
Review Problems & Solutions

The third in-class test will take place on Wednesday **11/28/07** from **2:30 to 4:00** pm. There will be a recitation with test review on Monday **11/26/07**.

The test is 'closed book,' but if you wish you may bring a one-sided sheet of formulas. The test will be composed entirely from a subset of the following problems. Thus if you are familiar and comfortable with these problems, there will be no surprises!

You may find the following information helpful:

Physical Constants

Electron mass	$m_e \approx 9.1 \times 10^{-31} kg$	Proton mass	$m_p \approx 1.7 \times 10^{-27} kg$
Electron Charge	$e \approx 1.6 \times 10^{-19} C$	Planck's const./ 2π	$\hbar \approx 1.1 \times 10^{-34} Js^{-1}$
Speed of light	$c \approx 3.0 \times 10^8 ms^{-1}$	Stefan's const.	$\sigma \approx 5.7 \times 10^{-8} Wm^{-2}K^{-4}$
Boltzmann's const.	$k_B \approx 1.4 \times 10^{-23} JK^{-1}$	Avogadro's number	$N_0 \approx 6.0 \times 10^{23} mol^{-1}$

Conversion Factors

$$1 atm \equiv 1.0 \times 10^5 Nm^{-2} \qquad 1 \text{\AA} \equiv 10^{-10} m \qquad 1 eV \equiv 1.1 \times 10^4 K$$

Thermodynamics

$$dE = TdS + dW \qquad \text{For a gas: } dW = -PdV \qquad \text{For a wire: } dW = Jdx$$

Mathematical Formulas

$$\int_0^\infty dx x^n e^{-\alpha x} = \frac{n!}{\alpha^{n+1}} \qquad \left(\frac{1}{2}\right)! = \frac{\sqrt{\pi}}{2}$$

$$\int_{-\infty}^\infty dx \exp\left[-ikx - \frac{x^2}{2\sigma^2}\right] = \sqrt{2\pi\sigma^2} \exp\left[-\frac{\sigma^2 k^2}{2}\right] \qquad \lim_{N \rightarrow \infty} \ln N! = N \ln N - N$$

$$\langle e^{-ikx} \rangle = \sum_{n=0}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle \qquad \ln \langle e^{-ikx} \rangle = \sum_{n=1}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle_c$$

$$\cosh(x) = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \dots \qquad \sinh(x) = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \dots$$

$$\text{Surface area of a unit sphere in } d \text{ dimensions} \qquad S_d = \frac{2\pi^{d/2}}{(d/2-1)!}$$

1. *Debye–Hückel theory and ring diagrams:* The virial expansion gives the gas pressure as an *analytic* expansion in the density $n = N/V$. Long range interactions can result in *non-analytic* corrections to the ideal gas equation of state. A classic example is the Coulomb interaction in plasmas, whose treatment by Debye–Hückel theory is equivalent to summing all the *ring diagrams* in a cumulant expansion.

For simplicity consider a gas of N electrons moving in a uniform background of positive charge density Ne/V to ensure overall charge neutrality. The Coulomb interaction takes the form

$$\mathcal{U}_Q = \sum_{i < j} \mathcal{V}(\vec{q}_i - \vec{q}_j), \quad \text{with} \quad \mathcal{V}(\vec{q}) = \frac{e^2}{4\pi|\vec{q}|} - c.$$

The constant c results from the background and ensures that the first order correction vanishes, i.e. $\int d^3\vec{q} \mathcal{V}(\vec{q}) = 0$.

(a) Show that the Fourier transform of $\mathcal{V}(\vec{q})$ takes the form

$$\tilde{\mathcal{V}}(\vec{\omega}) = \begin{cases} e^2/\omega^2 & \text{for } \vec{\omega} \neq 0 \\ 0 & \text{for } \vec{\omega} = 0 \end{cases}.$$

• The Fourier transform of $\mathcal{V}(\vec{q})$ is singular at the origin, and can be defined explicitly as

$$\tilde{\mathcal{V}}(\vec{\omega}) = \lim_{\varepsilon \rightarrow 0} \int d^3\vec{q} \mathcal{V}(\vec{q}) e^{i\vec{\omega} \cdot \vec{q} - \varepsilon q}.$$

The result at $\vec{\omega} = 0$ follows immediately from the definition of c . For $\vec{\omega} \neq 0$,

$$\begin{aligned} \tilde{\mathcal{V}}(\vec{\omega}) &= \lim_{\varepsilon \rightarrow 0} \int d^3\vec{q} \left(\frac{e^2}{4\pi q} - c \right) e^{i\vec{\omega} \cdot \vec{q} - \varepsilon q} = \lim_{\varepsilon \rightarrow 0} \int d^3\vec{q} \left(\frac{e^2}{4\pi q} \right) e^{i\vec{\omega} \cdot \vec{q} - \varepsilon q} \\ &= \lim_{\varepsilon \rightarrow 0} \left[2\pi \int_0^\pi \sin \theta d\theta \int_0^\infty q^2 dq \left(\frac{e^2}{4\pi q} \right) e^{i\omega q \cos \theta - \varepsilon q} \right] \\ &= -\frac{e^2}{2} \int_0^\infty \frac{e^{i\omega q - \varepsilon q} - e^{-i\omega q - \varepsilon q}}{i\omega} dq \\ &= \lim_{\varepsilon \rightarrow 0} \frac{e^2}{2i\omega} \left(\frac{1}{i\omega - \varepsilon} + \frac{1}{i\omega + \varepsilon} \right) = \lim_{\varepsilon \rightarrow 0} \left(\frac{e^2}{\omega^2 + \varepsilon^2} \right) = \frac{e^2}{\omega^2}. \end{aligned}$$

(b) In the cumulant expansion for $\langle \mathcal{U}_Q^\ell \rangle_c^0$, we shall retain only the diagrams forming a ring; which are proportional to

$$R_\ell = \int \frac{d^3\vec{q}_1}{V} \cdots \frac{d^3\vec{q}_\ell}{V} \mathcal{V}(\vec{q}_1 - \vec{q}_2) \mathcal{V}(\vec{q}_2 - \vec{q}_3) \cdots \mathcal{V}(\vec{q}_\ell - \vec{q}_1).$$

Use properties of Fourier transforms to show that

$$R_\ell = \frac{1}{V^{\ell-1}} \int \frac{d^3\vec{\omega}}{(2\pi)^3} \tilde{\mathcal{V}}(\vec{\omega})^\ell.$$

- In the cumulant expansion for $\langle \mathcal{U}_Q^\ell \rangle_c^0$, we retain only the diagrams forming a ring. The contribution of these diagrams to the partition function is

$$\begin{aligned} R_\ell &= \int \frac{d^3 \vec{q}_1}{V} \frac{d^3 \vec{q}_2}{V} \cdots \frac{d^3 \vec{q}_\ell}{V} \mathcal{V}(\vec{q}_1 - \vec{q}_2) \mathcal{V}(\vec{q}_2 - \vec{q}_3) \cdots \mathcal{V}(\vec{q}_\ell - \vec{q}_1) \\ &= \frac{1}{V^\ell} \int \cdots \int d^3 \vec{x}_1 d^3 \vec{x}_2 \cdots d^3 \vec{x}_{\ell-1} d^3 \vec{q}_\ell \mathcal{V}(\vec{x}_1) \mathcal{V}(\vec{x}_2) \cdots \mathcal{V}(\vec{x}_{\ell-1}) \mathcal{V} \left(- \sum_{i=1}^{\ell-1} \vec{x}_i \right), \end{aligned}$$

where we introduced the new set of variables $\{\vec{x}_i \equiv \vec{q}_i - \vec{q}_{i+1}\}$, for $i = 1, 2, \dots, \ell - 1$. Note that since the integrand is independent of \vec{q}_ℓ ,

$$R_\ell = \frac{1}{V^{\ell-1}} \int \cdots \int d^3 \vec{x}_1 d^3 \vec{x}_2 \cdots d^3 \vec{x}_{\ell-1} \mathcal{V}(\vec{x}_1) \mathcal{V}(\vec{x}_2) \cdots \mathcal{V} \left(- \sum_{i=1}^{\ell-1} \vec{x}_i \right).$$

Using the inverse Fourier transform

$$\mathcal{V}(\vec{q}) = \frac{1}{(2\pi)^3} \int d^3 \vec{\omega} \cdot \tilde{\mathcal{V}}(\vec{\omega}) e^{-i\vec{q} \cdot \vec{\omega}},$$

the integral becomes

$$\begin{aligned} R_\ell &= \frac{1}{(2\pi)^{3\ell} V^{\ell-1}} \int \cdots \int d^3 \vec{x}_1 \cdots d^3 \vec{x}_{\ell-1} \tilde{\mathcal{V}}(\vec{\omega}_1) e^{-i\vec{\omega}_1 \cdot \vec{x}_1} \tilde{\mathcal{V}}(\vec{\omega}_2) e^{-i\vec{\omega}_2 \cdot \vec{x}_2} \\ &\quad \cdots \tilde{\mathcal{V}}(\vec{\omega}_\ell) \exp \left(-i \sum_{k=1}^{\ell-1} \vec{\omega}_\ell \cdot \vec{x}_k \right) d^3 \vec{\omega}_1 \cdots d^3 \vec{\omega}_\ell. \end{aligned}$$

Since

$$\int \frac{d^3 \vec{q}}{(2\pi)^3} e^{-i\vec{\omega} \cdot \vec{q}} = \delta^3(\vec{\omega}),$$

we have

$$R_\ell = \frac{1}{(2\pi)^3 V^{\ell-1}} \int \cdots \int \left(\prod_{k=1}^{\ell-1} \delta(\vec{\omega}_k - \vec{\omega}_\ell) \tilde{\mathcal{V}}(\vec{\omega}_k) d^3 \vec{\omega}_k \right) d^3 \vec{\omega}_\ell,$$

resulting finally in

$$R_\ell = \frac{1}{V^{\ell-1}} \int \frac{d^3 \vec{\omega}}{(2\pi)^3} \tilde{\mathcal{V}}(\vec{\omega})^\ell.$$

(c) Show that the number of ring graphs generated in $\langle \mathcal{U}_Q^\ell \rangle_c^0$ is

$$S_\ell = \frac{N!}{(N-\ell)!} \times \frac{(\ell-1)!}{2} \approx \frac{(\ell-1)!}{2} N^\ell.$$

- The number of rings graphs generated in $\langle \mathcal{U}_Q^\ell \rangle_c^0$ is given by the product of the number of ways to choose ℓ particles out of a total of N ,

$$\frac{N!}{(N-\ell)!}.$$

multiplied by the number of ways to arrange the ℓ particles in a ring

$$\frac{\ell!}{2\ell}.$$

The numerator is the number of ways of distributing the ℓ labels on the ℓ points of the ring. This overcounts by the number of equivalent arrangements that appear in the denominator. The factor of $1/2$ comes from the equivalence of clockwise and counterclockwise arrangements (reflection), and there are ℓ equivalent choices for the starting point of the ring (rotations). Hence

$$S_\ell = \frac{N!}{(N-\ell)!} \times \frac{\ell!}{2\ell} = \frac{N!}{(N-\ell)!} \times \frac{(\ell-1)!}{2}.$$

For $N \gg \ell$, we can approximate $N(N-1)\cdots(N-\ell+1) \approx N^\ell$, and

$$S_\ell \approx \frac{(\ell-1)!}{2} N^\ell.$$

Another way to justify this result is by induction: A ring of length $\ell+1$ can be created from a ring of ℓ links by inserting an additional point in between any of the existing ℓ nodes. Hence $S_{\ell+1} = S_\ell \times (N-\ell-1) \times \ell$, leading to the above result, when starting with $S_2 = N(N-1)/2$.

(d) Show that the contribution of the ring diagrams can be summed as

$$\begin{aligned} \ln Z_{\text{rings}} &= \ln Z_0 + \sum_{\ell=2}^{\infty} \frac{(-\beta)^\ell}{\ell!} S_\ell R_\ell \\ &\approx \ln Z_0 + \frac{V}{2} \int_0^\infty \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \left[\left(\frac{\kappa}{\omega} \right)^2 - \ln \left(1 + \frac{\kappa^2}{\omega^2} \right) \right], \end{aligned}$$

where $\kappa = \sqrt{\beta e^2 N/V}$ is the inverse Debye screening length.

(Hint: Use $\ln(1+x) = -\sum_{\ell=1}^{\infty} (-x)^\ell/\ell$.)

