From Kardar.

Problem 3.1 (One-dimensional gas)**.** A thermalized gas particle is suddenly confined to a one-dimensional trap. The corresponding mixed state is described by an initial density function $\rho(q,p,t=0)=\delta(q)f(p)$, where $f(p)=\exp(-p^2/2mk_BT)/\sqrt{2\pi mk_BT}$.

(a) Starting from Liouville's equation, derive $\rho(q,p,t)$ and sketch it in the (q,p) plane.

(b) Derive the expressions for the averages $\langle q^2\rangle$ and $\langle p^2\rangle$ at $t>0$.

(c) Suppose that hard walls are placed at $q=\pm Q$. Describe $\rho(q,p,t\gg\tau)$, where τ is an appropriately large relaxation time.

(d) A "course-grained" density $\tilde{\rho}$ is obtained by ignoring variation of ρ below some small resolution in the (q,p) plane; for example, by averaging ρ over cells of the same resolution area. Find $\tilde{\rho}(q,p)$ for the situation in part (c), and show that it is stationary.

Solution. (a) Liouville's equation is

$$\frac{\partial\rho}{\partial t}=-\{\rho,H\}.$$

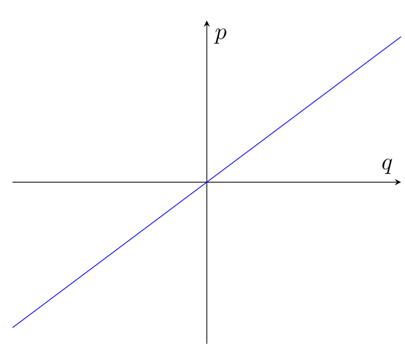
For a 1D gas particle, the Hamiltonian is simply $H=p^2/2m$. Thus, it follows that

$$\frac{\partial\rho}{\partial t}=-\frac{\partial\rho}{\partial q}\frac{p}{m}.$$

This is simply a 1D transport equation, so the solution is of the form

$$\rho(q,p,t)=\rho\left(q-\frac{p}{m}t,p,0\right)=\delta\left(q-\frac{p}{m}t\right)f(p).$$

This looks like



with slope m/t.

(b) The averages are given by

$$\begin{aligned}
\left\langle p^2 \right\rangle &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p^2 \delta\left(q - \frac{p}{m}t\right) \frac{\exp\left(-p^2/2mk_BT\right)}{\sqrt{2\pi m k_B T}}\, dq\, dp \\
&= \frac{1}{\sqrt{2\pi m k_B T}} \int_{-\infty}^{\infty} p^2 \exp\left(-\frac{p^2}{2mk_BT}\right) dx.
\end{aligned}$$

This is simply the variance of a normal distribution with $\sigma^2 = mk_BT$, so

$$\left\langle p^2 \right\rangle = mk_BT.$$

Then,

$$\begin{aligned}
\left\langle q^2 \right\rangle &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} q^2 \delta\left(q - \frac{p}{m}t\right) \frac{\exp\left(-p^2/2mk_BT\right)}{\sqrt{2\pi m k_B T}}\, dq\, dp \\
&= \int_{-\infty}^{\infty} \left(\frac{pt}{m}\right)^2 \frac{\exp\left(-p^2/2mk_BT\right)}{\sqrt{2\pi m k_B T}}\, dp \\
&= \frac{t^2}{m^2}\left\langle p^2 \right\rangle \\
&= \frac{t^2}{m^2\sqrt{2\pi m k_B T}}.
\end{aligned}$$

(c) Observe that the scenario of hard walls placed at $q = \pm Q$ is equivalent to solving the problem with initial periodic density

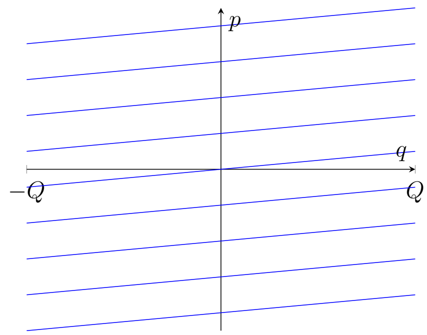
$$\rho'(q, p, t = 0) = \sum_{n=-\infty}^{\infty} \rho(q + 2nQ, p, t = 0),$$

then restricting to $|q| < Q$. This is because with hard walls, the particle reverses momentum $p \to -p$ at $\pm Q$, and this is equivalent to the original particle leaving and another particle entering with momentum p every time a particle reaches a wall. Periodically extending the initial distribution spaced $2Q$ with the same Hamiltonian achieves this.

