Physics 12c: Problem Set 7

Due: Thursday, May 30, 2019
Note: problem 3 is optional.

1. **Mechanical contact and volume fluctuations**

   Consider a system in thermal and mechanical contact with a reservoir at constant temperature τ and pressure p. The heat capacity at constant pressure is defined as

   $$C_p = \left(\frac{\partial U}{\partial \tau}\right)_p + p\left(\frac{\partial V}{\partial \tau}\right)_p . \tag{1}$$

   The isothermal compressibility is defined by

   $$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_\tau , \tag{2}$$

   and the thermal expansion coefficient is defined by

   $$\eta = \frac{1}{V}\left(\frac{\partial V}{\partial \tau}\right)_p . \tag{3}$$

   Here, $U = \langle E\rangle$ and $V = \langle V\rangle$. For a quantity X, we write $\Delta X = X - \langle X\rangle$.

   (a) Compute the expected fluctuations

   $$\langle \Delta E^2\rangle, \quad \langle \Delta E \Delta V\rangle, \quad \langle \Delta V^2\rangle \tag{4}$$

   in terms of C_p, κ, and η. *Hint:* Remember problem 1 on problem set 2. You will have to use an appropriate generalization of the canonical ensemble and study an appropriate generalization of the partition function. You may find it helpful to define the variables $\beta = 1/\tau$ and $\gamma = p/\tau$.

   (b) Compute C_p, κ, η for an ideal monatomic gas and plug them in to determine the fluctuations (4) in terms of N, τ, and V. In particular, show that $\langle \Delta V^2\rangle = \frac{V^2}{N}$.

2. **Kinetic model of a gas**

   The purpose of this problem is to introduce an important concrete model of a gas and to reproduce your result for $\langle \Delta V^2\rangle$ from problem 1 using that model. The computation in problem 1 is much simpler, and you might take this as evidence for the power of partition functions.

   Let us model a gas as a collection of N non-interacting classical particles with mass m and infinitesimal size, moving in a container with dimensions $L_x \times L_y \times L_z$. The gas is in thermal and mechanical contact with a reservoir with pressure p and temperature τ. Specifically, the right-hand wall of the container with area $A = L_y L_z$ is a movable piston with mass $M \gg m$. The reservoir applies pressure p to the piston, and this is balanced by a force from the gas.

The probability distribution of velocities of gas particles is described by the Maxwell-Boltzmann distribution that you computed in problem 4 of problem set 4:

$$f(\mathbf{v}) = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{\beta m(v_x^2+v_y^2+v_z^2)}{2}}. \tag{5}$$

For example, the total number of particles with velocity inside a velocity-space cube $[\mathbf{v}, \mathbf{v} + d\mathbf{v}] = [v_x, v_x + dv_x] \times [v_y, v_y + dv_x] \times [v_z, v_z + dv_z]$ is

$$N f(\mathbf{v}) d^3\mathbf{v} = N f(\mathbf{v}) dv_x dv_y dv_z. \tag{6}$$

You may find it helpful to factor $f(\mathbf{v})$ into a product of 1-dimensional MB distributions $f(\mathbf{v}) = g(v_x)g(v_y)g(v_z)$, where

$$g(v) = \left(\frac{\beta m}{2\pi}\right)^{1/2} e^{-\frac{\beta m v^2}{2}}. \tag{7}$$

(a) We can model the force from the gas as the collective result of many individual elastic collisions between gas particles and the piston. During a single collision, a gas particle with velocity $\mathbf{v}_i = (v_x, v_y, v_z)$ bounces off the wall and leaves with velocity $\mathbf{v}_f = (-v_x, v_y, v_z)$. During a bounce, what momentum does the gas particle transfer to the wall?

(b) Let the number of particles with velocity $\mathbf{v} = (v_x, v_y, v_z)$ inside a velocity-space cube $d^3\mathbf{v}$ that hit the wall in a time interval dt be

$$n(\mathbf{v}) f(\mathbf{v})\, dt\, d^3\mathbf{v} \tag{8}$$

Compute $n(\mathbf{v})$. What is the total momentum transfer to the wall from these particles?