- The contribution of the ring diagrams is summed as

$$\begin{aligned}
\ln Z_{\text{rings}} &= \ln Z_0 + \sum_{\ell=2}^{\infty} \frac{(-\beta)^\ell}{\ell!} S_\ell R_\ell \\
&= \ln Z_0 + \sum_{\ell=2}^{\infty} \frac{(-\beta)^\ell (\ell-1)!}{\ell!} N^\ell \frac{1}{V^{\ell-1}} \int \frac{d^3 \vec{\omega}}{(2\pi)^3} \tilde{\mathcal{V}}(\vec{\omega})^\ell \\
&= \ln Z_0 + \frac{V}{2} \int_0^\infty \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \sum_{\ell=2}^{\infty} \frac{1}{\ell} \left(-\frac{\beta N}{V} \tilde{\mathcal{V}}(\omega) \right)^\ell \\
&= \ln Z_0 + \frac{V}{2} \int_0^\infty \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \sum_{\ell=2}^{\infty} \frac{1}{\ell} \left(-\frac{\beta N e^2}{V\omega^2} \right)^\ell \\
&= \ln Z_0 + \frac{V}{2} \int_0^\infty \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \left[\frac{\beta N e^2}{V\omega^2} - \ln \left(1 + \frac{\beta N e^2}{V\omega^2} \right) \right],
\end{aligned}$$

where we have used $\ln(1+x) = -\sum_{\ell=1}^{\infty} (-x)^\ell / \ell$. Finally, substituting $\kappa = \sqrt{\beta e^2 N / V}$, leads to

$$\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{2} \int_0^\infty \frac{4\pi\omega^2 d\omega}{(2\pi)^3} \left[\left(\frac{\kappa}{\omega} \right)^2 - \ln \left(1 + \frac{\kappa^2}{\omega^2} \right) \right].$$

- (e) The integral in the previous part can be simplified by changing variables to $x = \kappa/\omega$, and performing integration by parts. Show that the final result is

$$\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{12\pi} \kappa^3.$$

- Changing variables to $x = \kappa/\omega$, and integrating the integrand by parts, gives

$$\begin{aligned}
\int_0^\infty \omega^2 d\omega \left[\left(\frac{\kappa}{\omega} \right)^2 - \ln \left(1 + \frac{\kappa^2}{\omega^2} \right) \right] &= \kappa^3 \int_0^\infty \frac{dx}{x^4} [x^2 - \ln(1+x^2)] \\
&= \frac{\kappa^3}{3} \int_0^\infty \frac{dx}{x^3} \left[2x - \frac{2x}{1+x^2} \right] = \frac{2\kappa^3}{3} \int_0^\infty \frac{dx}{1+x^2} = \frac{\pi\kappa^3}{3},
\end{aligned}$$

resulting in

$$\ln Z_{\text{rings}} = \ln Z_0 + \frac{V}{4\pi^2} \cdot \frac{\pi\kappa^3}{3} = \ln Z_0 + \frac{V}{12\pi} \kappa^3.$$

- (f) Calculate the correction to pressure from the above ring diagrams.

- The correction to the ideal gas pressure due to the Debye–Hückel approximation is

$$\begin{aligned}
P &= k_B T \left(\left. \frac{\partial \ln Z_{\text{rings}}}{\partial V} \right|_{T,N} \right) \\
&= P_0 + k_B T \left. \frac{\partial}{\partial V} \left(\frac{V \kappa^3}{12\pi} \right) \right|_{T,N} = P_0 - \frac{k_B T}{24\pi} \kappa^3 \\
&= P_0 - \frac{k_B T}{24\pi} \left(\frac{e^2 N}{k_B T V} \right)^{3/2}.
\end{aligned}$$

Note that the correction to the ideal gas behavior is non-analytic, and cannot be expressed by a virial series. This is due to the long range nature of the Coulomb interaction.

(g) We can introduce an effective potential $\bar{V}(\vec{q} - \vec{q}')$ between two particles by integrating over the coordinates of all the other particles. This is equivalent to an expectation value that can be calculated perturbatively in a cumulant expansion. If we include only the loop-less diagrams (the analog of the rings) between the particles, we have

$$\bar{V}(\vec{q} - \vec{q}') = V(\vec{q} - \vec{q}') + \sum_{\ell=1}^{\infty} (-\beta N)^{\ell} \int \frac{d^3 \vec{q}_1}{V} \cdots \frac{d^3 \vec{q}_{\ell}}{V} \mathcal{V}(\vec{q} - \vec{q}_1) \mathcal{V}(\vec{q}_1 - \vec{q}_2) \cdots \mathcal{V}(\vec{q}_{\ell} - \vec{q}').$$

Show that this sum leads to the screened Coulomb interaction $\bar{V}(\vec{q}) = \exp(-\kappa|\vec{q}|)/(4\pi|\vec{q}|)$.

- Introducing the effective potential $\bar{\mathcal{V}}(\vec{q} - \vec{q}')$, and summing over the loop-less diagrams gives

$$\begin{aligned}
\bar{\mathcal{V}}(\vec{q} - \vec{q}') &= \mathcal{V}(\vec{q} - \vec{q}') + \sum_{\ell=1}^{\infty} (-\beta N)^{\ell} \int \frac{d^3 \vec{q}_1}{V} \cdots \frac{d^3 \vec{q}_{\ell}}{V} \mathcal{V}(\vec{q} - \vec{q}_1) \mathcal{V}(\vec{q}_1 - \vec{q}_2) \cdots \mathcal{V}(\vec{q}_{\ell} - \vec{q}') \\
&= \mathcal{V}(\vec{q} - \vec{q}') - \beta N \int \frac{d^3 \vec{q}_1}{V} \mathcal{V}(\vec{q} - \vec{q}_1) \mathcal{V}(\vec{q}_1 - \vec{q}') \\
&\quad + (\beta N)^2 \int \frac{d^3 \vec{q}_1}{V} \frac{d^3 \vec{q}_2}{V} \mathcal{V}(\vec{q} - \vec{q}_1) \mathcal{V}(\vec{q}_1 - \vec{q}_2) \mathcal{V}(\vec{q}_2 - \vec{q}') - \cdots.
\end{aligned}$$

Using the changes of notation

$$\begin{aligned}
\vec{x}_1 &\equiv \vec{q}, & \vec{x}_2 &\equiv \vec{q}', & \vec{x}_3 &\equiv \vec{q}_1, & \vec{x}_4 &\equiv \vec{q}_2, & \cdots & \vec{x}_{\ell} &\equiv \vec{q}_{\ell}, \\
\mathcal{V}_{12} &\equiv \mathcal{V}(\vec{x}_1 - \vec{x}_2), & \text{and} & & n &\equiv N/V,
\end{aligned}$$

we can write

$$\bar{\mathcal{V}}_{12} = \mathcal{V}_{12} - \beta n \int d^3 \vec{x}_3 \mathcal{V}_{13} \mathcal{V}_{32} + (\beta n)^2 \int d^3 \vec{x}_3 d^3 \vec{x}_4 \mathcal{V}_{13} \mathcal{V}_{34} \mathcal{V}_{42} - \cdots.$$

Using the inverse Fourier transform (as in part (a)), and the notation $\vec{x}_{ij} \equiv \vec{x}_i - \vec{x}_j$,

$$\bar{\mathcal{V}}_{12} = \mathcal{V}_{12} - \beta n \int \frac{d^3 \vec{x}_3}{(2\pi)^6} \tilde{\mathcal{V}}(\vec{\omega}_{13}) \tilde{\mathcal{V}}(\vec{\omega}_{32}) e^{-i(\vec{x}_{13} \cdot \vec{\omega}_{13} + \vec{x}_{32} \cdot \vec{\omega}_{32})} d^3 \vec{\omega}_{13} d^3 \vec{\omega}_{32} + \cdots,$$

and employing the delta function, as in part (a)

$$\begin{aligned}\bar{\mathcal{V}}_{12} &= \mathcal{V}_{12} - \beta n \int \frac{d^3\vec{\omega}_{13} d^3\vec{\omega}_{32}}{(2\pi)^3} \delta^3(\vec{\omega}_{13} - \vec{\omega}_{32}) \tilde{\mathcal{V}}(\vec{\omega}_{13}) \tilde{\mathcal{V}}(\vec{\omega}_{32}) \exp[\vec{x}_1 \cdot \vec{\omega}_{13} - \vec{x}_2 \cdot \vec{\omega}_{32}] + \dots \\ &= \mathcal{V}_{12} - \beta n \int \frac{d^3\vec{\omega}}{(2\pi)^3} [\tilde{\mathcal{V}}(\vec{\omega})]^2 \exp[\vec{\omega} \cdot \vec{x}_{12}] + \dots\end{aligned}$$

Generalizing this result and dropping the subscript such that $\vec{x} \equiv \vec{x}_{12}$,

$$\bar{\mathcal{V}}_{12} = \mathcal{V}_{12} + \sum_{\ell=1}^{\infty} \frac{(-\beta n)^\ell}{(2\pi)^3} \int [\tilde{\mathcal{V}}(\vec{\omega})]^{\ell+1} e^{i\vec{x} \cdot \vec{\omega}} d^3\vec{\omega}.$$

Finally, including the Fourier transform of the direct potential (first term), gives

$$\begin{aligned}\bar{\mathcal{V}}_{12} &= \sum_{\ell=0}^{\infty} \int \frac{d^3\vec{\omega}}{(2\pi)^3} (-\beta n)^\ell \frac{e^{2\ell+2}}{\omega^{2\ell+2}} e^{i\vec{x} \cdot \vec{\omega}} = \sum_{\ell=0}^{\infty} \int \frac{d^3\vec{\omega}}{(2\pi)^3} \frac{(-1)^\ell e^2 \kappa^{2\ell}}{\omega^{2\ell+2}} e^{ix\omega \cos \theta} \\ &= \int_0^\infty d\omega \sum_{\ell=0}^{\infty} \frac{(-1)^\ell e^2}{2\pi^2} \left(\frac{\kappa}{\omega}\right)^{2\ell} \int_{-1}^1 e^{ix\omega \cos \theta} d \cos \theta \\ &= \int_0^\infty d\omega \frac{e^2}{2\pi^2} \frac{2 \sin x\omega}{x\omega} \sum_{\ell=0}^{\infty} (-1)^\ell \left(\frac{\kappa}{\omega}\right)^{2\ell}.\end{aligned}$$

Setting $y \equiv \omega/\kappa$, gives

$$\bar{\mathcal{V}}_{12} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{e^2}{2\pi^2} \kappa \frac{e^{ix\kappa y} - e^{-ix\kappa y}}{2ix\kappa y} \frac{-1}{y^2 + 1} dy.$$

Intergrating in the complex plane, via the residue theorem, gives

$$\bar{\mathcal{V}}_{12} = \frac{e^2}{4\pi^2} \left(\frac{e^{-\kappa x}}{2x} + \frac{e^{-\kappa x}}{2x} \right) \cdot \pi = \frac{e^2 e^{-\kappa x}}{4\pi x}.$$

Recalling our original notation, $x = |\vec{q} - \vec{q}'| \equiv |\vec{q}|$, we obtain the screened Coulomb potential

$$\bar{\mathcal{V}}(\vec{q}) = \frac{e^2}{4\pi} \frac{e^{-\kappa|\vec{q}|}}{|\vec{q}|}.$$

2. Virial coefficients: Consider a gas of particles in d -dimensional space interacting through a pair-wise central potential, $\mathcal{V}(r)$, where

$$\mathcal{V}(r) = \begin{cases} +\infty & \text{for } 0 < r < a, \\ -\varepsilon & \text{for } a < r < b, \\ 0 & \text{for } b < r < \infty. \end{cases}$$

(a) Calculate the second virial coefficient $B_2(T)$, and comment on its high and low temperature behaviors.

- The second virial coefficient is obtained from

$$B_2 \equiv -\frac{1}{2} \int d^d r_{12} \{ \exp[-\beta \mathcal{V}(r_{12})] - 1 \},$$

where $r_{12} \equiv |\vec{r}_1 - \vec{r}_2|$, as

$$\begin{aligned} B_2 &= -\frac{1}{2} \left[\int_0^a d^d r_{12} (-1) + \int_a^b d^d r_{12} (e^{\beta \varepsilon} - 1) \right] \\ &= -\frac{1}{2} \{ V_d(a)(-1) + [V_d(b) - V_d(a)] \cdot [\exp(\beta \varepsilon) - 1] \}, \end{aligned}$$

where

$$V_d(r) = \frac{S_d}{d} r^d = \frac{2\pi^{d/2}}{d(d/2 - 1)!} r^d,$$

is the volume of a d -dimensional sphere of radius r . Thus,

$$B_2(T) = \frac{1}{2} V_d(b) - \frac{1}{2} \exp(\beta \varepsilon) [V_d(b) - V_d(a)].$$

For high temperatures $\exp(\beta \varepsilon) \approx 1 + \beta \varepsilon$, and

$$B_2(T) \approx \frac{1}{2} V_d(a) - \frac{\beta \varepsilon}{2} [V_d(b) - V_d(a)].$$

At the highest temperatures, $\beta \varepsilon \ll 1$, the hard-core part of the potential is dominant, and

$$B_2(T) \approx \frac{1}{2} V_d(a).$$

For low temperatures $\beta \gg 1$, the attractive component takes over, and

$$\begin{aligned} B_2 &= -\frac{1}{2} \{ V_d(a)(-1) + [V_d(b) - V_d(a)] \cdot [\exp(\beta \varepsilon) - 1] \} \\ &\approx -\frac{1}{2} [V_d(b) - V_d(a)] \exp(\beta \varepsilon), \end{aligned}$$

resulting in $B_2 < 0$.

