

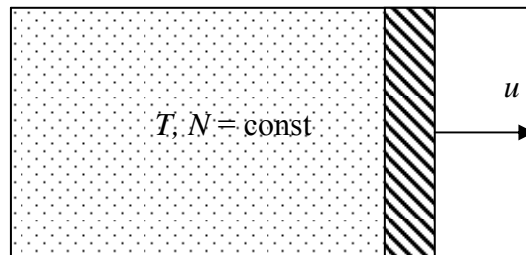
Homework 10 with Solutions

Problem 10.1. Starting from the Maxwell distribution of velocities, calculate explicitly:

(i) the damping constant $\eta \equiv -\partial\langle p \rangle / \partial u$, and

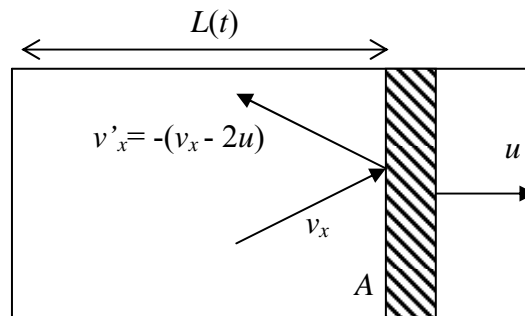
(ii) constant C in the (approximate) expression $\langle p(t)p(t + \tau) \rangle = C\delta(\tau)$,

for the pressure $p(t)$ exerted by molecules on a slowly moving piston, in the simplest experiment with an ideal classical gas - see Fig. below. Check that the relation between the calculated constants obeys the (classical version of) the fluctuation-dissipation theorem.



Solution:

(i) Consider a molecule hitting the piston, with the initial horizontal velocity $v_x > 0$ (in the lab frame). In the reference frame bound to the piston, this component is $(v_x - u)$. Since the collision is elastic, in the piston frame the modulus of velocity is conserved, so that the horizontal velocity after the collision is $-(v_x - u) = -v_x + u$, and in the lab frame it is $v'_x = (-v_x + u) - u = -(v_x - 2u)$ - see Fig. below. Hence the momentum transferred to the piston is $-\Delta m v_x = -m[(-v_x - 2u) - v_x] = 2m(v_x - u)$.



The time interval between the previous collision and the analyzed one can be found from the evident equation $v_x \Delta t = L(t - L/v_x) + L(t - 2L/v_x)$, and the next interval from the similar equation $v'_x \Delta t' = L(t + L/v'_x) + L(t + 2L/v'_x)$. At small piston velocities, $|u| \ll \langle v_x \rangle$, we can use the Taylor expansion $L(t) \approx L(t_0) + u(t - t_0)$, and the above equations yield $\Delta t \approx L(2 - 3u/v_x)/v_x$, $\Delta t' \approx L(2 + 3u/v'_x)/v'_x \approx L(2 + 7u/v_x)/v_x$, so that the average interval is $\Delta t_{\text{av}} = (\Delta t + \Delta t')/2 = 2L(1 + u/v_x)/v_x$. Thus the average force exerted on a piston by the molecule,

$$f = \frac{2m(v_x - u)}{2L(1 + u/v_x)/v_x} \approx \frac{m}{L}(v_x^2 - 2uv_x), \quad \text{for } v_x > 0.$$

Since a molecules moving in the opposite direction will apply the similar force (after its reflection from the immobile end of the cylinder), we can use the following formula,

$$f \approx \frac{m}{L}(v_x^2 - 2u|v_x|),$$

for any molecule. This force should be averaged over the 1D Maxwell distribution

$$dw = \frac{1}{\sqrt{2\pi\sigma}} \exp\left\{-\frac{v_x^2}{2\sigma^2}\right\} dv_x, \quad \sigma^2 = \frac{T}{m},$$

of all molecules with velocities $v_x > 0$. The resulting average pressure of N molecules of the piston is