It then follows that the solution is simply

$$\rho(q, p, t) = \sum_{n=-\infty}^{\infty} \delta\left(q - \frac{p}{m}t + 2nQ\right) f(p), \quad |q| < Q.$$

This looks like



with each line again having slope m/t, and the vertical spacing between the lines is $2Qm/t$. To find a characteristic time τ, the length of the system is $2Q$, and taking the root-mean-square velocity

$$\sqrt{\langle \dot{q}^2 \rangle} = \frac{\sqrt{\langle p^2 \rangle}}{m} = \sqrt{\frac{k_B T}{m}}$$

as the characteristic speed, we get

$$\tau \sim 2Q\sqrt{\frac{m}{k_B T}}.$$

For $t \gg \tau$, both the slopes of the lines as well as the spacing go to zero, while the density at each point on the lines is still $f(p)$.

(d) For the situation in part (c), after sufficiently long $t \gg \tau$, the lines approximately flat and the density becomes approximately constant along the lines. We then get that the coarse-grained density is simply

$$\tilde{\rho}(p, q, t \gg \tau) = \frac{1}{2Q\sqrt{2\pi m k_B T}} \exp\left(-\frac{p^2}{2mk_B T}\right).$$

To verify that this is stationary, Liouville's equation gives that

$$\frac{\partial \tilde{\rho}}{\partial t} = -\frac{p}{m}\frac{\partial \tilde{\rho}}{\partial q} = 0$$

as $\tilde{\rho}$ has no q dependence. □

Problem 3.2 (Evolution of entropy)**.** The normalized ensemble density is a probability in the phase space Γ. This probability has an associated entropy $S(t) = -\int d\Gamma\, \rho(\Gamma, t) \ln \rho(\Gamma, t)$.

(a) Show that if $\rho(\Gamma, t)$ satisfies Liouville's equation for a Hamiltonian $\mathcal{H}$, $dS/dt = 0$.

(b) Using the method of Lagrange multipliers, find the function $\rho_{\max}(\Gamma)$ that maximizes the functional $S[\rho]$, subject to the constraint of fixed average energy, $\langle \mathcal{H} \rangle = \int d\Gamma\, \rho \mathcal{H} = E$.

(c) Show that the solution to part (b) is stationary, that is, $\partial\rho_{\max}/\partial t = 0$.

(d) How can one reconcile the result in (a) with the observed increase in entropy as the system approaches the equilibrium density in (b)? (*Hint.* Think of the situation encountered in the previous problem.)

Solution. (a) Suppose $\rho(\Gamma, t)$ satisfies Liouville's equation for a Hamiltonian $\mathcal{H}$. Then

$$\begin{aligned}
\frac{dS}{dt} &= -\frac{d}{dt}\int \rho(\Gamma,t)\ln\rho(\Gamma,t)\,d\Gamma \\
&= -\int \frac{\partial\rho}{\partial t}\ln\rho + \frac{\partial\rho}{\partial t}\,d\Gamma \\
&= -\int \frac{\partial\rho}{\partial t}\ln\rho\,d\Gamma - \frac{d}{dt}\int\rho\,d\Gamma \\
&= \int \ln\rho\,\{\rho,\mathcal{H}\}\;d\Gamma \\
&= \int \prod_{i=1}^{N} dq_i dp_i \ln\rho\left[\sum_{i=1}^{N}\frac{\partial\rho}{\partial q_i}\frac{\partial\mathcal{H}}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial\mathcal{H}}{\partial q_i}\right] \\
&= -\int \prod_{i=1}^{N} dq_i dp_i \rho\ln\rho\left[\sum_{i=1}^{N}\frac{\partial^2\mathcal{H}}{\partial q_i\partial p_i} - \frac{\partial^2\mathcal{H}}{\partial p_i\partial q_i}\right] + \left[\sum_{i=1}^{N}\frac{\partial\rho}{\partial q_i}\frac{\partial\mathcal{H}}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial\mathcal{H}}{\partial q_i}\right] \\
&= -\int \{\rho,\mathcal{H}\}\;d\Gamma \\
&= 0,
\end{aligned}$$

where we differentiate by parts to get that the integral vanishes.