(b) Calculate the first correction to isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_{T,N}.$$

- The isothermal compressibility is defined by

$$\kappa_T \equiv -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_{T,N}.$$

From the expansion

$$\frac{P}{k_B T} = \frac{N}{V} + \frac{N^2}{V^2} B_2,$$

for constant temperature and particle number, we get

$$\frac{1}{k_B T} dP = -\frac{N}{V^2} dV - 2B_2 \frac{N^2}{V^3} dV.$$

Thus

$$\left. \frac{\partial V}{\partial P} \right|_{T,N} = -\frac{1}{k_B T} \frac{1}{N/V^2 + 2B_2 N^2/V^3} = -\frac{V^2}{N k_B T} \left(\frac{1}{1 + 2B_2 N/V} \right),$$

and

$$\kappa_T = \frac{V}{N k_B T} \left(\frac{1}{1 + 2B_2 N/V} \right) \approx \frac{V}{N k_B T} \left(1 - 2B_2 \frac{N}{V} \right).$$

(c) In the high temperature limit, reorganize the equation of state into the van der Waals form, and identify the van der Waals parameters.

- Including the correction introduced by the second virial coefficient, the equation of state becomes

$$\frac{PV}{N k_B T} = 1 + \frac{N}{V} B_2(T).$$

Using the expression for B_2 in the high temperature limit,

$$\frac{PV}{N k_B T} = 1 + \frac{N}{2V} \{V_d(a) - \beta \varepsilon [V_d(b) - V_d(a)]\},$$

and

$$P + \frac{N^2}{2V^2} \varepsilon [V_d(b) - V_d(a)] = k_B T \frac{N}{V} \left(1 + \frac{N}{2V} V_d(a) \right).$$

Using the variable $n = N/V$, and noting that for low concentrations

$$1 + \frac{n}{2} V_d(a) \approx \left(1 - \frac{n}{2} V_d(a) \right)^{-1} = V \left(V - \frac{N}{2} V_d(a) \right)^{-1},$$

the equation of state becomes

$$\left(P + \frac{n^2 \varepsilon}{2} [V_d(b) - V_d(a)] \right) \cdot \left(V - \frac{N}{2} V_d(a) \right) = N k_B T.$$

This can be recast in the usual van der Waals form

$$(P - an^2) \cdot (V - Nb) = Nk_B T,$$

with

$$a = \frac{\varepsilon}{2} [V_d(b) - V_d(a)], \quad \text{and} \quad b = \frac{1}{2} V_d(a).$$

(d) For $b = a$ (a hard sphere), and $d = 1$, calculate the third virial coefficient $B_3(T)$.

- By definition, the third virial coefficient is

$$B_3 = -\frac{1}{3} \int d^d r d^d r' f(r) f(r') f(r - r'),$$

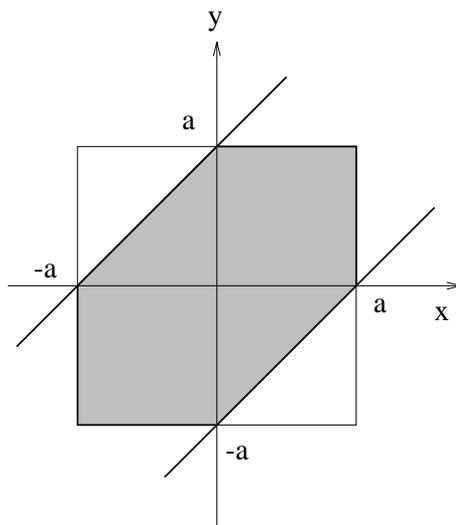
where, for a hard core gas

$$f(r) \equiv \exp\left(-\frac{\mathcal{V}(r)}{k_B T}\right) - 1 = \begin{cases} -1 & \text{for } 0 < r < a, \\ 0 & \text{for } a < r < \infty. \end{cases}$$

In one-dimension, the only contributions come from $0 < r$, and $r' < a$, where $f(r) = f(r') = -1$. Using the notations $|x| \equiv r$, $|y| \equiv r'$ (i.e. $-a < x$, and $y < a$),

$$B_3 = -\frac{1}{3} \int_{-a}^a dx \int_{-a}^a dy \cdot f(x - y) = \frac{1}{3} \int \int_{-a < x, y < a, -a < x - y < a} (-1) = \frac{1}{3} \frac{6}{8} (2a)^2 = a^2,$$

where the relevant integration area is plotted below.



3. *Dieterici's equation:* A gas obeys Dieterici's equation of state:

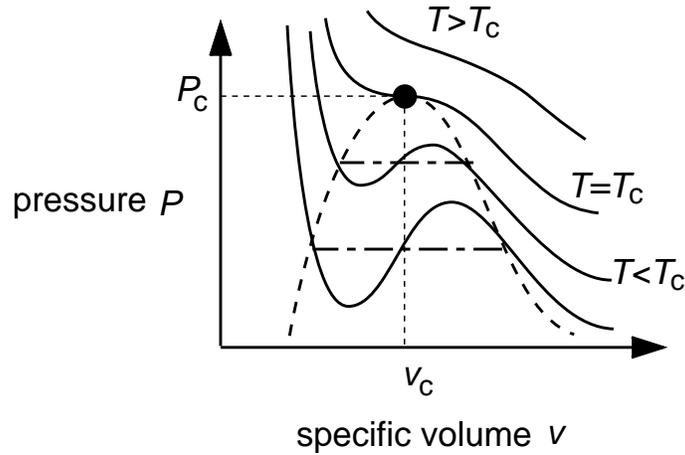
$$P(v - b) = k_B T \exp\left(-\frac{a}{k_B T v}\right),$$

where $v = V/N$.

(a) Find the ratio $Pv/k_B T$ at the critical point.

- The critical point is the point of inflection, described by

$$\left.\frac{\partial P}{\partial v}\right|_{T_c, N} = 0, \quad \text{and} \quad \left.\frac{\partial^2 P}{\partial v^2}\right|_{T_c, N} = 0.$$



The first derivative of P is

$$\begin{aligned} \left.\frac{\partial P}{\partial v}\right|_{T_c, N} &= \frac{\partial}{\partial v} \left[\frac{k_B T}{v - b} \exp\left(-\frac{a}{k_B T v}\right) \right] = \frac{k_B T}{v - b} \exp\left(-\frac{a}{k_B T v}\right) \left(\frac{a}{k_B T v^2} - \frac{1}{v - b} \right) \\ &= P \left(\frac{a}{k_B T v^2} - \frac{1}{v - b} \right), \end{aligned}$$

while a second derivative gives

$$\begin{aligned} \left.\frac{\partial^2 P}{\partial v^2}\right|_{T_c, N} &= \frac{\partial}{\partial v} \left[P \left(\frac{a}{k_B T v^2} - \frac{1}{v - b} \right) \right] \\ &= \frac{\partial P}{\partial v} \left(\frac{a}{k_B T v^2} - \frac{1}{v - b} \right) - P \left(\frac{2a}{k_B T v^3} - \frac{1}{(v - b)^2} \right). \end{aligned}$$

Therefore v_c and T_c are determined by

$$\frac{a}{k_B T_c v_c^2} - \frac{1}{v_c - b} = 0, \quad \text{and} \quad \frac{2a}{k_B T_c v_c^3} - \frac{1}{(v_c - b)^2} = 0,$$

with the solutions

$$v_c = 2b, \quad \text{and} \quad k_B T_c = \frac{a}{4b}.$$

The critical pressure is

$$P_c = \frac{k_B T_c}{v_c - b} \exp\left(-\frac{a}{k_B T_c v_c}\right) = \frac{a}{4b^2} e^{-2},$$

resulting in the ratio

$$\frac{P_c v_c}{k_B T_c} = 2e^{-2} \approx 0.27.$$

Note that for the van der Waals gas

$$\frac{P_c v_c}{k_B T_c} = \frac{3}{8} = 0.375,$$

while for some actual gases

$$\left(\frac{P_c v_c}{k_B T_c}\right)_{\text{water}} = 0.230, \quad \text{and} \quad \left(\frac{P_c v_c}{k_B T_c}\right)_{\text{Argon}} = 0.291.$$

(b) Calculate the isothermal compressibility κ_T for $v = v_c$ as a function of $T - T_c$.

- The isothermal compressibility is defined by

$$\kappa_T \equiv -\frac{1}{v} \frac{\partial v}{\partial P} \Big|_{T,N},$$

and from part (a), given by

$$\frac{\partial P}{\partial v} \Big|_{T_c, N} = P \left(\frac{a}{k_B T v^2} - \frac{1}{v - b} \right).$$

Expanding this expression, at $v = v_c$, in terms of $t \equiv k_B T - k_B T_c$ (for $T > T_c$), yields

$$\frac{\partial P}{\partial v} \Big|_{T_c, N} \approx P_c \left(\frac{a}{(a/4b + t) 4b^2} - \frac{1}{b} \right) \approx -\frac{P_c}{b} \frac{4bt}{a} = -\frac{2P_c}{v_c k_B T_c} t,$$

and thus

$$\kappa_T = \frac{k_B T_c}{2P_c} \frac{1}{t} = \frac{be^2}{2k_B(T - T_c)}.$$

Note that expanding any analytic equation of state will yield the same simple pole for the divergence of the compressibility.

(c) On the critical isotherm expand the pressure to the lowest non-zero order in $(v - v_c)$.

- Perform a Taylor–series expansion along the critical isotherm $T = T_c$, as

$$P(v, T_c) = P_c + \left. \frac{\partial P}{\partial v} \right|_{T_c, v_c} (v - v_c) + \frac{1}{2!} \left. \frac{\partial^2 P}{\partial v^2} \right|_{T_c, v_c} (v - v_c)^2 + \frac{1}{3!} \left. \frac{\partial^3 P}{\partial v^3} \right|_{T_c, v_c} (v - v_c)^3 + \dots$$

The first two terms are zero at the critical point, and

$$\begin{aligned} \left. \frac{\partial^3 P}{\partial v^3} \right|_{T_c, v_c} &= -P_c \frac{\partial}{\partial v} \left(\frac{2a}{k_B T_c v^3} - \frac{1}{(v-b)^2} \right) \\ &= -P_c \left(\frac{6a}{k_B T_c v_c^4} - \frac{2}{(v_c - b)^3} \right) \\ &= -\frac{P_c}{2b^3}. \end{aligned}$$

Substituting this into the Taylor expansion for $P(v, T_c)$, results in

$$P(v, T_c) = P_c \left(1 - \frac{(v - v_c)^3}{12b^3} \right),$$

which is equivalent to

$$\frac{P}{P_c} - 1 = -\frac{2}{3} \left(\frac{v}{v_c} - 1 \right)^3.$$

4. Two dimensional Coulomb gas: Consider a classical mixture of N positive, and N negative charged particles in a *two dimensional* box of area $A = L \times L$. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{2N} \frac{\vec{p}_i^2}{2m} - \sum_{i < j} c_i c_j \ln |\vec{q}_i - \vec{q}_j|, \quad ,$$

where $c_i = +c_0$ for $i = 1, \dots, N$, and $c_i = -c_0$ for $i = N + 1, \dots, 2N$, denote the charges of the particles; $\{\vec{q}_i\}$ and $\{\vec{p}_i\}$ their coordinates and momenta respectively.

(a) Note that in the interaction term each pair appears only once, and that there is no self interaction $i = j$. How many pairs have repulsive interactions, and how many have attractive interactions?

- There are N positively charged particles, and N negatively charged particles. Hence there are $N \cdot N = N^2$ pairs of opposite charges, and $n_{\text{attractive}} = N^2$. For like charges, we can choose pairs from the N particles of positive charge, or from the N particles with negative charges. Hence the number of pairs of like pairs is

$$n_{\text{repulsive}} = 2 \times \binom{N}{2} = 2 \times \frac{N!}{2!(N-2)!} = N(N-1).$$

(b) Write down the expression for the partition function $Z(N, T, A)$ in terms of integrals over $\{\vec{q}_i\}$ and $\{\vec{p}_i\}$. Perform the integrals over the momenta, and rewrite the contribution of the coordinates as a product involving powers of $\{\vec{q}_i\}$, using the identity $e^{\ln x} = x$.

