

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

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

Thermodynamics

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

Mathematical Formulas

$$\begin{aligned} \int_0^\infty dx \, x^n e^{-\alpha x} &= \frac{n!}{\alpha^{n+1}} & \left(\frac{1}{2}\right)! &= \frac{\sqrt{\pi}}{2} \\ \int_{-\infty}^\infty dx \exp\left[-ikx - \frac{x^2}{2\sigma^2}\right] &= \sqrt{2\pi\sigma^2} \exp\left[-\frac{\sigma^2 k^2}{2}\right] & \lim_{N \rightarrow \infty} \ln N! &= N \ln N - N \\ \langle e^{-ikx} \rangle &= \sum_{n=0}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle & \ln \langle e^{-ikx} \rangle &= \sum_{n=1}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle_c \\ \cosh(x) &= 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \dots & \ln(1-x) &= -\sum_{n=1}^\infty \frac{x^n}{n} \\ \text{Surface area of a unit sphere in } d \text{ dimensions} & & S_d &= \frac{2\pi^{d/2}}{(d/2-1)!} \end{aligned}$$

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, $PV = Nk_B T$, implies that internal energy E can only depend on the temperature T .

- Since there is only one form of work, we can choose any two parameters as independent variables. For example, selecting T and V , such that $E = E(T, V)$, and $S = S(T, V)$, we obtain

$$dE = TdS - PdV = T \left. \frac{\partial S}{\partial T} \right|_V dT + T \left. \frac{\partial S}{\partial V} \right|_T dV - PdV,$$

resulting in

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial S}{\partial V} \right|_T - P.$$

Using the Maxwell's relation[†]

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V,$$

we obtain

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial P}{\partial T} \right|_V - P.$$

Since $T \left. \frac{\partial P}{\partial T} \right|_V = T \frac{Nk_B}{V} = P$, for an ideal gas, $\left. \frac{\partial E}{\partial V} \right|_T = 0$.

Thus E depends only on T , i.e. $E = E(T)$.

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

- If $E = E(T)$,

$$\left. \frac{\partial E}{\partial V} \right|_T = 0, \implies T \left. \frac{\partial P}{\partial T} \right|_V = P.$$

The solution for this equation is $P = f(V)T$, where $f(V)$ is any function of only V .

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

- The van der Waals equation of state is given by

$$\left[P - a \left(\frac{N}{V} \right)^2 \right] \cdot (V - Nb) = Nk_B T,$$

[†] $dL = Xdx + Ydy + \dots, \implies \left. \frac{\partial X}{\partial y} \right|_x = \left. \frac{\partial Y}{\partial x} \right|_y = \frac{\partial^2 L}{\partial x \partial y}.$

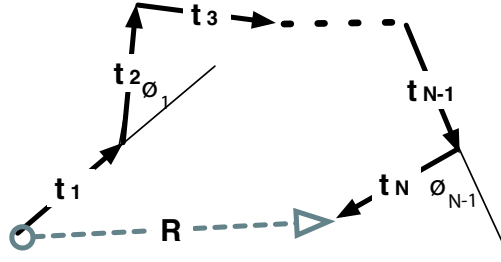
or

$$P = \frac{Nk_B T}{(V - Nb)} + a \left(\frac{N}{V} \right)^2.$$

From these equations, we conclude that

$$C_V \equiv \left. \frac{\partial E}{\partial T} \right|_V, \quad \Rightarrow \quad \left. \frac{\partial C_V}{\partial V} \right|_T = \frac{\partial^2 E}{\partial V \partial T} = \frac{\partial}{\partial T} \left\{ T \left. \frac{\partial P}{\partial T} \right|_V - P \right\} = T \left. \frac{\partial^2 P}{\partial T^2} \right|_V = 0.$$

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 $i = 1, \dots, N$), 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 of 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 $\{\phi_i\}$.

- In terms of the angles, the dot product can be written as

$$\mathbf{t}_m \cdot \mathbf{t}_n = a^2 \cos(\phi_m + \phi_{m+1} + \dots + \phi_{n-1}) = a^2 \Re e^{i(\phi_m + \phi_{m+1} + \dots + \phi_{n-1})}.$$

Note that the angles $\{\phi_n\}$ are *independent variables*, distributed according to the Boltzmann weight

$$p[\{\phi_n\}] \propto \prod_{n=1}^{N-1} \exp\left(\frac{\kappa a^2}{k_B T} \cos \phi_n\right) \quad .$$

Hence the average of the product is the product of averages, and

$$\langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle = a^2 \Re \prod_{k=m}^{n-1} \langle e^{i\phi_k} \rangle = a^2 \left[\frac{\int d\phi \cos \phi e^{\frac{\kappa a^2}{k_B T} \cos \phi}}{\int d\phi e^{\frac{\kappa a^2}{k_B T} \cos \phi}} \right]^{|n-m|}.$$

The persistence length is thus given by

$$\ell_p = \frac{a}{\ln \left[\int d\phi e^{\frac{\kappa a^2}{k_B T} \cos \phi} / \int d\phi \cos \phi e^{\frac{\kappa a^2}{k_B T} \cos \phi} \right]}.$$

(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 $\{\mathbf{t}_i\}$.