(b) With the constraints

$$\int\rho\,d\Gamma = 1, \quad \int\rho\mathcal{H}\,d\Gamma = E,$$

we get that we need to minimize $\tilde{S}[\rho] = \int F(\rho)\,d\Gamma$, where

$$F(\rho) = \rho\ln\rho + \lambda_1\rho + \lambda_2\rho\mathcal{H},$$

with $\lambda_{1,2}$ being the Lagrange multipliers. Since F only depends on ρ, the associated Euler-Lagrange equation is simply $\partial F/\partial\rho = 0$. Thus,

$$\begin{aligned}
\frac{\partial F}{\partial\rho} &= \ln\rho + 1 + \lambda_1 + \lambda_2\mathcal{H} = 0 \\
\implies \rho_{\max} &= \exp\left(-1-\lambda_1-\lambda_2\mathcal{H}\right) = \alpha\exp\left(-\beta\mathcal{H}\right),
\end{aligned}$$

with α, β chosen so that the constraints are satisfied.

(c) To see that $\rho_{\max}$ is stationary, by Liouville's equation,

$$\begin{aligned}\frac{\partial \rho_{\max}}{\partial t} &= -\frac{\partial \rho_{\max}}{\partial q}\frac{\partial \mathcal{H}}{\partial p} + \frac{\partial \rho_{\max}}{\partial p}\frac{\partial \mathcal{H}}{\partial q} \\ &= \alpha\beta \exp(-\beta\mathcal{H}) \left[\frac{\partial \mathcal{H}}{\partial q}\frac{\partial \mathcal{H}}{\partial p} - \frac{\partial \mathcal{H}}{\partial p}\frac{\partial \mathcal{H}}{\partial q}\right] \\ &= 0.\end{aligned}$$

(d) By time-reversal symmetry, a system satisfying Liouville's equation must conserve entropy. However, following the situation in the previous problem, we can find that the entropy increases as the system approaches equilibrium if we observed the coarse-grained density $\tilde{\rho}$. This is because as the system approaches equilibrium, the fluctuations about the equilibrium distribution $\rho_{\max}$ get averaged out by $\tilde{\rho}$ (causing information loss), so $\tilde{\rho} \to \rho_{\max}$ and the coarse-grained entropy approaches the maximum entropy even though the entropy of ρ remains constant. $\square$

Problem 3.10 (Light and matter)**.** In this problem we use kinetic theory to explore the equilibrium between atoms and radiation.

(a) The atoms are assumed to be either in their ground state a_0, or in an excited state a_1, which has a higher energy ε. By considering the atoms as a collection of N fixed two-state systems of energy E (i.e., ignoring their coordinates and momenta), calculate the ratio n_1/n_0 of densities of atoms in the two states as a function of temperature T.

Consider photons γ of frequency $\omega = \varepsilon/\hbar$ and momentum $|\mathbf{p}| = \hbar\omega/c$, which can interact with the atoms through the following processes:

(i) *Spontaneous emission:* $a \to a_0 + \gamma$.

(ii) *Adsorption:* $a_0 + \gamma \to a_1$.

(iii) *Stimulated emission:* $a_1 + \gamma \to a_0 + \gamma + \gamma$.

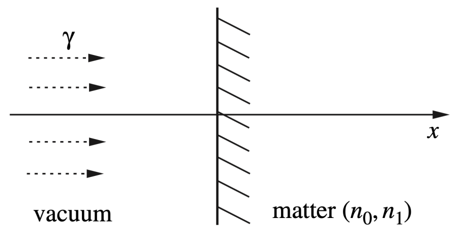
Assume that spontaneous emission occurs with a probability σ_{sp}, and that adsorption and stimulated emission have constant (angle-independent) differential cross-sections of $\sigma_{\text{ad}}/4\pi$ and $\sigma_{\text{st}}/4\pi$, respectively.

(b) Write down the Boltzmann equation governing the density f of the photon gas, by treating the atoms as fixed scatters of densities n_0 and n_1.

(c) Find the equilibrium density $f_{\text{eq.}}$ for photons of the above frequency.

(d) According to Planck's law, the density of photons at a temperature T depends on their frequency ω as $f_{\text{eq.}} = \left[\exp(\hbar\omega/k_BT) - 1\right]^{-1}/h^3$. What does this imply about the above cross-sections?

(e) Consider a situation in which light shines along the x axis on a collection of atoms whose boundary coincides with the $x = 0$ plane, as illustrated in the figure. Clearly, f will depend on x (and p_x), but will be independent of y and z.