- The partition function is

$$\begin{aligned} Z(N, T, A) &= \frac{1}{(N!)^2 h^{4N}} \int \prod_{i=1}^{2N} d^2 \vec{q}_i d^2 \vec{p}_i \exp \left[-\beta \sum_{i=1}^{2N} \frac{p_i^2}{2m} + \beta \sum_{i<j} c_i c_j \ln |\vec{q}_i - \vec{q}_j| \right] \\ &= \frac{1}{\lambda^{4N} (N!)^2} \int \prod_{i=1}^{2N} d^2 \vec{q}_i \exp [\beta \ln |\vec{q}_i - \vec{q}_j|^{c_i c_j}], \end{aligned}$$

where $\lambda = h/\sqrt{2\pi m k_B T}$. Further simplifying the expression for the partition function

$$Z(N, T, A) = \frac{1}{\lambda^{4N} (N!)^2} \int \prod_{i=1}^{2N} d^2 \vec{q}_i \prod_{i<j} |\vec{q}_i - \vec{q}_j|^{\beta c_i c_j},$$

where we have used the fact that $e^{\ln x} = x$.

(c) Although it is not possible to perform the integrals over $\{\vec{q}_i\}$ exactly, the dependence of Z on A can be obtained by the simple rescaling of coordinates, $\vec{q}_i' = \vec{q}_i/L$. Use the results in parts (a) and (b) to show that $Z \propto A^{2N - \beta c_0^2 N/2}$.

- The only length scale appearing in the problem is set by the system size L . Rescaling the expression using $\vec{q}_i' = \vec{q}_i/L$, then yields

$$Z(N, T, A) = \frac{1}{\lambda^{4N} (N!)^2} \int \prod_{i=1}^{2N} (L^2 d^2 \vec{q}_i') \prod_{i<j} L^{\beta c_i c_j} |\vec{q}_i' - \vec{q}_j'|^{\beta c_i c_j}.$$

Note that there are N^2 terms for which the interaction is attractive ($\beta c_i c_j = -\beta c_0^2$), and $N(N-1)$ terms for which the interaction is repulsive ($\beta c_i c_j = \beta c_0^2$). Thus

$$\begin{aligned} Z(N, T, A) &= L^{4N} \cdot L^{\beta c_0^2 N(N-1)} \cdot L^{-\beta c_0^2 N^2} \frac{1}{\lambda^{4N} (N!)^2} \int \prod_{i=1}^{2N} d^2 \vec{q}_i' \prod_{i<j} |\vec{q}_i' - \vec{q}_j'|^{\beta c_i c_j} \\ &= L^{4N - \beta N c_0^2} Z_0(N, T, A' = L'^2 = 1) \propto A^{2N - \beta c_0^2 N/2}, \end{aligned}$$

since $A = L^2$.

(d) Calculate the two dimensional pressure of this gas, and comment on its behavior at high and low temperatures.

- The pressure is then calculated from

$$\begin{aligned}
P &= -\frac{1}{\beta} \left. \frac{\partial \ln Z}{\partial A} \right|_{N,T} = k_B T \frac{\partial}{\partial A} \ln \left(A^{2N - \beta c_0^2 N/2} Z_0 \right) \\
&= k_B T (2N - \beta c_0^2 N/2) \frac{\partial}{\partial A} \ln A = \frac{2N k_B T}{A} - \frac{N c_0^2}{2A}.
\end{aligned}$$

At high temperatures,

$$P = \frac{2N k_B T}{A},$$

which is the ideal gas behavior for $2N$ particles. The pressure becomes negative at temperature below

$$T_c^0 = \frac{c_0^2}{4k_B},$$

which is unphysical, indicating the collapse of the particles due to their attractions.

(e) The unphysical behavior at low temperatures is avoided by adding a hard-core which prevents the coordinates of any two particles from coming closer than a distance a . The appearance of two length scales a and L , makes the scaling analysis of part (c) questionable. By examining the partition function for $N = 1$, obtain an estimate for the temperature T_c at which the short distance scale a becomes important in calculating the partition function, invalidating the result of the previous part. What are the phases of this system at low and high temperatures?

- A complete collapse of the system (to a single point) can be avoided by adding a hard core repulsion which prevents any two particles from coming closer than a distance a . The partition function for two particles (i.e. $N = 1$) is now given by

$$Z(N = 1, T, A) = \frac{1}{\lambda^4} \int d^2 \vec{q}_1 d^2 \vec{q}_2 \cdot |\vec{q}_1 - \vec{q}_2|^{-\beta c_0^2}.$$

To evaluate this integral, first change to center of mass and relative coordinates

$$\begin{cases} \vec{Q} = \frac{1}{2}(\vec{q}_1 + \vec{q}_2), \\ \vec{q} = \vec{q}_1 - \vec{q}_2. \end{cases}$$

Integrating over the center of mass gives

$$\begin{aligned}
Z(N = 1, T, A) &= \frac{A}{\lambda^4} \int d^2 \vec{q} q^{-\beta c_0^2} \approx \frac{2\pi A}{\lambda^4} \int_a^L dq \cdot q^{1 - \beta c_0^2} \\
&= \frac{2\pi A}{\lambda^4} \left. \frac{q^{2 - \beta c_0^2}}{2 - \beta c_0^2} \right|_a^L = \frac{2\pi A}{\lambda^4} \frac{L^{2 - \beta c_0^2} - a^{2 - \beta c_0^2}}{2 - \beta c_0^2}.
\end{aligned}$$

If $2 - \beta c_0^2 < 0$, as $L \rightarrow \infty$,

$$Z \approx \frac{2\pi A}{\lambda^4} \frac{a^{2-\beta c_0^2}}{2 - \beta c_0^2},$$

is controlled by the short distance cutoff a ; while if $2 - \beta c_0^2 > 0$, the integral is controlled by the system size L , as assumed in part (c). Hence the critical temperature can be estimated by $\beta c_0^2 = 2$, giving

$$T_c = \frac{c_0^2}{2k_B},$$

which is larger than T_c^0 by a factor of 2. Thus the unphysical collapse at low temperatures is preempted at the higher temperature where the hard cores become important. The high temperature phase ($T > T_c$) is a dissociated plasma; while the low temperature phase is a gas of paired dipoles.

5. Exact solutions for a one dimensional gas: In statistical mechanics, there are very few systems of interacting particles that can be solved *exactly*. Such exact solutions are very important as they provide a check for the reliability of various approximations. A one dimensional gas with short-range interactions is one such solvable case.

(a) Show that for a potential with a hard core that screens the interactions from further neighbors, the Hamiltonian for N particles can be written as

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=2}^N \mathcal{V}(x_i - x_{i-1}).$$

The (indistinguishable) particles are labelled with coordinates $\{x_i\}$ such that

$$0 \leq x_1 \leq x_2 \leq \cdots \leq x_N \leq L,$$

where L is the length of the box confining the particles.

• Each particle i interacts only with adjacent particles $i - 1$ and $i + 1$, as the hard cores from these nearest neighbors screen the interactions with any other particle. Thus we need only consider nearest neighbor interactions, and, included the kinetic energies, the Hamiltonian is given by

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=2}^N \mathcal{V}(x_i - x_{i-1}), \quad \text{for} \quad 0 \leq x_1 \leq x_2 \leq \cdots \leq x_N \leq L.$$

(b) Write the expression for the partition function $Z(T, N, L)$. Change variables to $\delta_1 = x_1$, $\delta_2 = x_2 - x_1$, \cdots , $\delta_N = x_N - x_{N-1}$, and carefully indicate the allowed ranges of integration and the constraints.

- The partition function is

$$\begin{aligned}
Z(T, N, L) &= \frac{1}{h^N} \int_0^L dx_1 \int_{x_1}^L dx_2 \cdots \int_{x_{N-1}}^L dx_N \exp \left[-\beta \sum_{i=2}^N \mathcal{V}(x_i - x_{i-1}) \right] \\
&\quad \cdot \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_N \exp \left[-\beta \sum_{i=1}^N N \frac{p_i^2}{2m} \right] \\
&= \frac{1}{\lambda^N} \int_0^L dx_1 \int_{x_1}^L dx_2 \cdots \int_{x_{N-1}}^L dx_N \exp \left[-\beta \sum_{i=2}^N \mathcal{V}(x_i - x_{i-1}) \right],
\end{aligned}$$

where $\lambda = h/\sqrt{2\pi mk_B T}$. (Note that there is no $N!$ factor, as the ordering of the particles is specified.) Introducing a new set of variables

$$\delta_1 = x_1, \quad \delta_2 = x_2 - x_1, \quad \cdots \quad \delta_n = x_N - x_{N-1},$$

or equivalently

$$x_1 = \delta_1, \quad x_2 = \delta_1 + \delta_2, \quad \cdots \quad x_N = \sum_{i=1}^N \delta_i,$$

the integration becomes

$$Z(T, N, L) = \frac{1}{\lambda^N} \int_0^L d\delta_1 \int_0^{L-\delta_1} d\delta_2 \int_0^{L-(\delta_1+\delta_2)} d\delta_3 \cdots \int_0^{L-\sum_{i=1}^N \delta_i} d\delta_N e^{-\beta \sum_{i=2}^N \mathcal{V}(\delta_i)}.$$

This integration can also be expressed as

$$Z(T, N, L) = \frac{1}{\lambda^N} \left[\int d\delta_1 d\delta_2 \cdots d\delta_N \right]' \exp \left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i) \right],$$

with the constraint

$$0 \leq \sum_{i=1}^N \delta_i \leq L.$$

This constraint can be put into the equation explicitly with the use of the step function

$$\Theta(x) = \begin{cases} 0 & \text{for } x < 0 \\ 1 & \text{for } x \geq 0 \end{cases},$$

as

$$Z(T, N, L) = \frac{1}{\lambda^N} \int_0^{\infty} d\delta_1 \int_0^{\infty} d\delta_2 \cdots \int_0^{\infty} d\delta_N \exp \left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i) \right] \Theta \left(L - \sum_{i=1}^N \delta_i \right).$$

(c) Consider the Gibbs partition function obtained from the Laplace transformation

$$\mathcal{Z}(T, N, P) = \int_0^\infty dL \exp(-\beta PL) Z(T, N, L),$$

and by extremizing the integrand find the standard formula for P in the canonical ensemble.

- The Gibbs partition function is

$$\mathcal{Z}(T, N, P) = \int_0^\infty dL \exp(-\beta PL) Z(T, N, L).$$

The saddle point is obtained by extremizing the integrand with respect to L ,

$$\left. \frac{\partial}{\partial L} \exp(-\beta PL) Z(T, N, L) \right|_{T, N} = 0,$$

which implies that

$$\beta P = \left. \frac{\partial}{\partial L} \ln Z(T, N, L) \right|_{T, N}, \quad \implies \quad P = k_B T \left. \frac{\partial \ln Z}{\partial L} \right|_{T, N}.$$

From thermodynamics, for a one-dimensional gas we have

$$dF = -SdT - PdL, \quad \implies \quad P = - \left. \frac{\partial F}{\partial L} \right|_{T, N}.$$

Further noting that

$$F = -k_B T \ln Z,$$

again results in

$$P_{\text{canonical}} = k_B T \left. \frac{\partial \ln Z}{\partial L} \right|_{T, N}.$$

(d) Change variables from L to $\delta_{N+1} = L - \sum_{i=1}^N \delta_i$, and find the expression for $\mathcal{Z}(T, N, P)$ as a product over one-dimensional integrals over each δ_i .

- The expression for the partition function given above is

$$Z(T, N, L) = \frac{1}{\lambda^N} \int_0^\infty d\delta_1 \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \exp \left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i) \right] \Theta \left(L - \sum_{i=1}^N \delta_i \right).$$

The Laplace transform of this equation is

$$\begin{aligned}
\mathcal{Z}(T, N, P) &= \frac{1}{\lambda^N} \int_0^\infty dL \exp(-\beta PL) \int_0^\infty d\delta_1 \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \\
&\quad \cdot \exp \left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i) \right] \Theta \left(L - \sum_{i=1}^N \delta_i \right) \\
&= \frac{1}{\lambda^N \beta P} \int_0^\infty d\delta_1 \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \exp \left[-\beta \sum_{i=2}^N \mathcal{V}(\delta_i) \right] \exp \left[-\beta P \left(\sum_{i=1}^N \delta_i \right) \right] \\
&= \frac{1}{\lambda^N (\beta P)^2} \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \exp \left\{ -\sum_{i=2}^N [\beta \mathcal{V}(\delta_i) + \beta P \delta_i] \right\}.
\end{aligned}$$

Since the integrals for different δ'_i 's are equivalent, we obtain

$$\mathcal{Z}(T, N, P) = \frac{1}{\lambda^N (\beta P)^2} \left\{ \int_0^\infty d\delta \exp [-\beta (\mathcal{V}(\delta) + P\delta)] \right\}^{N-1}.$$

This expression can also be obtained directly, without use of the step function as follows.