• Using $\mathbf{R} = \sum_{n=1}^{N-1} \mathbf{t}_n$, we obtain

$$\langle R^2 \rangle = \sum_{m,n} \langle \mathbf{t}_m \cdot \mathbf{t}_n \rangle = \sum_{m,n} a^2 e^{-|n-m|/\xi}.$$

The above sum decays exponentially around each point. Ignoring corrections from end effects, which are asymptotically negligible for $N \rightarrow \infty$, we obtain

$$\langle R^2 \rangle \simeq a^2 N \left[1 + 2 \frac{e^{-1/\xi}}{1 - e^{-1/\xi}} \right] = a^2 N \coth \frac{1}{2\xi}.$$

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

• Since $\mathbf{R} = \sum_{n=1}^{N-1} \mathbf{t}_n$, we can use the central limit theorem to conclude that in the limit of $N \rightarrow \infty$, the probability distribution $p(\mathbf{R})$ approaches a Gaussian form. Thus, we just need to evaluate the mean and variance of \mathbf{R} . Since the mean $\langle \mathbf{R} \rangle = 0$ by symmetry, the variance is equal to $\langle R^2 \rangle$ calculated in part (b). Noting that in two dimensions, $\langle R_x^2 \rangle = \langle R_y^2 \rangle = \langle R^2 \rangle / 2$, the properly normalized Gaussian form is

$$p(\mathbf{R}) = \frac{1}{\pi \langle R^2 \rangle} \exp \left[-\frac{\mathbf{R} \cdot \mathbf{R}}{\langle R^2 \rangle} \right].$$

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

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

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

(a) For the zeroth order density

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

calculate the pressure tensor $P_{\alpha\beta}^0 = mn \langle c_\alpha c_\beta \rangle^0$, and the heat flux $h_\alpha^0 = nm \langle c_\alpha c^2/2 \rangle^0$.

- The PDF for \vec{c} is proportional to the Gaussian $\exp(-mc^2/(2k_B T))$, from which we immediately get

$$\langle c_\alpha c_\beta \rangle^0 = \frac{k_B T}{m} \delta_{\alpha\beta} \implies P_{\alpha\beta}^0 = n k_B T \delta_{\alpha\beta}, \quad \text{and} \quad \varepsilon = \frac{3}{2} k_B T.$$

All odd expectation values of the symmetric weight are zero, specifically $\langle \vec{c} \rangle = 0$, and $\langle \vec{h}^0 \rangle = 0$.

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

- Substituting $P_{\alpha\beta}^0 = n k_B T \delta_{\alpha\beta}$, $\varepsilon = 3k_B T/2$, and $\langle \vec{h}^0 \rangle = 0$ in the hydrodynamic equations gives:

$$\begin{cases} \partial_t n + u_\alpha \partial_\alpha n = -n \partial_\alpha u_\alpha \\ \partial_t u_\alpha + u_\beta \partial_\beta u_\alpha = -\frac{k_B}{mn} \partial_\alpha (nT) \\ \frac{3}{2} (\partial_t T + u_\alpha \partial_\alpha T) = -T \partial_\alpha u_\alpha \end{cases}.$$

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

- Using $D_t = \partial_t + u_\beta \partial_\beta$, the above equations can be written as

$$\begin{cases} D_t \ln n = -\partial_\alpha u_\alpha \\ D_t u_\alpha = -\frac{k_B}{mn} \partial_\alpha (nT) \\ \frac{3}{2} D_t \ln T = -\partial_\alpha u_\alpha \end{cases}.$$

Eliminating $\partial_\alpha u_\alpha$ between the first and third equations gives the required result of $D_t \ln (nT^{-3/2}) = 0$.

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

- Using the expression for f_1^0 ,

$$H^0(t) = \int d^3 \vec{q} d^3 \vec{p} \frac{n}{(2\pi m k_B T)^{3/2}} \exp \left[-\frac{(\vec{p} - m\vec{u})^2}{2m k_B T} \right] \times \left[\ln (nT^{-3/2}) - \frac{3}{2} \ln (2\pi m k_B) - \frac{(\vec{p} - m\vec{u})^2}{2m k_B T} \right].$$

The Gaussian averages over \vec{p} are easily performed to yield

$$H^0(t) = \int d^3 \vec{q} n \left[\ln (nT^{-3/2}) - \frac{3}{2} \ln (2\pi m k_B) - \frac{3}{2} \right].$$

(e) Using the hydrodynamic equations in (b) calculate dH^0/dt .

- Taking the time derivative inside the integral gives

$$\frac{dH^0}{dT} = \int d^3 \vec{q} \left[\partial_t n \ln (nT^{-3/2}) + n \partial_t \ln (nT^{-3/2}) \right].$$

Use the results of parts (b) and (c) to substitute for $\partial_t n$ and $\partial_t \ln (nT^{-3/2})$, to get

$$\begin{aligned} \frac{dH^0}{dT} &= - \int d^3 \vec{q} \left[\ln (nT^{-3/2}) \partial_\alpha (n u_\alpha) + n u_\alpha \partial_\alpha \ln (nT^{-3/2}) \right] \\ &= - \int d^3 \vec{q} \partial_\alpha \left[n u_\alpha \ln (nT^{-3/2}) \right] = 0, \end{aligned}$$

since the integral of a complete derivative is zero.

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

- The expression for $-H^0$ is related to the entropy of the gas. The result in (f) implies that the entropy of the gas does not change if its n , \vec{u} , and T vary according to the zeroth order equations. The corrections due to first order hydrodynamics are necessary in order to describe the increase in entropy.