Adapt the Boltzmann equation you propose in part (b) to the case of a uniform incoming flux of photons with momentum $\mathbf{p} = \hbar\omega\hat{\mathbf{x}}/c$. What is the *penetration length* across which the incoming flux decays?

Solution. (a) By the Gibbs distribution, we know $n_i \sim \exp(-\beta H)$, so the ratio of the densities will be

$$\frac{n_1}{n_0} = \exp\left(-\beta\epsilon\right) = \exp\left(-\frac{\epsilon}{k_B T}\right).$$

(b) The energy of photons is given by $E = |\mathbf{p}|\, c$, so the Boltzmann equation for the photon gas is

$$\left[\frac{\partial}{\partial t} + \hat{\mathbf{p}}c \cdot \frac{\partial}{\partial \mathbf{q}}\right] f = n_1\sigma_{\text{sp}} + c\left[\sigma_{\text{st}}n_1 - \sigma_{\text{ad}}n_0\right] f$$

(c) The equilibrium density is then

$$\frac{\partial f}{\partial t} = 0 \implies \hat{\mathbf{p}}c \cdot \frac{\partial f}{\partial \mathbf{q}} = n_1\sigma_{\text{sp}} + c\left[\sigma_{\text{st}}n_1 - \sigma_{\text{ad}}n_0\right] f.$$

By symmetry, $\partial f_{\text{eq.}}/\partial \mathbf{q} = 0$, so

$$f_{\text{eq}} = \frac{n_1\sigma_{\text{sp}}}{c(\sigma_{\text{ad}}n_0 - \sigma_{\text{st}}n_1)} = \frac{1}{c}\frac{\sigma_{\text{sp}}}{\sigma_{\text{ad}}\exp\left(\epsilon/k_B T\right) - \sigma_{\text{st}}}.$$

(d) By Planck's law, we get that

$$f_{\text{eq.}} = \frac{1}{h^3}\left[\exp\left(\frac{\epsilon}{k_B T} - 1\right)\right]^{-1} = \frac{\sigma_{\text{sp}}}{c\sigma_{\text{ad}}}\left[\exp\left(\frac{\epsilon}{k_B T} - \frac{\sigma_{\text{st}}}{\sigma_{\text{ad}}}\right)\right]^{-1}$$
$$\implies \frac{\sigma_{\text{sp}}}{\sigma_{\text{ad}}} = \frac{c}{h^3}, \quad \frac{\sigma_{\text{st}}}{\sigma_{\text{ad}}} = 1.$$

(e) The Boltzmann equation for $x > 0$ remains the same, being

$$\left[\frac{\partial}{\partial t} + \hat{\mathbf{p}}c \cdot \frac{\partial}{\partial \mathbf{q}}\right] f = n_1\sigma_{\mathrm{sp}} + c\left[\sigma_{\mathrm{st}}n_1 - \sigma_{\mathrm{ad}}n_0\right] f.$$

However, at equilibrium, the symmetry in x is broken, so we get that

$$c\frac{\partial f}{\partial x} = n_1\sigma_{\mathrm{sp}} + c\left[\sigma_{\mathrm{st}}n_1 - \sigma_{\mathrm{ad}}n_0\right] f.$$

This is a inhomogeneous first-order differential equation with solution

$$f_{\mathrm{eq.}} = \frac{1}{c}\frac{n_1\sigma_{\mathrm{sp}}}{\sigma_{\mathrm{ad.}}n_0 - \sigma_{\mathrm{st}}n_1} + C\exp\left[(\sigma_{\mathrm{st}}n_1 - \sigma_{\mathrm{ad}}n_0)x\right],$$

where C is a constant which depends on the boundary conditions. The boundary condition in this case is that

$$f_{\mathrm{eq.}}(x=0) = \frac{1}{c}\frac{n_1\sigma_{\mathrm{sp}}}{\sigma_{\mathrm{ad.}}n_0 - \sigma_{\mathrm{st}}n_1} + C = f_{\mathrm{incoming}},$$

where f_{incoming} is the density of the incoming photons. We can then read off the penetration length as

$$\sigma_{\mathrm{ad}}n_0 - \sigma_{\mathrm{st}}n_1 = n_0\sigma_{\mathrm{ad}}\left[1 - \exp\left(-\frac{\epsilon}{k_BT}\right)\right]. \qquad \square$$

Problem 3.14 (Effusion)**.** A box contains a perfect gas at temperature T and density n.