$$\begin{aligned}
\mathcal{Z}(T, N, P) &= \frac{1}{\lambda^N} \int_0^L d\delta_1 \int_0^{L-\delta_1} d\delta_2 \int_0^{L-(\delta_1+\delta_2)} d\delta_3 \cdots \int_0^{L-\sum_{i=1}^N \delta_i} d\delta_N \\
&\quad \cdot \int_0^\infty dL \exp \left[-\beta PL - \beta \left(\sum_{i=2}^N \mathcal{V}(\delta) \right) \right] \\
&= \frac{1}{\lambda^N} \int_0^L d\delta_1 \int_0^{L-\delta_1} d\delta_2 \cdots \int_0^{L-\sum_{i=1}^N \delta_i} d\delta_N \int_{-\sum_{i=1}^N \delta_i}^\infty d \left(L - \sum_{i=1}^N \delta_i \right) \\
&\quad \cdot \exp \left\{ -\beta P \left[\sum_{i=1}^N \delta_i + \left(L - \sum_{i=1}^N \delta_i \right) \right] - \beta \left(\sum_{i=2}^N \mathcal{V}(\delta_i) \right) \right\}.
\end{aligned}$$

Change variables to $\delta_{N+1} \equiv L - \sum_{i=1}^N \delta_i$, and note that each of the δ 's indicates the distance between neighboring particles. The size of the gas L , has been extended to any value, hence each δ can be varied independently from 0 to ∞ . Thus the Gibbs partition

function is

$$\begin{aligned}
\mathcal{Z}(T, N, P) &= \frac{1}{\lambda^N} \int_0^\infty d\delta_1 \int_0^\infty d\delta_2 \cdots \int_0^\infty d\delta_N \int_0^\infty d\delta_{N+1} \\
&\quad \cdot \exp \left[-\beta P \left(\sum_{i=1}^{N+1} \delta_i \right) - \beta \left(\sum_{i=2}^N \mathcal{V}(\delta_i) \right) \right] \\
&= \frac{1}{\lambda^N} \left(\int_0^\infty d\delta \cdot \exp[-\beta \mathcal{V}(\delta) - \beta P \delta] \right)^{N-1} \int_0^\infty d\delta_1 \exp(-\beta P \delta_1) \\
&\quad \cdot \int_0^\infty d\delta_{N+1} \exp(-\beta P \delta_{N+1}) \\
&= \frac{1}{\lambda^N (\beta P)^2} \left\{ \int_0^\infty d\delta \exp[-\beta (\mathcal{V}(\delta) + P\delta)] \right\}^{N-1}.
\end{aligned}$$

(e) At a fixed pressure P , find expressions for the mean length $L(T, N, P)$, and the density $n = N/L(T, N, P)$ (involving ratios of integrals which should be easy to interpret).

- The mean length is

$$\begin{aligned}
L(T, N, P) &= -k_B T \left. \frac{\partial}{\partial (\beta P)} \ln \mathcal{Z}(T, N, P) \right|_{T, N} \\
&= \frac{2}{\beta P} + (N-1) \frac{\int_0^\infty d\delta \cdot \delta \cdot \exp[-\beta \mathcal{V}(\delta) - \beta P \delta]}{\int_0^\infty d\delta \cdot \exp[-\beta \mathcal{V}(\delta) - \beta P \delta]},
\end{aligned}$$

and the density n is given by

$$n = \frac{N}{L(T, N, P)} = N \left\{ \frac{2k_B T}{P} + (N-1) \frac{\int_0^\infty d\delta \cdot \delta \cdot \exp[-\beta (\mathcal{V}(\delta) - P\delta)]}{\int_0^\infty d\delta \cdot \exp[-\beta (\mathcal{V}(\delta) - P\delta)]} \right\}^{-1}.$$

Note that for an ideal gas $\mathcal{V}_{\text{i.g.}}(\delta) = 0$, and

$$L_{\text{i.g.}}(T, N, P) = \frac{(N+1)k_B T}{P},$$

leading to

$$n(p)_{\text{i.g.}} = \frac{N}{N+1} \frac{P}{k_B T}.$$

Since the expression for $n(T, P)$ in part (e) is continuous and non-singular for any choice of potential, there is in fact no condensation transition for the one-dimensional gas. By contrast, the approximate van der Waals equation (or the mean-field treatment) incorrectly predicts such a transition.

(f) For a hard sphere gas, with minimum separation a between particles, calculate the equation of state $P(T, n)$. Compare the excluded volume factor with the approximate result obtained in earlier problems, and also obtain the general virial coefficient $B_\ell(T)$.

- For a hard sphere gas

$$\delta_i \geq a, \quad \text{for } i = 2, 3, \dots, N,$$

the Gibbs partition function is

$$\begin{aligned} \mathcal{Z}(T, N, P) &= \frac{1}{\lambda^N (\beta P)^2} \left[\int_a^\infty d\delta \exp(-\beta \mathcal{V}(\delta) - \beta P \delta) \right]^{N-1} \\ &= \frac{1}{\lambda^N (\beta P)^2} \left[\int_a^\infty d\delta \exp(-\beta P \delta) \right]^{N-1} \\ &= \frac{1}{\lambda^N} \left(\frac{1}{\beta P} \right)^{N+1} \exp(-\beta P a)^{N-1}. \end{aligned}$$

From the partition function, we can calculate the mean length

$$L = -k_B T \left. \frac{\partial \ln \mathcal{Z}}{\partial P} \right|_{T, N} = \frac{(N+1)k_B T}{P} + (N-1)a,$$

which after rearrangement yields

$$\beta P = \frac{(N+1)}{L - (N-1)a} = \frac{n + 1/L}{1 - (n - 1/L)a} \approx (n + 1/l)(1 + (n - 1/L)a + (n - 1/L)^2 a^2 + \dots).$$

For $N \gg 1$, $n \gg 1/L$, and

$$\beta P \approx n(1 + na + n^2 a^2 + \dots) = n + an^2 + a^2 n^3 + \dots,$$

which gives the virial coefficients

$$B_\ell(T) = a^{\ell-1}.$$

The value of $B_3 = a^2$ agrees with the result obtained in an earlier problem. Also note that the exact ‘excluded volume’ is $(N-1)a$, as opposed to the estimate of $Na/2$ used in deriving the van der Waals equation.

6. One dimensional chain: A chain of $N+1$ particles of mass m is connected by N massless springs of spring constant K and relaxed length a . The first and last particles are held fixed at the equilibrium separation of Na . Let us denote the longitudinal displacements

of the particles from their equilibrium positions by $\{u_i\}$, with $u_0 = u_N = 0$ since the end particles are fixed. The Hamiltonian governing $\{u_i\}$, and the conjugate momenta $\{p_i\}$, is

$$\mathcal{H} = \sum_{i=1}^{N-1} \frac{p_i^2}{2m} + \frac{K}{2} \left[u_1^2 + \sum_{i=1}^{N-2} (u_{i+1} - u_i)^2 + u_{N-1}^2 \right].$$

(a) Using the appropriate (sine) Fourier transforms, find the normal modes $\{\tilde{u}_k\}$, and the corresponding frequencies $\{\omega_k\}$.

- From the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N-1} \frac{p_i^2}{2m} + \frac{K}{2} \left[u_1^2 + \sum_{i=2}^{N-1} (u_i - u_{i-1})^2 + u_{N-1}^2 \right],$$

the classical equations of motion are obtained as

$$m \frac{d^2 u_j}{dt^2} = -K(u_j - u_{j-1}) - K(u_j - u_{j+1}) = K(u_{j-1} - 2u_j + u_{j+1}),$$

for $j = 1, 2, \dots, N-1$, and with $u_0 = u_N = 0$. In a normal mode, the particles oscillate in phase. The usual procedure is to obtain the modes, and corresponding frequencies, by diagonalizing the matrix of coefficients coupling the displacements on the right hand side of the equation of motion. For any linear system, we have $m d^2 u_i / dt^2 = \mathcal{K}_{ij} u_j$, and we must diagonalize \mathcal{K}_{ij} . In the above example, \mathcal{K}_{ij} is only a function of the difference $i - j$. This is a consequence of translational symmetry, and allows us to diagonalize the matrix using Fourier modes. Due to the boundary conditions in this case, the appropriate transformation involves the sine, and the motion of the j -th particle in a normal mode is given by

$$\tilde{u}_{k(n)}(j) = \sqrt{\frac{2}{N}} e^{\pm i \omega_n t} \sin(k(n) \cdot j).$$

The origin of time is arbitrary, but to ensure that $u_N = 0$, we must set

$$k(n) \equiv \frac{n\pi}{N}, \quad \text{for } n = 1, 2, \dots, N-1.$$

Larger values of n give wave-vectors that are simply shifted by a multiple of π , and hence coincide with one of the above normal modes. The number of normal modes thus equals the number of original displacement variables, as required. Furthermore, the amplitudes are chosen such that the normal modes are also orthonormal, i.e.

$$\sum_{j=1}^{N-1} \tilde{u}_{k(n)}(j) \cdot \tilde{u}_{k(m)}(j) = \delta_{n,m}.$$

By substituting the normal modes into the equations of motion we obtain the dispersion relation

$$\omega_n^2 = 2\omega_0^2 \left[1 - \cos \left(\frac{n\pi}{N} \right) \right] = \omega_0^2 \sin^2 \left(\frac{n\pi}{2N} \right),$$

where $\omega_0 \equiv \sqrt{K/m}$.

The potential energy for each normal mode is given by

$$\begin{aligned} U_n &= \frac{K}{2} \sum_{i=1}^N |u_i - u_{i-1}|^2 = \frac{K}{N} \sum_{i=1}^N \left\{ \sin \left(\frac{n\pi}{N} i \right) - \sin \left[\frac{n\pi}{N} (i-1) \right] \right\}^2 \\ &= \frac{4K}{N} \sin^2 \left(\frac{n\pi}{2N} \right) \sum_{i=1}^N \cos^2 \left[\frac{n\pi}{N} \left(i - \frac{1}{2} \right) \right]. \end{aligned}$$

Noting that

$$\sum_{i=1}^N \cos^2 \left[\frac{n\pi}{N} \left(i - \frac{1}{2} \right) \right] = \frac{1}{2} \sum_{i=1}^N \left\{ 1 + \cos \left[\frac{n\pi}{N} (2i-1) \right] \right\} = \frac{N}{2},$$

we have

$$U_{k(n)} = 2K \sin^2 \left(\frac{n\pi}{2N} \right).$$

(b) Express the Hamiltonian in terms of the amplitudes of normal modes $\{\tilde{u}_k\}$, and evaluate the *classical* partition function. (You may integrate the $\{u_i\}$ from $-\infty$ to $+\infty$).

- Before evaluating the classical partition function, let's evaluate the potential energy by first expanding the displacement using the basis of normal modes, as

$$u_j = \sum_{n=1}^{N-1} a_n \cdot \tilde{u}_{k(n)}(j).$$

The expression for the total potential energy is

$$U = \frac{K}{2} \sum_{i=1}^N (u_i - u_{i-1})^2 = \frac{K}{2} \sum_{i=1}^N \left\{ \sum_{n=1}^{N-1} a_n [\tilde{u}_{k(n)}(i) - \tilde{u}_{k(n)}(i-1)] \right\}^2.$$

Since

$$\sum_{j=1}^{N-1} \tilde{u}_{k(n)}(j) \cdot \tilde{u}_{k(m)}(j-1) = \frac{1}{N} \delta_{n,m} \sum_{j=1}^{N-1} \{-\cos[k(n)(2j-1)] + \cos k(n)\} = \delta_{n,m} \cos k(n),$$

the total potential energy has the equivalent forms

$$\begin{aligned} U &= \frac{K}{2} \sum_{i=1}^N (u_i - u_{i-1})^2 = K \sum_{n=1}^{N-1} a_n^2 (1 - \cos k(n)), \\ &= \sum_{i=1}^{N-1} a_{k(n)}^2 \varepsilon_{k(n)}^2 = 2K \sum_{i=1}^{N-1} a_{k(n)}^2 \sin^2 \left(\frac{n\pi}{2N} \right). \end{aligned}$$

The next step is to change the coordinates of phase space from u_j to a_n . The Jacobian associated with this change of variables is unity, and the classical partition function is now obtained from

$$Z = \frac{1}{\lambda^{N-1}} \int_{-\infty}^{\infty} da_1 \cdots \int_{-\infty}^{\infty} da_{N-1} \exp \left[-2\beta K \sum_{n=1}^{N-1} a_n^2 \sin^2 \left(\frac{n\pi}{2N} \right) \right],$$

where $\lambda = h/\sqrt{2\pi mk_B T}$ corresponds to the contribution to the partition function from each momentum coordinate. Performing the Gaussian integrals, we obtain

$$\begin{aligned} Z &= \frac{1}{\lambda^{N-1}} \prod_{n=1}^{N-1} \left\{ \int_{-\infty}^{\infty} da_n \exp \left[-2\beta K a_n^2 \sin^2 \left(\frac{n\pi}{2N} \right) \right] \right\}, \\ &= \frac{1}{\lambda^{N-1}} \left(\frac{\pi k_B T}{2K} \right)^{\frac{N-1}{2}} \prod_{n=1}^{N-1} \left[\sin \left(\frac{n\pi}{2N} \right) \right]^{-1}. \end{aligned}$$

(c) First evaluate $\langle |\tilde{u}_k|^2 \rangle$, and use the result to calculate $\langle u_i^2 \rangle$. Plot the resulting squared displacement of each particle as a function of its equilibrium position.

