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

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

Thermodynamics

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

Mathematical Formulas

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

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

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

$$\cosh(x) = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots \qquad\qquad \ln(1-x) = -\sum_{n=1}^\infty \frac{x^n}{n}$$

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

1. *Attractive shell potential:* Consider a gas of particles in three dimensions 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 $B_2(T)$.

• **(2 points)** The second virial coefficient is obtained from

$$B_2 \equiv -\frac{1}{2} \int d^3 r_{12} \left\{ \exp[-\beta \mathcal{V}(r_{12})] - 1 \right\},$$

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

$$B_2 = -\frac{1}{2} \left[\int_0^a d^3 r_{12}(-1) + \int_a^b d^3 r_{12} \left(e^{\beta \varepsilon} - 1 \right) \right]$$

$$= -\frac{1}{2} \left\{ V_3(a)(-1) + [V_3(b) - V_3(a)] \cdot [\exp(\beta \varepsilon) - 1] \right\},$$

where

$$V_3(r) = \frac{4\pi}{3} r^3,$$

is the volume of a 3–dimensional sphere of radius r. Thus,

$$B_2(T) = \frac{1}{2} V_3(b) - \frac{1}{2} \exp(\beta \varepsilon) \left[V_3(b) - V_3(a) \right] = \frac{2\pi}{3} \left[b^3 - (b^3 - a^3) e^{\beta \varepsilon} \right].$$

(b) Find the limiting behavior of $B_2(T)$ at high temperature (including the first correction to order of β), and comment on the low temperature behavior of $B_2(T)$.

• **(2 points)** For high temperatures $\exp(\beta \varepsilon) \approx 1 + \beta \varepsilon$, and

$$B_2(T) \approx \frac{1}{2} V_3(a) - \frac{\beta \varepsilon}{2} [V_3(b) - V_3(a)] = \frac{2\pi}{3} \left[a^3 - \beta \varepsilon (b^3 - a^3) \right].$$

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

$$B_2(T) \approx \frac{1}{2} V_3(a) = \frac{2\pi}{3} a^3.$$

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

$$B_2 = -\frac{1}{2} \left\{ V_3(a)(-1) + [V_3(b) - V_3(a)] \cdot [\exp(\beta \varepsilon) - 1] \right\}$$

$$\approx -\frac{1}{2} [V_3(b) - V_3(a)] \exp(\beta \varepsilon) = -\frac{2\pi}{3} (b^3 - a^3) e^{\beta \varepsilon},$$

2

resulting in $B_2 < 0$.

(c) In the high temperature limit, reorganize the equation of state into the van der Waals form $(P + an^2)(V - Nb) = Nk_BT$, and identify the van der Waals parameters a and b.

- **(2 points)** Including the correction introduced by the second virial coefficient, the equation of state becomes

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

Using the expression for B_2 in the high temperature limit,

$$\frac{PV}{Nk_BT} = 1 + \frac{N}{2V}\{V_3(a) - \beta\varepsilon[V_3(b) - V_3(a)]\},$$

and

$$P + \frac{N^2}{2V^2}\varepsilon[V_3(b) - V_3(a)] = k_BT\frac{N}{V}\left(1 + \frac{N}{2V}V_3(a)\right).$$

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

$$1 + \frac{n}{2}V_3(a) \approx \left(1 - \frac{n}{2}V_3(a)\right)^{-1} = V\left(V - \frac{N}{2}V_3(a)\right)^{-1},$$

the equation of state becomes

$$\left(P + \frac{n^2\varepsilon}{2}[V_3(b) - V_3(a)]\right) \cdot \left(V - \frac{N}{2}V_3(a)\right) = Nk_BT.$$

This can be recast in the usual van der Waals form

$$(P + an^2) \cdot (V - Nb) = Nk_BT,$$

with

$$a = \frac{\varepsilon}{2}[V_3(b) - V_3(a)] = \frac{2\pi}{3}(b^3 - a^3)\varepsilon,$$

and

$$b = \frac{1}{2}V_3(a) = \frac{2\pi}{3}a^3.$$

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2. *Interacting point particles:* Consider a system of N classical point particles at temperature T, in a volume V. Unspecified interactions between the particles modify the energy

3

of any configuration by $-NU(V/N)$, where $U(v)$ if some function of the inverse density $v = V/N$. The partition function is thus given by

$$Z(T, N, V) = Z_{\text{ideal gas}}(T, N, V) \times \exp\left[\beta N U(v)\right],$$

where $Z_{\text{ideal gas}}(T, N, V)$ is the partition function of a classical gas, and $\beta = (k_B T)^{-1}$,

(a) The ideal gas partition function depends on volume V and temperature T as $Z_{\text{ideal gas}}(T, N, V) \propto V^x T^y$. What are the values of x and y?

• **(1 points)** From the N coordinate integrations we find $Z_{\text{ideal gas}} \propto V^N$, while the $3N$ momentum integrations give $Z_{\text{gas}} \propto T^{3N/2}$, i.e. $x = N$ and $y = 3N/2$.

(b) Using the partition function, or otherwise, compute the energy $E = \langle \mathcal{H} \rangle$.

• **(2 points)** Since the ideal gas partition function is proportional to $\beta^{-3N/2}$, we have

$$\ln Z = -\frac{3N}{2} \ln \beta + \beta N U\left(\frac{V}{N}\right) + (\beta - \text{independent terms}).$$

The mean energy is obtained from

$$E = \langle \mathcal{H} \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{3N}{2}\frac{1}{\beta} - NU(v) = \frac{3N}{2}k_B T - NU(v).$$

(c) Find the heat capacity C_V at constant volume.

• **(1 points)** The heat capacity is given by

$$C_V = \left.\frac{dQ}{dT}\right|_V = \left.\frac{dE}{dT}\right|_V = \frac{3N}{2}k_B.$$

(d) Using the partition function, or otherwise, compute the pressure $P(n, T)$, as a function of the density $n = N/V$.

• **(2 points)** Since the ideal gas partition function is proportional to V^N, we have

$$\ln Z = N \ln V + \beta N U\left(\frac{V}{N}\right) + (V - \text{independent terms}).$$

The pressure is obtained from

$$\beta P = \frac{\partial \ln Z}{\partial V} = \frac{N}{V} + \beta U'(v), \implies P = n k_B T + U'(v).$$

(e) Compute the isothermal compressibility $\kappa_T(n) = -\frac{1}{V}\frac{\partial V}{\partial P}\big|_T$.

$\bullet$ **(2 points)** From the above expression for pressure, we obtain

$$\frac{\partial P}{\partial V}\Big|_T = -\frac{Nk_BT}{V^2} + \frac{1}{N}U''(v) \quad \Longrightarrow \quad -V\frac{\partial P}{\partial V}\Big|_T = nk_BT - \frac{1}{n}U''(v)\,,$$

and thus

$$\kappa_T(n) = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T = \frac{n}{n^2k_BT - U''(v)}\,.$$

(f) What is the necessary condition for $U(v)$ for stability of the system of particles.

$\bullet$ **(1 points)** Stability requires $-\Delta P\delta V \geq 0$, and hence $\kappa(T) \geq 0$. For this to be satisfied, we need

$$v^2 U''(v) \leq k_BT\,.$$

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