$$\begin{aligned} \langle p \rangle &\equiv N \frac{\langle f \rangle}{A} = \frac{Nm \langle v_x^2 \rangle}{V} - 2u \frac{Nm \langle |v_x| \rangle}{V} = \frac{NT}{V} - \eta u, \\ \eta &= 2 \frac{Nm}{V} \frac{2}{\sqrt{2\pi\sigma}} \int_0^\infty v_x \exp\left\{-\frac{v_x^2}{2\sigma^2}\right\} dv_x = \frac{2N}{V} \sqrt{\frac{2mT}{\pi}}. \end{aligned}$$

The first component of the pressure is the usual (static) pressure of the ideal classical gas, while the second one presents the damping force.

(ii) For one molecule, constant F in the approximate formula $\langle f(t)f(t + \tau) \rangle = F\delta(\tau)$ may be calculated as the integral

$$F = \int \langle f(t)f(t + \tau) \rangle d\tau$$

over the time interval of the order of the collision duration. Even small angular scattering of the molecule between its collisions with the piston makes the process ergodic, so that we can replace the statistical ensemble average with the average over time t :

$$\langle \dots \rangle = \frac{1}{2L/v_x} \int \dots dt,$$

where the denominator is the time between the adjacent collisions. Introducing, instead of τ , a new independent variable $t' \equiv t + \tau$, we get

$$F = \frac{1}{2L/v_x} \int dt \int d\tau f(t)f(t + \tau) = \frac{1}{2L/v_x} \int dt \int dt' f(t)f(t') = \frac{1}{2L/v_x} \left[\int f(t) dt \right]^2,$$

where the integration has to be limited by the time of one collision.

For the calculation of pressure fluctuations, we can neglect the piston velocity, so that the momentum transferred to the piston by a molecule, i.e. the time integral in the last formula is just $2m|v_x|$, so that

$$F = \frac{m}{L} |v_x^3|.$$

Constants F due to uncorrelated hits of the piston by different molecules add up, so that averaging the result over the Maxwell distribution, for the constant C in the expression for pressure we get

$$C = \frac{N}{A} \langle F \rangle = \frac{Nm}{AL} \langle |v_x^3| \rangle = \frac{Nm}{V} \frac{2}{\sqrt{2\pi}\sigma} \int_0^\infty v_x^3 \exp\left\{-\frac{v_x^2}{2\sigma^2}\right\} dv_x = \frac{4N}{V} \sqrt{\frac{2mT^3}{\pi}}.$$

We immediately see that $C = 2\eta T$, in accordance with the classical version of the fluctuation-dissipation theorem.

Problem 10.2. A particle may occupy any of N similar sites, and jump from that site to any other one classically (i.e., without quantum-mechanical coherence between the jumps), with the same rate Γ . Find the correlation function and spectral density of fluctuations of the instant occupancy $n(t)$ (equal to either 1 or 0) of any particular cite.

Solution:

Similarly to the two-site problem discussed in class, let write the “master” equation for the probability for the particle to occupy the (arbitrary) j -th site:

$$\dot{w}_j = -(N-1)\Gamma w_j + \sum_{j' \neq j} \Gamma w_{j'}.$$

Since the sum of all $w_{j'}$ should be equal to 1, the fact that all the rates are equal allow us to transform this equation into a linear differential equation for one variable

$$\dot{w}_j = -(N-1)\Gamma w_j + \Gamma \sum_{j' \neq j} w_{j'} = -(N-1)\Gamma w_j + \Gamma(1 - w_j) = \Gamma(1 - Nw_j),$$

and immediately write its general solution (whose structure has been discussed in class):

$$w_j(t) = w_j(0) \exp\{-N\Gamma t\} + w_j(\infty)(1 - \exp\{-N\Gamma t\}), \quad w_j(\infty) = \frac{1}{N}. \quad (*)$$

Now we can readily calculate all the averages of interest, starting from the (ensemble!) average of the occupancy:¹

$$\langle n(t) \rangle = \sum_{n=0,1} n w(n,t) = w(1,t).$$

But $w(1,t)$ is just the probability to have this particular (e.g., j -th) site occupied at time t , i.e. the $w_j(t)$ given by Eq. (*), so that

$$\langle n(t) \rangle = \langle n(0) \rangle \exp\{-N\Gamma t\} + \frac{1}{N}(1 - \exp\{-N\Gamma t\}).$$

¹ It is evident that in this uniform system all averages are independent of the site number.