- The average squared amplitude of each normal mode is

$$\begin{aligned} \langle a_n^2 \rangle &= \frac{\int_{-\infty}^{\infty} da_n (a_n^2) \exp \left[-2\beta K a_n^2 \sin^2 \left(\frac{n\pi}{2N} \right) \right]}{\int_{-\infty}^{\infty} da_n \exp \left[-2\beta K a_n^2 \sin^2 \left(\frac{n\pi}{2N} \right) \right]} \\ &= \left[4\beta K \sin^2 \left(\frac{n\pi}{2N} \right) \right]^{-1} = \frac{k_B T}{4K} \frac{1}{\sin^2 \left(\frac{n\pi}{2N} \right)}. \end{aligned}$$

The variation of the displacement is then given by

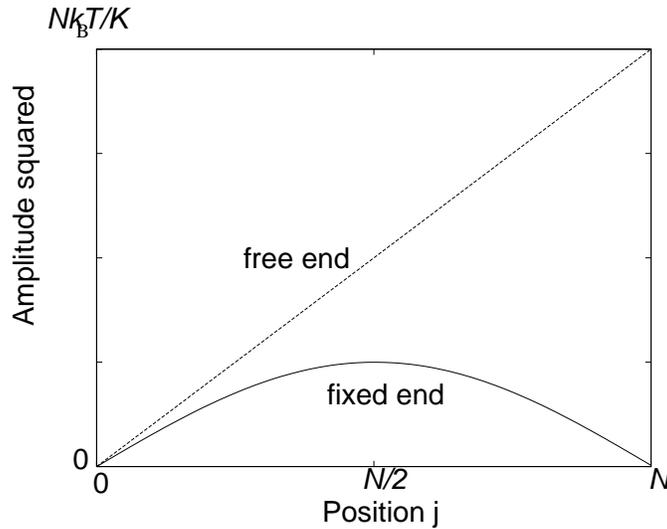
$$\begin{aligned} \langle u_j^2 \rangle &= \left\langle \left[\sum_{n=1}^{N-1} a_n \tilde{u}_n(j) \right]^2 \right\rangle = \sum_{n=1}^{N-1} \langle a_n^2 \rangle \tilde{u}_n^2(j) \\ &= \frac{2}{N} \sum_{n=1}^{N-1} \langle a_n^2 \rangle \sin^2 \left(\frac{n\pi}{N} j \right) = \frac{k_B T}{2KN} \sum_{n=1}^{N-1} \frac{\sin^2 \left(\frac{n\pi}{N} j \right)}{\sin^2 \left(\frac{n\pi}{2N} \right)}. \end{aligned}$$

The evaluation of the above sum is considerably simplified by considering the combination

$$\begin{aligned}\langle u_{j+1}^2 \rangle + \langle u_{j-1}^2 \rangle - 2\langle u_j^2 \rangle &= \frac{k_B T}{2KN} \sum_{n=1}^{N-1} \frac{2 \cos \left[\frac{2n\pi}{N} j \right] - \cos \left[\frac{2n\pi}{N} (j+1) \right] - \cos \left[\frac{2n\pi}{N} (j-1) \right]}{1 - \cos \left(\frac{n\pi}{N} \right)} \\ &= \frac{k_B T}{2KN} \sum_{n=1}^{N-1} \frac{2 \cos \left(\frac{2n\pi}{N} j \right) \left[1 - \cos \left(\frac{n\pi}{N} \right) \right]}{1 - \cos \left(\frac{n\pi}{N} \right)} = -\frac{k_B T}{KN},\end{aligned}$$

where we have used $\sum_{n=1}^{N-1} \cos(\pi n/N) = -1$. It is easy to check that subject to the boundary conditions of $\langle u_0^2 \rangle = \langle u_N^2 \rangle = 0$, the solution to the above recursion relation is

$$\langle u_j^2 \rangle = \frac{k_B T}{K} \frac{j(N-j)}{N}.$$



(d) How are the results modified if only the first particle is fixed ($u_0 = 0$), while the other end is free ($u_N \neq 0$)? (Note that this is a much simpler problem as the partition function can be evaluated by changing variables to the $N - 1$ spring extensions.)

- When the last particle is free, the overall potential energy is the sum of the contributions of each spring, i.e. $U = K \sum_{j=1}^{N-1} (u_j - u_{j-1})^2/2$. Thus each extension can be treated independently, and we introduce a new set of independent variables $\Delta u_j \equiv u_j - u_{j-1}$. (In the previous case, where the two ends are fixed, these variables were not independent.)

The partition function can be calculated separately for each spring as

$$\begin{aligned}Z &= \frac{1}{\lambda^{N-1}} \int_{-\infty}^{\infty} du_1 \cdots \int_{-\infty}^{\infty} du_{N-1} \exp \left[-\frac{K}{2k_B T} \sum_{j=1}^{N-1} (u_j - u_{j-1})^2 \right] \\ &= \frac{1}{\lambda^{N-1}} \int_{-\infty}^{\infty} d\Delta u_1 \cdots \int_{-\infty}^{\infty} d\Delta u_{N-1} \exp \left[-\frac{K}{2k_B T} \sum_{j=1}^{N-1} \Delta u_j^2 \right] = \left(\frac{2\pi k_B T}{\lambda^2 K} \right)^{(N-1)/2}.\end{aligned}$$

For each spring extension, we have

$$\langle \Delta u_j^2 \rangle = \langle (u_j - u_{j-1})^2 \rangle = \frac{k_B T}{K}.$$

The displacement

$$u_j = \sum_{i=1}^j \Delta u_i,$$

is a sum of *independent* random variables, leading to the variance

$$\langle u_j^2 \rangle = \left\langle \left(\sum_{i=1}^j \Delta u_i \right)^2 \right\rangle = \sum_{i=1}^j (\Delta u_i)^2 = \frac{k_B T}{K} j.$$

The results for displacements of open and closed chains are compared in the above figure.

7. Black hole thermodynamics: According to Bekenstein and Hawking, the entropy of a black hole is proportional to its area A , and given by

$$S = \frac{k_B c^3}{4G\hbar} A \quad .$$

(a) Calculate the escape velocity at a radius R from a mass M using classical mechanics. Find the relationship between the radius and mass of a black hole by setting this escape velocity to the speed of light c . (Relativistic calculations do not modify this result which was originally obtained by Laplace.)

- The classical escape velocity is obtained by equating the gravitational energy and the kinetic energy on the surface as,

$$G \frac{Mm}{R} = \frac{mv_E^2}{2},$$

leading to

$$v_E = \sqrt{\frac{2GM}{r}}.$$

Setting the escape velocity to the speed of light, we find

$$R = \frac{2G}{c^2} M.$$

For a mass larger than given by this ratio (i.e. $M > c^2 R / 2G$), nothing will escape from distances closer than R .

(b) Does entropy increase or decrease when two black holes collapse into one? What is the entropy change for the universe (in equivalent number of bits of information), when two solar mass black holes ($M_{\odot} \approx 2 \times 10^{30} \text{ kg}$) coalesce?

- When two black holes of mass M collapse into one, the entropy change is

$$\begin{aligned}\Delta S &= S_2 - 2S_1 = \frac{k_B c^3}{4G\hbar} (A_2 - 2A_1) = \frac{k_B c^3}{4G\hbar} 4\pi (R_2^2 - 2R_1^2) \\ &= \frac{\pi k_B c^3}{G\hbar} \left[\left(\frac{2G}{c^2} 2M \right)^2 - 2 \left(\frac{2G}{c^2} M \right)^2 \right] = \frac{8\pi G k_B M^2}{c\hbar} > 0.\end{aligned}$$

Thus the merging of black holes increases the entropy of the universe.

Consider the coalescence of two solar mass black holes. The entropy change is

$$\begin{aligned}\Delta S &= \frac{8\pi G k_B M_{\odot}^2}{c\hbar} \\ &\approx \frac{8\pi \cdot 6.7 \times 10^{-11} (N \cdot \text{m}^2/\text{kg}^2) \cdot 1.38 \times 10^{-23} (\text{J}/\text{K}) \cdot (2 \times 10^{30})^2 \text{kg}^2}{3 \times 10^8 (\text{m}/\text{s}) \cdot 1.05 \times 10^{-34} (\text{J} \cdot \text{s})} \\ &\approx 3 \times 10^{54} (\text{J}/\text{K}).\end{aligned}$$

In units of bits, the information lost is

$$N_I = \frac{\Delta S \ln 2}{k_B} = 1.5 \times 10^{77}.$$

(c) The internal energy of the black hole is given by the Einstein relation, $E = Mc^2$. Find the temperature of the black hole in terms of its mass.

- Using the thermodynamic definition of temperature $\frac{1}{T} = \frac{\partial S}{\partial E}$, and the Einstein relation $E = Mc^2$,

$$\frac{1}{T} = \frac{1}{c^2} \frac{\partial}{\partial M} \left[\frac{k_B c^3}{4G\hbar} 4\pi \left(\frac{2G}{c^2} M \right)^2 \right] = \frac{8\pi k_B G}{\hbar c^3} M, \quad \implies \quad T = \frac{\hbar c^3}{8\pi k_B G} \frac{1}{M}.$$

(d) A “black hole” actually emits thermal radiation due to pair creation processes on its event horizon. Find the rate of energy loss due to such radiation.

- The (quantum) vacuum undergoes fluctuations in which particle–antiparticle pairs are constantly created and destroyed. Near the boundary of a black hole, sometimes one member of a pair falls into the black hole while the other escapes. This is a hand-waving explanation for the emission of radiation from black holes. The decrease in energy E of a black body of area A at temperature T is given by the Stefan-Boltzmann law,

$$\frac{1}{A} \frac{\partial E}{\partial t} = -\sigma T^4, \quad \text{where} \quad \sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}.$$

(e) Find the amount of time it takes an isolated black hole to evaporate. How long is this time for a black hole of solar mass?

- Using the result in part (d) we can calculate the time it takes a black hole to evaporate. For a black hole

$$A = 4\pi R^2 = 4\pi \left(\frac{2G}{c^2} M \right)^2 = \frac{16\pi G^2}{c^4} M^2, \quad E = Mc^2, \quad \text{and} \quad T = \frac{\hbar c^3}{8\pi k_B G} \frac{1}{M}.$$

Hence

$$\frac{d}{dt} (Mc^2) = -\frac{\pi^2 k_B^4}{60 \hbar^3 c^2} \left(\frac{16\pi G^2}{c^4} M^2 \right) \left(\frac{\hbar c^3}{8\pi k_B G} \frac{1}{M} \right)^4,$$

which implies that

$$M^2 \frac{dM}{dt} = -\frac{\hbar c^4}{15360 G^2} \equiv -b.$$

This can be solved to give

$$M(t) = (M_0^3 - 3bt)^{1/3}.$$

The mass goes to zero, and the black hole evaporates after a time

$$\tau = \frac{M_0^3}{3b} = \frac{5120 G^2 M_\odot^3}{\hbar c^4} \approx 2.2 \times 10^{74} \text{ s},$$

which is considerably longer than the current age of the universe (approximately $\times 10^{18} \text{ s}$).

(f) What is the mass of a black hole that is in thermal equilibrium with the current cosmic background radiation at $T = 2.7\text{K}$?

- The temperature and mass of a black hole are related by $M = \hbar c^3 / (8\pi k_B G T)$. For a black hole in thermal equilibrium with the current cosmic background radiation at $T = 2.7^\circ \text{K}$,

$$M \approx \frac{1.05 \times 10^{-34} (\text{J} \cdot \text{s}) (3 \times 10^8 \text{ m/s})^3}{8\pi \cdot 1.38 \times 10^{-23} (\text{J/K}) \cdot 6.7 \times 10^{-11} (\text{N} \cdot \text{m}^2/\text{kg}^2) \cdot 2.7^\circ \text{K}} \approx 4.5 \times 10^{22} \text{ kg}.$$

(g) Consider a spherical volume of space of radius R . According to the recently formulated *Holographic Principle* there is a maximum to the amount of entropy that this volume of space can have, independent of its contents! What is this maximal entropy?

- The mass inside the spherical volume of radius R must be less than the mass that would make a black hole that fills this volume. Bring in additional mass (from infinity) inside the volume, so as to make a volume-filling black hole. Clearly the entropy of the system

will increase in the process, and the final entropy, which is the entropy of the black hole is larger than the initial entropy in the volume, leading to the inequality

$$S \leq S_{BH} = \frac{k_B c^3}{4G\hbar} A,$$

where $A = 4\pi R^2$ is the area enclosing the volume. The surprising observation is that the upper bound on the entropy is proportional to area, whereas for any system of particles we expect the entropy to be proportional to N . This should remain valid even at very high temperatures when interactions are unimportant. The ‘holographic principle’ is an allusion to the observation that it appears as if the degrees of freedom are living on the surface of the system, rather than its volume. It was formulated in the context of string theory which attempts to construct a consistent theory of quantum gravity, which replaces particles as degrees of freedom, with strings.