(c) Integrate your answer to the previous part over $\mathbf{v}$ to obtain the total momentum transfer to the piston in time dt. Be careful: only one sign of v_x contributes. You should recover the ideal gas law $p = \frac{N\tau}{V}$. *Note:* there is also a slick way to compute the above integral using equipartition of energy. However you want to do it is fine.

Let us now consider fluctuations in the position of the piston. We write its position as $L_x + x$, where $\langle x \rangle = 0$ in equilibrium. There are three important effects:

- The piston experiences a position-dependent force from the volume-dependence of the ideal gas law.
- The piston experiences a velocity-dependent drag force from increased/decreased impulse of gas particles.
- Fluctuations in the number of particles hitting the piston cause the force on the piston to fluctuate around its average value.

Overall, the position of the piston satisfies the differential equation

$$M\ddot{x} = -kx - \gamma\dot{x} + \zeta(t), \tag{9}$$

where $-xk$ is the position-dependent force, $-\gamma\dot{x}$ is the velocity-dependent drag force, and $\zeta(t)$ is a random driving force satisfying

$$\begin{aligned} \langle\zeta(t)\rangle &= 0, \\ \langle\zeta(t)\zeta(t')\rangle &= r\delta(t-t') \end{aligned} \tag{10}$$

coming from fluctuations in the number of particles hitting the piston. Our goal is to compute k, γ, r.

(d) The reservoir exerts a constant force $-pA = -\frac{N\tau}{L_x}$ on the piston. The gas exerts an average force $\frac{N\tau A}{V}$ on the piston, where $V = A(L_x + x)$. Compute k by linearizing the total force around $x = 0$.

(e) The term $-\gamma\dot{x}$ is a velocity-dependent drag force. Suppose the piston has velocity $\dot{x}$. In the frame of the piston, the distribution of velocities of the gas molecules is shifted

$$f(v_x, v_y, v_z) \to f(v_x + \dot{x}, v_y, v_z) \tag{11}$$

Linearize this distribution around $\dot{x} = 0$ and redo your calculation in part (2c) to compute γ.

We would now like to compute r. Let us model each bounce as an instantaneous force:

$$2mv_{i,x}\delta(t - t_i), \tag{12}$$

where t_i is the time of the bounce and $\mathbf{v}_i$ is the velocity of the particle participating in the bounce. Consider a long time interval T, during which $B \gg 1$ bounces occur. The force at time t is

$$F(t; t_1, \mathbf{v}_1, \ldots, t_B, \mathbf{v}_B) = \sum_{i=1}^{B} 2mv_{i,x}\delta(t - t_i). \tag{13}$$

In addition to depending on t, the force also depends on the bounce times $t_1, \ldots, t_B$ and bounce velocities $\mathbf{v}_1, \ldots, \mathbf{v}_B$. Note that t is not a bounce time — it is the time at which we measure the force.

The probability of bounce i occurring in a time interval dt_i and velocity cube $d^3\mathbf{v}_i$ is

$$\rho(t_i, \mathbf{v}_i)dt_i\, d^3\mathbf{v}_i, \equiv \frac{1}{B} n(\mathbf{v}_i) f(\mathbf{v}_i) dt_i\, d^3\mathbf{v}_i \tag{14}$$

where $n(\mathbf{v})$ is the function you computed in part (2b). Given a function $h(t_1, \mathbf{v}_1)$ of a single bounce time and bounce velocity, its expectation value is

$$\langle h \rangle = \int_0^T dt_1 \int d^3\mathbf{v}_1 \rho(t_1, \mathbf{v}_1) h(t_1, \mathbf{v}_1). \tag{15}$$

Similarly, for a function $h(t_1, \mathbf{v}_1, \ldots, t_k, \mathbf{v}_k)$ of multiple bounce times and bounce velocities, its expectation value is

$$\langle h \rangle = \int_0^T dt_1 \int d^3\mathbf{v}_1 \cdots \int_0^T dt_k \int d^3\mathbf{v}_k \rho(t_1, \mathbf{v}_1) \cdots \rho(t_k, \mathbf{v}_k) h(t_1, \mathbf{v}_1, \ldots, t_k, \mathbf{v}_k). \tag{16}$$

The number of bounces B can be fixed by demanding that $\langle 1 \rangle = 1$. You do not need to actually compute B for this problem, but you should convince yourself that it grows linearly with T.[1]

(f) Show that

$$F_0 \equiv \langle F(t; t_1, \mathbf{v}_1, \ldots, t_B, \mathbf{v}_B) \rangle = \frac{N\tau}{L_x}, \tag{17}$$

in agreement with your answer to part (2c). *Hint:* t is not a bounce time, so you should not integrate over t.

