = -\epsilon_0$. At negative and positive μ, $\overline{N}$ also vanishes. Clearly, N cannot be negative, so the unphysical range of μ is $\mu \leq -1$. This model, since it allows for infinite occupation, can intuitively lead to $\overline{N}$ blowing up. By restricting the maximum occupation for each site, it should give a more physical answer. □