On the background of Eq. (*), this is probably an evident result, but it is a good preparation for the calculation of the correlation function² of the instant occupancy:

$$K_n(\tau) \equiv \langle n_j(t)n_j(t+\tau) \rangle = \sum_{n=1,0} n w(n, \infty) \sum_{n'=1,0} n' w(n', \tau | n, 0).$$

Since one of two possible occupancy numbers is zero, in this sum of generally four terms, only one term (with $n = n' = 1$) gives a nonvanishing contribution:

$$K_n(\tau) \equiv \langle n_j(t)n_j(t+\tau) \rangle = w(1, \infty)w(1, \tau | 1, 0).$$

The first operand of this product equals $w_j(\infty) = 1/N$, while the second one is $w_j(\tau)$ with the initial condition $w_j(0) = 1$, so that Eq. (*) yields

$$K_n(\tau) = \frac{1}{N} \left[\exp\{-N\Gamma\tau\} + \frac{1}{N}(1 - \exp\{-N\Gamma\tau\}) \right] = \frac{1}{N} \left[\frac{1}{N} + \left(1 - \frac{1}{N}\right) \exp\{-N\Gamma\tau\} \right].$$

As a sanity check, the particular result

$$K_n(0) \equiv \langle n^2 \rangle = \frac{1}{N}$$

may be readily checked by a direct calculation:

$$\langle n^2 \rangle = \sum_{n=1,0} n^2 w_n = w_1 = w_j(\infty) = \frac{1}{N}.$$

Now, before going after the spectral density of occupancy fluctuations, one should be careful to distinguish the calculated correlation function $K_n(\tau)$ of the instant occupancies, and that of their fluctuations:

$$K_{\tilde{n}}(\tau) \equiv \langle \tilde{n}(t)\tilde{n}(t+\tau) \rangle = \langle [n(t) - \langle n \rangle][n(t+\tau) - \langle n \rangle] \rangle = K_n(\tau) - \langle n \rangle^2.$$

For our problem,

$$K_{\tilde{n}}(\tau) = \frac{1}{N} \left[\frac{1}{N} + \left(1 - \frac{1}{N}\right) \exp\{-N\Gamma\tau\} \right] - \frac{1}{N^2} = \frac{N-1}{N^2} \exp\{-N\Gamma\tau\},$$

so that

$$\begin{aligned} S_{\tilde{n}}(\omega) &= \frac{1}{\pi} \operatorname{Re} \int_0^{+\infty} K_{\tilde{n}}(\tau) \exp\{i\omega\tau\} d\tau = \frac{N-1}{\pi N^2} \operatorname{Re} \int_0^{+\infty} \exp\{(-N\Gamma + i\omega)\tau\} d\tau \\ &= \frac{N-1}{\pi N^2} \operatorname{Re} \frac{1}{-N\Gamma + i\omega} = \frac{N-1}{\pi N} \frac{\Gamma}{N^2\Gamma^2 + \omega^2}. \end{aligned}$$

The result describes a Lorentzian spectrum (typical for such problems), with the low-frequency density scaling as $(N-1)/N^3\Gamma$. As an additional sanity check, for a system consisting of just one site ($N=1$), the occupancy does not fluctuate – of course.

² $K_n(\tau)$ is frequently called the *autocorrelation* function in order to contrast it with a more general correlation function $\langle n_j(t)n_j'(t+\tau) \rangle$.