(g) Show that for any function $h(\mathbf{v})$,

$$\langle h(\mathbf{v}_i) h(\mathbf{v}_j) \delta(t - t_i) \delta(t' - t_j) \rangle = \begin{cases} \frac{\langle h(\mathbf{v}_i)^2 \rangle}{T} \delta(t - t') & \text{if } i = j \\ \frac{\langle h(\mathbf{v}_i) \rangle^2}{T^2} & \text{if } i \neq j. \end{cases} \tag{18}$$

(h) Let the fluctuating part of the force be $\zeta(t) = F(t; t_1, \mathbf{v}_1, \ldots, t_B, \mathbf{v}_B) - F_0$. Using (18), show that

$$\lim_{T \to \infty} \langle \zeta(t) \zeta(t') \rangle = r\delta(t - t') \tag{19}$$

and compute r.

[1] For the sums over bounces to make sense, B must be an integer. You can assume that T is such that this is the case. Because T is large, this doesn't really matter. You may also assume $L_x / \langle v_x \rangle \gg T$, so that a single particle doesn't experience multiple bounces. Also, for the purposes of computing fluctuations, you can use the value of $n(\mathbf{v})$ at $x = 0, \dot{x} = 0$.

(i) Equation (9) is an example of a stochastic differential equation. The random driving force repeatedly kicks the piston making it undergo a sort of random walk called "Brownian motion" in the potential defined by the position-dependent force $-kx$. You will (optionally) show in problem 3 that

$$\langle x^2 \rangle = \frac{r}{2\gamma k}. \tag{20}$$

Plugging in your values for k, γ, r, show that

$$\langle \Delta V^2 \rangle = \frac{V^2}{N}. \tag{21}$$

3. **Optional: solving the stochastic diffeq**

In this completely optional problem, we prove equation (20).[2]

(a) Define $\dot{x} = v$ (not to be confused with the velocity of a gas particle) and write (9) as a first-order matrix differential equation

$$\dot{\mathbf{y}} = A\mathbf{y} + \mathbf{z}(t), \tag{22}$$

where

$$\mathbf{y} \equiv \begin{pmatrix} x \\ v \end{pmatrix}, \qquad \mathbf{z}(t) \equiv \begin{pmatrix} 0 \\ \zeta(t)/M \end{pmatrix} \tag{23}$$

compute the 2×2 matrix A.

(b) Show that the solution is

$$\mathbf{y}(t) = \int_{-\infty}^{t} dt' e^{A(t-t')} \mathbf{z}(t'). \tag{24}$$

(Recall that the exponential of a matrix can be defined by its Taylor series.) Thus

$$x(0) = \frac{1}{M} \int_{-\infty}^{0} dt' (e^{-At'})_{12} \zeta(t'), \tag{25}$$

where $(e^{-At'})_{ij}$ are the matrix elements of $e^{-At'}$.

(c) Show that

$$\langle x(0)^2 \rangle = \frac{r}{M^2} \int_{-\infty}^{0} dt' (e^{-At'})^2_{12}. \tag{26}$$

[2] The canonical way to do this is via Fourier analysis and contour integrals. Since many of you haven't studied complex analysis, we will do things in a different way.

(d) Using any method you like (Mathematica is ok), show

$$(e^{-At})_{12} = -2M \frac{e^{\frac{\gamma t}{2M}}}{\sqrt{4kM - \gamma^2}} \sin\left(\frac{t\sqrt{4kM - \gamma^2}}{2M}\right). \tag{27}$$

Perform the integral (26) to derive

$$\langle x(0)^2 \rangle = \frac{r}{2k\gamma}. \tag{28}$$

From the point of view of this calculation, it is remarkable that M drops out of the final answer — i.e. the volume fluctuations do not depend on the mass of the piston. Of course, this is obvious from the approach of problem 1 (since the mass of the piston doesn't appear anywhere).