8. Quantum harmonic oscillator: Consider a single harmonic oscillator with the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}, \quad \text{with} \quad p = \frac{\hbar}{i} \frac{d}{dq} \quad .$$

(a) Find the partition function Z , at a temperature T , and calculate the energy $\langle \mathcal{H} \rangle$.

- The partition function Z , at a temperature T , is given by

$$Z = \text{tr } \rho = \sum_n e^{-\beta E_n}.$$

As the energy levels for a harmonic oscillator are given by

$$\epsilon_n = \hbar\omega \left(n + \frac{1}{2} \right),$$

the partition function is

$$\begin{aligned} Z &= \sum_n \exp \left[-\beta \hbar \omega \left(n + \frac{1}{2} \right) \right] = e^{-\beta \hbar \omega / 2} + e^{-3\beta \hbar \omega / 2} + \dots \\ &= \frac{1}{e^{\beta \hbar \omega / 2} - e^{-\beta \hbar \omega / 2}} = \frac{1}{2 \sinh(\beta \hbar \omega / 2)}. \end{aligned}$$

The expectation value of the energy is

$$\langle \mathcal{H} \rangle = -\frac{\partial \ln Z}{\partial \beta} = \left(\frac{\hbar\omega}{2} \right) \frac{\cosh(\beta \hbar \omega / 2)}{\sinh(\beta \hbar \omega / 2)} = \left(\frac{\hbar\omega}{2} \right) \frac{1}{\tanh(\beta \hbar \omega / 2)}.$$

(b) Write down the formal expression for the canonical density matrix ρ in terms of the eigenstates ($\{|n\rangle\}$), and energy levels ($\{\epsilon_n\}$) of \mathcal{H} .

- Using the formal representation of the energy eigenstates, the density matrix ρ is

$$\rho = 2 \sinh\left(\frac{\beta\hbar\omega}{2}\right) \left(\sum_n |n\rangle \exp\left[-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right] \langle n| \right).$$

In the coordinate representation, the eigenfunctions are in fact given by

$$\langle n|q\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{H_n(\xi)}{\sqrt{2^n n!}} \exp\left(-\frac{\xi^2}{2}\right),$$

where

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}} q,$$

with

$$\begin{aligned} H_n(\xi) &= (-1)^n \exp(\xi^2) \left(\frac{d}{d\xi}\right)^n \exp(-\xi^2) \\ &= \frac{\exp(\xi^2)}{\pi} \int_{-\infty}^{\infty} (-2iu)^n \exp(-u^2 + 2i\xi u) du. \end{aligned}$$

For example,

$$H_0(\xi) = 1, \quad \text{and} \quad H_1(\xi) = -\exp(\xi^2) \frac{d}{d\xi} \exp(-\xi^2) = 2\xi,$$

result in the eigenstates

$$\langle 0|q\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar} q^2\right),$$

and

$$\langle 1|q\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{2m\omega}{\hbar}} q \cdot \exp\left(-\frac{m\omega}{2\hbar} q^2\right).$$

Using the above expressions, the matrix elements are obtained as

$$\begin{aligned} \langle q'|\rho|q\rangle &= \sum_{n,n'} \langle q'|n'\rangle \langle n'|\rho|n\rangle \langle n|q\rangle = \frac{\sum_n \exp\left[-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right] \cdot \langle q'|n\rangle \langle n|q\rangle}{\sum_n \exp\left[-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right]} \\ &= 2 \sinh\left(\frac{\beta\hbar\omega}{2}\right) \cdot \sum_n \exp\left[-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right] \cdot \langle q'|n\rangle \langle n|q\rangle. \end{aligned}$$

(c) Show that for a general operator $A(x)$,

$$\frac{\partial}{\partial x} \exp[A(x)] \neq \frac{\partial A}{\partial x} \exp[A(x)], \quad \text{unless} \quad \left[A, \frac{\partial A}{\partial x} \right] = 0,$$

while in all cases

$$\frac{\partial}{\partial x} \text{tr} \{ \exp[A(x)] \} = \text{tr} \left\{ \frac{\partial A}{\partial x} \exp[A(x)] \right\}.$$

• By definition

$$e^A = \sum_{n=0}^{\infty} \frac{1}{n!} A^n,$$

and

$$\frac{\partial e^A}{\partial x} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial A^n}{\partial x}.$$

But for a product of n operators,

$$\frac{\partial}{\partial x} (A \cdot A \cdots A) = \frac{\partial A}{\partial x} \cdot A \cdots A + A \cdot \frac{\partial A}{\partial x} \cdots A + \cdots + A \cdot A \cdots \frac{\partial A}{\partial x}.$$

The $\frac{\partial A}{\partial x}$ can be moved through the A 's surrounding it only if $[A, \frac{\partial A}{\partial x}] = 0$, in which case

$$\frac{\partial A}{\partial x} = n \frac{\partial A}{\partial x} A^{n-1}, \quad \text{and} \quad \frac{\partial e^A}{\partial x} = \frac{\partial A}{\partial x} e^A.$$

However, as we can always reorder operators inside a trace, i.e. $\text{tr}(BC) = \text{tr}(CB)$, and

$$\text{tr} \left(A \cdots A \cdots \frac{\partial A}{\partial x} \cdots A \right) = \text{tr} \left(\frac{\partial A}{\partial x} \cdot A^{n-1} \right),$$

and the identity

$$\frac{\partial}{\partial x} \text{tr} (e^A) = \text{tr} \left(\frac{\partial A}{\partial x} \cdot e^A \right),$$

can always be satisfied, independent of any constraint on $[A, \frac{\partial A}{\partial x}]$.

(d) Note that the partition function calculated in part (a) does not depend on the mass m , i.e. $\partial Z/\partial m = 0$. Use this information, along with the result in part (c), to show that

$$\left\langle \frac{p^2}{2m} \right\rangle = \left\langle \frac{m\omega^2 q^2}{2} \right\rangle.$$

• The expectation values of the kinetic and potential energy are given by

$$\left\langle \frac{p^2}{2m} \right\rangle = \text{tr} \left(\frac{p^2}{2m} \rho \right), \quad \text{and} \quad \left\langle \frac{m\omega^2 q^2}{2} \right\rangle = \text{tr} \left(\frac{m\omega^2 q^2}{2} \rho \right).$$

Noting that the expression for the partition function derived in part (a) is independent of mass, we know that $\partial Z/\partial m = 0$. Starting with $Z = \text{tr} \left(e^{-\beta\mathcal{H}} \right)$, and differentiating

$$\frac{\partial Z}{\partial m} = \frac{\partial}{\partial m} \text{tr} \left(e^{-\beta\mathcal{H}} \right) = \text{tr} \left[\frac{\partial}{\partial m} (-\beta\mathcal{H}) e^{-\beta\mathcal{H}} \right] = 0,$$

where we have used the result in part (c). Differentiating the Hamiltonian, we find that

$$\text{tr} \left[\beta \frac{p^2}{2m^2} e^{-\beta\mathcal{H}} \right] + \text{tr} \left[-\beta \frac{m\omega^2 q^2}{2} e^{-\beta\mathcal{H}} \right] = 0.$$

Equivalently,

$$\text{tr} \left[\frac{p^2}{2m} e^{-\beta\mathcal{H}} \right] = \text{tr} \left[\frac{m\omega^2 q^2}{2} e^{-\beta\mathcal{H}} \right],$$

which shows that the expectation values of kinetic and potential energies are equal.

(e) Using the results in parts (d) and (a), or otherwise, calculate $\langle q^2 \rangle$. How are the results in Problem #6 modified at low temperatures by inclusion of quantum mechanical effects.

• In part (a) it was found that $\langle \mathcal{H} \rangle = (\hbar\omega/2) (\tanh(\beta\hbar\omega/2))^{-1}$. Note that $\langle \mathcal{H} \rangle = \langle p^2/2m \rangle + \langle m\omega^2 q^2/2 \rangle$, and that in part (d) it was determined that the contribution from the kinetic and potential energy terms are equal. Hence,

$$\langle m\omega^2 q^2/2 \rangle = \frac{1}{2} (\hbar\omega/2) (\tanh(\beta\hbar\omega/2))^{-1}.$$

Solving for $\langle q^2 \rangle$,

$$\langle q^2 \rangle = \frac{\hbar}{2m\omega} (\tanh(\beta\hbar\omega/2))^{-1} = \frac{\hbar}{2m\omega} \coth(\beta\hbar\omega/2).$$

While the classical result $\langle q^2 \rangle = k_B T/m\omega^2$, vanishes as $T \rightarrow 0$, the quantum result saturates at $T = 0$ to a constant value of $\langle q^2 \rangle = \hbar/(2m\omega)$. The amplitude of the displacement curves in Problem #6 are effected by exactly the same saturation factors.

(f) In a coordinate representation, calculate $\langle q' | \rho | q \rangle$ in the high temperature limit. One approach is to use the result

$$\exp(\beta A) \exp(\beta B) = \exp \left[\beta(A + B) + \beta^2[A, B]/2 + \mathcal{O}(\beta^3) \right].$$

• Using the general operator identity

$$\exp(\beta A) \exp(\beta B) = \exp \left[\beta(A + B) + \beta^2[A, B]/2 + \mathcal{O}(\beta^3) \right],$$

the Boltzmann operator can be decomposed in the high temperature limit into those for kinetic and potential energy; to the lowest order as

$$\exp\left(-\beta\frac{p^2}{2m} - \beta\frac{m\omega^2 q^2}{2}\right) \approx \exp(-\beta p^2/2m) \cdot \exp(-\beta m\omega^2 q^2/2).$$

The first term is the Boltzmann operator for an ideal gas. The second term contains an operator diagonalized by $|q\rangle$. The density matrix element

$$\begin{aligned} \langle q'|\rho|q\rangle &= \langle q'|\exp(-\beta p^2/2m)\exp(-\beta m\omega^2 q^2/2)|q\rangle \\ &= \int dp' \langle q'|\exp(-\beta p^2/2m)|p'\rangle \langle p'|\exp(-\beta m\omega^2 q^2/2)|q\rangle \\ &= \int dp' \langle q'|p'\rangle \langle p'|q\rangle \exp(-\beta p'^2/2m) \exp(-\beta q^2 m\omega^2/2). \end{aligned}$$

Using the free particle basis $\langle q'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-iq\cdot p/\hbar}$,

$$\begin{aligned} \langle q'|\rho|q\rangle &= \frac{1}{2\pi\hbar} \int dp' e^{ip'(q-q')/\hbar} e^{-\beta p'^2/2m} e^{-\beta q^2 m\omega^2/2} \\ &= e^{-\beta q^2 m\omega^2/2} \frac{1}{2\pi\hbar} \int dp' \exp\left[-\left(p'\sqrt{\frac{\beta}{2m}} + \frac{i}{2\hbar}\sqrt{\frac{2m}{\beta}}(q-q')\right)^2\right] \exp\left(-\frac{1}{4}\frac{2m}{\beta\hbar^2}(q-q')^2\right), \end{aligned}$$

where we completed the square. Hence

$$\langle q'|\rho|q\rangle = \frac{1}{2\pi\hbar} e^{-\beta q^2 m\omega^2/2} \sqrt{2\pi m k_B T} \exp\left[-\frac{m k_B T}{2\hbar^2}(q-q')^2\right].$$

The proper normalization in the high temperature limit is

$$\begin{aligned} Z &= \int dq \langle q|e^{-\beta p^2/2m} \cdot e^{-\beta m\omega^2 q^2/2}|q\rangle \\ &= \int dq \int dp' \langle q|e^{-\beta p^2/2m}|p'\rangle \langle p'|e^{-\beta m\omega^2 q^2/2}|q\rangle \\ &= \int dq \int dp |\langle q|p\rangle|^2 e^{-\beta p^2/2m} e^{-\beta m\omega^2 q^2/2} = \frac{k_B T}{\hbar\omega}. \end{aligned}$$

Hence the properly normalized matrix element in the high temperature limit is

$$\langle q'|\rho|q\rangle_{\lim T \rightarrow \infty} = \sqrt{\frac{m\omega^2}{2\pi k_B T}} \exp\left(-\frac{m\omega^2}{2k_B T} q^2\right) \exp\left[-\frac{m k_B T}{2\hbar^2}(q-q')^2\right].$$

(g) At low temperatures, ρ is dominated by low energy states. Use the ground state wave-function to evaluate the limiting behavior of $\langle q'|\rho|q \rangle$ as $T \rightarrow 0$.

