Answer all three problems, but note that the first parts of each problem are easier than its last parts. Therefore, make sure to proceed to the next problem when you get stuck.

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

$dE = TdS + đW$ $\qquad$ For a gas: $đW = -PdV$ $\qquad$ For a wire: $đW = Jdx$

Mathematical Formulas

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

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

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

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

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

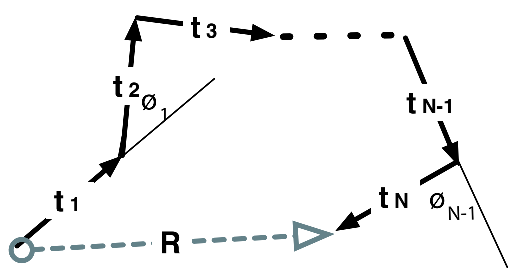
1. *Equations of State:* This problem appeared in the second problem set, and is related to how the equation of state constrains the internal energy of a gas.

(a) Show that the ideal gas equation of state, $PV = Nk_BT$, implies that internal energy E can only depend on the temperature T.

(b) What is the most general equation of state, $P(V,T)$, consistent with an internal energy that depends only on temperature?

(c) Show that for a van der Waals gas, with $\left[P - a\left(N/V\right)^2\right]\left(V - Nb\right) = Nk_BT$, the heat capacity C_V is a function of temperature alone.

2. *Semi-flexible polymer in two dimensions:* Configurations of a polymer are described by a set of vectors $\{\mathbf{t}_i\}$ of length a in two dimensions (for $i = 1, \cdots, N$), or alternatively by the angles $\{\phi_i\}$ between successive vectors, as indicated in the figure below.



The (joint) probability to find the polymer at a given configuration is $p(\{\mathbf{t}_i\}) \propto \exp(-\mathcal{H}/k_B T)$, where T is the temperature, and $\mathcal{H}$ is the energy of the configuration, given by

$$\mathcal{H} = -\kappa \sum_{i=1}^{N-1} \mathbf{t}_i \cdot \mathbf{t}_{i+1} = -\kappa a^2 \sum_{i=1}^{N-1} \cos\phi_i \quad .$$

(The parameter κ is related to the bending rigidity or the polymer.)

(a) Show that $\langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle \propto \exp(-|n-m|/\xi)$, and obtain an expression for the *persistence length* $\ell_p = a\xi$. (You can leave the answer as the ratio of simple integrals.)

Hint: Relate the angle between $\mathbf{t}_m$ and $\mathbf{t}_n$ to the angles $\{\phi_i\}$.

(b) Consider the end–to–end distance $\mathbf{R}$ as illustrated in the figure. Obtain an expression for $\langle R^2 \rangle$ in the limit of $N \gg 1$.

Hint: Relate $\mathbf{R}$ to $\{\mathbf{t}_i\}$.

(c) Find the probability $p(\mathbf{R})$ in the limit of $N \gg 1$.

3. *Zeroth-order hydrodynamics:* The hydrodynamic equations resulting from the conservation of particle number, momentum, and energy in collisions are (in a uniform box):

$$\begin{cases} \partial_t n + \partial_\alpha \left(n u_\alpha \right) = 0 \\ \partial_t u_\alpha + u_\beta \partial_\beta u_\alpha = -\dfrac{1}{mn} \partial_\beta P_{\alpha\beta} \\ \partial_t \varepsilon + u_\alpha \partial_\alpha \varepsilon = -\dfrac{1}{n} \partial_\alpha h_\alpha - \dfrac{1}{n} P_{\alpha\beta} u_{\alpha\beta} \end{cases},$$

where n is the local density, $\vec{u} = \langle \vec{p}/m \rangle$, $u_{\alpha\beta} = \left(\partial_\alpha u_\beta + \partial_\beta u_\alpha \right)/2$, and $\varepsilon = \left\langle mc^2/2 \right\rangle$, with $\vec{c} = \vec{p}/m - \vec{u}$.

(a) For the zeroth order density

$$f_1^0(\vec{p}, \vec{q}, t) = \frac{n(\vec{q}, t)}{\left(2\pi m k_B T(\vec{q}, t) \right)^{3/2}} \exp\left[-\frac{\left(\vec{p} - m\vec{u}(\vec{q}, t) \right)^2}{2 m k_B T(\vec{q}, t)} \right],$$

calculate the pressure tensor $P^0_{\alpha\beta} = mn \;\; c_\alpha c_\beta \;^0$, and the heat flux $h^0_\alpha = nm \;\; c_\alpha c^2/2 \;^0$.

(b) Obtain the zeroth order hydrodynamic equations governing the evolution of $n(\vec{q}, t)$, $\vec{u}(\vec{q}, t)$, and $T(\vec{q}, t)$.

(c) Show that the above equations imply $D_t \ln \left(n T^{-3/2} \right) = 0$, where $D_t = \partial_t + u_\beta \partial_\beta$ is the material derivative along streamlines.

(d) Write down the expression for the function $\mathrm{H}^0(t) = \int d^3\vec{q}d^3\vec{p}f_1^0(\vec{p},\vec{q},t)\ln f_1^0(\vec{p},\vec{q},t)$, after performing the integrations over $\vec{p}$, in terms of $n(\vec{q},t)$, $\vec{u}(\vec{q},t)$, and $T(\vec{q},t)$.

(e) Using the hydrodynamic equations in (b) calculate $d\mathrm{H}^0/dt$.

(f) Discuss the implications of the result in (e) for approach to equilibrium.