Nonequilibrium Statistical Mechanics (Honours)
Assignment 3

1. **Thermal conductivity of a monatomic gas.** In this problem, we calculate "rigorously" the thermal conductivity of a monatomic gas, composed of molecules of mass m, by solving the Boltzmann equation approximately using the perturbation expansion invented by Chapman and Enskog circa 1917.

   The fundamental assumption underlying the Chapman-Enskog expansion is that the mean free path for intermolecular collisions is much shorter than the distance over which (macroscopic) thermodynamic quantities vary, such as the temperature (whose gradient drives heat transport). Under these conditions, the gas is (nearly) in thermodynamic equilibrium locally, with number density $n(t, \mathbf{x})$ and temperature $T(t, \mathbf{x})$. As we are only interested in the steady-state thermal conductivity here, we restrict attention to a gas whose density and temperature are constant but not uniform, with $n(t, \mathbf{x}) = n(\mathbf{x})$ and $T(t, \mathbf{x}) = T(\mathbf{x})$. We also consider a situation where the gas is held at constant pressure P_0, and where there are no external fields (like gravity).

   (a) Split the distribution function $f(t, \mathbf{x}, \mathbf{v})$ into two parts, the local equilibrium distribution,

   $$f^{(0)}(\mathbf{x}, \mathbf{v}) = \frac{n(\mathbf{x}) m^{3/2}}{[2\pi k_{\mathrm{B}} T(\mathbf{x})]^{3/2}} \exp\left[-\frac{mv^2}{2k_{\mathrm{B}} T(\mathbf{x})}\right] , \tag{1}$$

   plus a small perturbation $f^{(1)}(t, \mathbf{x}, \mathbf{v})$. Show that, *to leading order*,[1] the left-hand side of Boltzmann's equation reduces to

   $$\frac{f^{(0)}(\mathbf{x}, \mathbf{v})}{T(\mathbf{x})} \left[\frac{mv^2}{2k_B T(\mathbf{x})} - \frac{5}{2}\right] (\mathbf{v} \cdot \nabla) T(\mathbf{x}) . \tag{2}$$

   (b) Without loss of generality, write the perturbation in the form $f^{(1)}(t, \mathbf{x}, \mathbf{v}) = f^{(0)}(\mathbf{x}, \mathbf{v}) g(\mathbf{x}, \mathbf{v}) / T(\mathbf{x})$. Note that $g(\mathbf{x}, \mathbf{v})$ is arbitrary at this stage; we still need to solve for it. Show that, *to leading order*, the right-hand side of Boltzmann's equation reduces to

   $$\frac{f^{(0)}(\mathbf{x}, \mathbf{v})}{T(\mathbf{x})} \int d^3\mathbf{v}_2 d^3\mathbf{v}_1' d^3\mathbf{v}_2' \, \sigma V f^{(0)}(\mathbf{x}, \mathbf{v}_2) [g(\mathbf{x}, \mathbf{v}_1') + g(\mathbf{x}, \mathbf{v}_2') - g(\mathbf{x}, \mathbf{v}) - g(\mathbf{x}, \mathbf{v}_2)] , \tag{3}$$

   where $d^3\mathbf{v}_1' d^3\mathbf{v}_2' \, \sigma = d\sigma$ denotes the differential collision cross-section (as a function of solid angle), and $V = |\mathbf{v} - \mathbf{v}_2| = |\mathbf{v}_1' - \mathbf{v}_2'|$ denotes the relative velocity. (*Beware!* This is not as "simple" as it looks; keep careful track of your dummy integration variables.)

   (c) By comparing (2) and (3), and appealing to the symmetry of the system, argue that the unknown function g should take the form

   $$g(\mathbf{x}, \mathbf{v}) = h(\mathbf{x}, v) (\mathbf{v} \cdot \nabla) T(\mathbf{x}) , \tag{4}$$

   where $h(\mathbf{x}, v)$ is another unknown function.

[1] Formally speaking, the small parameter at the heart of the Chapman-Enskog expansion is the ratio of the mean free path to $T/|\nabla T|$, but you should not attempt a formal series expansion here. Simply justify in words why you keep certain terms and discard others.

(d) Write down the integral equation for $h(\mathbf{x}, v)$. Solve it approximately by looking for a polynomial solution of the form

$$h(\mathbf{x}, v) = C(\mathbf{x}) \left[\frac{5}{2} - \frac{mv^2}{2k_B T(\mathbf{x})} \right] . \tag{5}$$

This is the first term in an expansion in generalised Laguerre polynomials. (You are spared the pain of taking the expansion to higher orders in this assignment.) You should find

$$C(\mathbf{x}) = \frac{15m}{8P_0 c_0(\mathbf{x})} , \tag{6}$$

with

$$c_0(\mathbf{x}) = \frac{m^{9/2}}{256\pi^{3/2}[k_\mathrm{B}T(\mathbf{x})]^{9/2}} \int d\Omega \sin^2\theta \int_0^\infty dV\, V^7 \exp\left[-\frac{mV^2}{2k_\mathrm{B}T(\mathbf{x})} \right] \frac{d\sigma}{d\Omega} . \tag{7}$$

In (7), θ is the scattering angle, defined by $V^2 \cos\theta = (\mathbf{v} - \mathbf{v}_2) \cdot (\mathbf{v}_1' - \mathbf{v}_2')$.

(e) (*Optional extension.*) Evaluate $c_0(\mathbf{x})$ for hard-sphere collisions between molecules of radius a.

(f) Calculate the first-order heat flux $\mathbf{Q}$. Hence prove that the thermal conductivity κ, which is defined by $\mathbf{Q} = -\kappa\nabla T$ is given by

$$\kappa = \frac{15k_\mathrm{B}P_0C(\mathbf{x})}{2m} . \tag{8}$$

Hint for part (d). Change integration variables to the centre-of-mass velocity and relative velocity.

Hint for part (f). You can answer this question even if you got stuck on part (d).