- In the low temperature limit, we retain only the first terms in the summation

$$\rho_{\lim T \rightarrow 0} \approx \frac{|0\rangle e^{-\beta\hbar\omega/2} \langle 0| + |1\rangle e^{-3\beta\hbar\omega/2} \langle 1| + \dots}{e^{-\beta\hbar\omega/2} + e^{-3\beta\hbar\omega/2}}.$$

Retaining only the term for the ground state in the numerator, but evaluating the geometric series in the denominator,

$$\langle q'|\rho|q \rangle_{\lim T \rightarrow 0} \approx \langle q'|0\rangle \langle 0|q\rangle e^{-\beta\hbar\omega/2} \cdot \left(e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2} \right).$$

Using the expression for $\langle q|0\rangle$ given in part (b),

$$\langle q'|\rho|q \rangle_{\lim T \rightarrow 0} \approx \sqrt{\frac{m\omega}{\pi\hbar}} \exp\left[-\frac{m\omega}{2\hbar}(q^2 + q'^2)\right] (1 - e^{-\beta\hbar\omega}).$$

(h) Calculate the exact expression for $\langle q'|\rho|q \rangle$.

9. Relativistic Coulomb gas: Consider a *quantum* system of N positive, and N negative charged relativistic particles in box of volume $V = L^3$. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{2N} c|\vec{p}_i| + \sum_{i<j}^{2N} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|},$$

where $e_i = +e_0$ for $i = 1, \dots, N$, and $e_i = -e_0$ for $i = N + 1, \dots, 2N$, denote the charges of the particles; $\{\vec{r}_i\}$ and $\{\vec{p}_i\}$ their coordinates and momenta respectively. While this is too complicated a system to solve, we can nonetheless obtain some exact results.

(a) Write down the Schrödinger equation for the eigenvalues $\varepsilon_n(L)$, and (in coordinate space) eigenfunctions $\Psi_n(\{\vec{r}_i\})$. State the constraints imposed on $\Psi_n(\{\vec{r}_i\})$ if the particles are bosons or fermions?

- In the coordinate representation \vec{p}_i is replaced by $-i\hbar\nabla_i$, leading to the Schrödinger equation

$$\left[\sum_{i=1}^{2N} c| -i\hbar\nabla_i | + \sum_{i<j}^{2N} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|} \right] \Psi_n(\{\vec{r}_i\}) = \varepsilon_n(L) \Psi_n(\{\vec{r}_i\}).$$

There are N identical particles of charge $+e_0$, and N identical particles of charge $-e_0$. We can examine the effect of permutation operators P_+ and P_- on these two sets. The symmetry constraints can be written compactly as

$$P_+ P_- \Psi_n(\{\vec{r}_i\}) = \eta_+^{P_+} \cdot \eta_-^{P_-} \Psi_n(\{\vec{r}_i\}),$$

where $\eta = +1$ for bosons, $\eta = -1$ for fermions, and $(-1)^P$ denotes the parity of the permutation. Note that there is no constraint associated with exchange of particles with opposite charge.

(b) By a change of scale $\vec{r}_i' = \vec{r}_i/L$, show that the eigenvalues satisfy a scaling relation $\varepsilon_n(L) = \varepsilon_n(1)/L$.

• After the change of scale $\vec{r}_i' = \vec{r}_i/L$ (and corresponding change in the derivative $\nabla_i' = L\nabla_i$), the above Schrödinger equation becomes

$$\left[\sum_{i=1}^{2N} c \left| -i\hbar \frac{\nabla_i'}{L} \right| + \sum_{i<j}^{2N} \frac{e_i e_j}{L |\vec{r}_i' - \vec{r}_j'|} \right] \Psi_n \left(\left\{ \frac{\vec{r}_i'}{L} \right\} \right) = \varepsilon_n(L) \Psi_n \left(\left\{ \frac{\vec{r}_i'}{L} \right\} \right).$$

The coordinates in the above equation are confined to a box of unit size. We can regard it as the Schrödinger equation in such a box, with wave-functions $\Psi_n'(\{\vec{r}_i\}) = \Psi_n(\{\vec{r}_i'/L\})$. The corresponding eigenvalues are $\varepsilon_n(1) = L\varepsilon_n(L)$ (obtained after multiplying both sides of the above equation by L). We thus obtain the scaling relation

$$\varepsilon_n(L) = \frac{\varepsilon_n(1)}{L}.$$

(c) Using the formal expression for the partition function $Z(N, V, T)$, in terms of the eigenvalues $\{\varepsilon_n(L)\}$, show that Z does not depend on T and V separately, but only on a specific scaling combination of them.

• The formal expression for the partition function is

$$\begin{aligned} Z(N, V, T) &= \text{tr} \left(e^{-\beta\mathcal{H}} \right) = \sum_n \exp \left(-\frac{\varepsilon_n(L)}{k_B T} \right) \\ &= \sum_n \exp \left(-\frac{\varepsilon_n(1)}{k_B T L} \right), \end{aligned}$$

where we have used the scaling form of the energy levels. Clearly, in the above sum T and L always occur in the combination TL . Since $V = L^3$, the appropriate scaling variable is VT^3 , and

$$Z(N, V, T) = \mathcal{Z}(N, VT^3).$$

(d) Relate the energy E , and pressure P of the gas to variations of the partition function. Prove the exact result $E = 3PV$.

• The average energy in the canonical ensemble is given by

$$E = -\frac{\partial \ln Z}{\partial \beta} = k_B T^2 \frac{\partial \ln Z}{\partial T} = k_B T^2 (3VT^2) \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)} = 3k_B VT^4 \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)}.$$

The free energy is $F = -k_B T \ln Z$, and its variations are $dF = -SdT - PdV + \mu dN$. Hence the gas pressure is given by

$$P = -\frac{\partial F}{\partial V} = k_B T \frac{\partial \ln Z}{\partial V} = k_B T^4 \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)}.$$

The ratio of the above expressions gives the exact identity $E = 3PV$.

(e) The Coulomb interaction between charges in d -dimensional space falls off with separation as $e_i e_j / |\vec{r}_i - \vec{r}_j|^{d-2}$. (In $d = 2$ there is a logarithmic interaction.) In what dimension d can you construct an exact relation between E and P for *non-relativistic* particles (kinetic energy $\sum_i \vec{p}_i^2 / 2m$)? What is the corresponding exact relation between energy and pressure?

- The above exact result is a consequence of the simple scaling law relating the energy eigenvalues $\varepsilon_n(L)$ to the system size. We could obtain the scaling form in part (b) since the kinetic and potential energies scaled in the same way. The kinetic energy for *non-relativistic* particles $\sum_i \vec{p}_i^2 / 2m = -\sum_i \hbar^2 \nabla_i^2 / 2m$, scales as $1/L^2$ under the change of scale $\vec{r}_i' = \vec{r}_i / L$, while the interaction energy $\sum_{i < j}^{2N} e_i e_j / |\vec{r}_i - \vec{r}_j|^{d-2}$ in d space dimensions scales as $1/L^{d-2}$. The two forms will scale the same way in $d = 4$ dimensions, leading to

$$\varepsilon_n(L) = \frac{\varepsilon_n(1)}{L^2}.$$

The partition function now has the scaling form

$$Z(N, V = L^4, T) = \mathcal{Z}(N, (TL^2)^2) = \mathcal{Z}(N, VT^2).$$

Following steps in the previous part, we obtain the exact relationship $E = 2PV$.

(f) Why are the above ‘exact’ scaling laws not expected to hold in dense (liquid or solid) Coulomb mixtures?

- The scaling results were obtained based on the assumption of the existence of a single scaling length L , relevant to the statistical mechanics of the problem. This is a good approximation in a gas phase. In a dense (liquid or solid) phase, the short-range repulsion between particles is expected to be important, and the particle size a is another relevant length scale which will enter in the solution to the Schrödinger equation, and invalidate the scaling results.

10. *The virial theorem* is a consequence of the invariance of the phase space for a system of N (classical or quantum) particles under canonical transformations, such as a change of scale. In the following, consider N particles with coordinates $\{\vec{q}_i\}$, and conjugate momenta $\{\vec{p}_i\}$ (with $i = 1, \dots, N$), and subject to a Hamiltonian $\mathcal{H}(\{\vec{p}_i\}, \{\vec{q}_i\})$.

(a) *Classical version:* Write down the expression for the classical partition function, $Z \equiv Z[\mathcal{H}]$. Show that it is invariant under the rescaling $\vec{q}_1 \rightarrow \lambda\vec{q}_1$, $\vec{p}_1 \rightarrow \vec{p}_1/\lambda$ of a pair of conjugate variables, i.e. $Z[\mathcal{H}_\lambda]$ is independent of λ , where \mathcal{H}_λ is the Hamiltonian obtained after the above rescaling.

- The classical partition function is obtained by appropriate integrations over phase space as

$$Z = \frac{1}{N!h^{3N}} \int \left(\prod_i d^3 p_i d^3 q_i \right) e^{-\beta\mathcal{H}}.$$

The rescaled Hamiltonian $\mathcal{H}_\lambda = \mathcal{H}(\vec{p}_1/\lambda, \{\vec{p}_{i \neq 1}\}, \lambda\vec{q}_1, \{\vec{q}_{i \neq 1}\})$ leads to a rescaled partition function

$$Z[\mathcal{H}_\lambda] = \frac{1}{N!h^{3N}} \int \left(\prod_i d^3 p_i d^3 q_i \right) e^{-\beta\mathcal{H}_\lambda},$$

which reduces to

$$Z[\mathcal{H}_\lambda] = \frac{1}{N!h^{3N}} \int (\lambda^3 d^3 p'_1) (\lambda^{-3} d^3 q'_1) \left(\prod_i d^3 p_i d^3 q_i \right) e^{-\beta\mathcal{H}} = Z,$$

under the change of variables $\vec{q}'_1 = \lambda\vec{q}_1$, $\vec{p}'_1 = \vec{p}_1/\lambda$.

(b) *Quantum mechanical version:* Write down the expression for the quantum partition function. Show that it is also invariant under the rescalings $\vec{q}_1 \rightarrow \lambda\vec{q}_1$, $\vec{p}_1 \rightarrow \vec{p}_1/\lambda$, where \vec{p}_i and \vec{q}_i are now quantum mechanical operators. (Hint: start with the time-independent Schrödinger equation.)

- Using the energy basis

$$Z = \text{tr} \left(e^{-\beta\mathcal{H}} \right) = \sum_n e^{-\beta E_n},$$

where E_n are the energy eigenstates of the system, obtained from the Schrödinger equation

$$\mathcal{H}(\{\vec{p}_i\}, \{\vec{q}_i\}) |\psi_n\rangle = E_n |\psi_n\rangle,$$

where $|\psi_n\rangle$ are the eigenstates. After the rescaling transformation, the corresponding equation is

$$\mathcal{H}(\vec{p}_1/\lambda, \{\vec{p}_{i \neq 1}\}, \lambda\vec{q}_1, \{\vec{q}_{i \neq 1}\}) \left| \psi_n^{(\lambda)} \right\rangle = E_n^{(\lambda)} \left| \psi_n^{(\lambda)} \right\rangle.$$

In the coordinate representation, the momentum operator is $\vec{p}_i = -i\hbar\partial/\partial\vec{q}_i$, and therefore $\psi_\lambda(\{\vec{q}_i\}) = \psi(\{\lambda\vec{q}_i\})$ is a solution of the rescaled equation with eigenvalue $E_n^{(\lambda)} = E_n$. Since the eigen-energies are invariant under the transformation, so is the partition function which is simply the sum of corresponding exponentials.

(c) Now assume a Hamiltonian of the form

$$\mathcal{H} = \sum_i \frac{\vec{p}_i^2}{2m} + V(\{\vec{q}_i\}).$$

Use the result that $Z[\mathcal{H}_\lambda]$ is independent of λ to prove the *virial* relation

$$\left\langle \frac{\vec{p}_1^2}{m} \right\rangle = \left\langle \frac{\partial V}{\partial \vec{q}_1} \cdot \vec{q}_1 \right\rangle,$$

where the brackets denote thermal averages.

- Differentiating the free energy with respect to λ at $\lambda = 1$, we obtain

$$0 = \frac{\partial \ln Z_\lambda}{\partial \lambda} \Big|_{\lambda=1} = -\beta \left\langle \frac{\partial H_\lambda}{\partial \lambda} \Big|_{\lambda=1} \right\rangle = -\beta \left\langle -\frac{\vec{p}_1^2}{m} + \frac{\partial V}{\partial \vec{q}_1} \cdot \vec{q}_1 \right\rangle,$$

i.e.,

$$\left\langle \frac{\vec{p}_1^2}{m} \right\rangle = \left\langle \frac{\partial V}{\partial \vec{q}_1} \cdot \vec{q}_1 \right\rangle.$$

(d) The above relation is sometimes used to estimate the mass of distant galaxies. The stars on the outer boundary of the G-8.333 galaxy have been measured to move with velocity $v \approx 200$ km/s. Give a numerical estimate of the ratio of the G-8.333's mass to its size.

- The virial relation applied to a gravitational system gives

$$\langle mv^2 \rangle = \left\langle \frac{GMm}{R} \right\rangle.$$

Assuming that the kinetic and potential energies of the stars in the galaxy have reached some form of equilibrium gives

$$\frac{M}{R} \approx \frac{v^2}{G} \approx 6 \times 10^{20} \text{ kg/m}.$$

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