(a) What is the one-particle density, $\rho_1(\mathbf{v})$, for particles with velocity $\mathbf{v}$?

A small hole is opened in the wall of the box for a short time to allow some particles to escape into a previously empty container.

(b) During the time that the hole is open what is the flux (number of particles per unit time and per unit area) of particles into the container? (Ignore the possibility of any particles returning to the box).

(c) Show that the average kinetic energy of escaping particles is $2k_BT$. (*Hint.* Calculate contributions to kinetic energy of velocity components parallel and perpendicular to the wall separately.)

(d) The hole is closed and the container (now thermally insulated) is allowed to reach equilibrium. What is the final temperature of the gas in the container?

(e) A vessel partially filled with mercury (atomic weight 201), and closed except for a hole of area 0.1 mm^2 above the liquid level, is kept at 0°C in a continuously evacuated enclosure. After 30 days it is found that 24 mg of mercury has been lost. What is the vapor pressure of mercury at 0°C?

Solution. (a) The one-particle density (PDF) is given by the Gibbs distribution

$$P(\mathbf{v}) \sim \exp\left(-\frac{mv^2}{2k_BT}\right) \implies \rho_1(\mathbf{v}) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_BT}\right),$$

where we have normalized so that $\iiint \rho_1(\mathbf{v})\, d^3\mathbf{v} = 1$. Note that the density f_1 is related to ρ_1 by $f_1 = n\rho_1/m^3$, which is normalized to $\int d^3\mathbf{p} d^3\mathbf{q}\, f_1 = N$.

(b) For particles of velocity $\mathbf{v}$, the number of particles that can go through the hole in a time dt is $dN(\mathbf{v}) = n\rho_1(\mathbf{v})Av_x dt$. Integrating over all $\mathbf{v}$ with $v_x > 0$ gives us that the flux of particles into the container is

$$\begin{aligned}
\frac{dN}{Adt} &= n\left(\frac{m}{2\pi k_BT}\right)^{3/2} \iiint_{v_x>0} v_x \exp\left(-\frac{mv^2}{2k_BT}\right) d^3\mathbf{v} \\
&= n\sqrt{\frac{m}{2\pi k_BT}} \int_0^\infty v_x \exp\left(-\frac{mv_x^2}{2k_BT}\right) dv_x \\
&= n\sqrt{\frac{m}{2\pi k_BT}} \left(\frac{k_BT}{m}\right) \int_0^\infty e^{-u}\, du \\
&= n\sqrt{\frac{k_BT}{2\pi m}}.
\end{aligned}$$

(c) The average kinetic energy of particles escaping is given by

$$\begin{aligned}
\langle K\rangle_{\text{esc}} &= \left[n\sqrt{\frac{k_BT}{2\pi m}}\right]^{-1} \cdot n\left(\frac{m}{2\pi k_BT}\right)^{3/2} \iiint_{v_x>0} \left(\frac{1}{2}mv^2\right) v_x \exp\left(-\frac{mv^2}{2k_BT}\right) d^3\mathbf{v} \\
&= \frac{1}{2\pi}\left(\frac{m}{k_BT}\right)^2 \iiint_{v_x>0} -\frac{\partial}{\partial\beta} v_x \exp\left(-\beta\frac{mv^2}{2}\right) d^3\mathbf{v} \\
&= -\frac{1}{2\pi}\left(\frac{m}{k_BT}\right)^2 \frac{d}{d\beta}\left(\frac{2\pi}{m^2\beta^2}\right) \\
&= -\beta^2\left(-\frac{2}{\beta^3}\right) \\
&= \frac{2}{\beta} \\
&= 2k_BT.
\end{aligned}$$

(d) For an ideal gas, the average kinetic energy at equilibrium is

$$\begin{aligned}\langle K\rangle &= -\frac{\partial}{\partial\beta}\ln\left(\frac{2\pi}{m\beta}\right)^{3/2}\\ &= -\frac{3}{2}\left(\frac{m\beta}{2\pi}\right)\left(-\frac{2\pi}{m\beta^2}\right)\\ &= \frac{3}{2\beta}\\ &= \frac{3}{2}k_BT\end{aligned}$$

(also obtained from the equipartition theorem). Thus, the temperature of the container is

$$T_{\text{cont.}} = \frac{2}{3k_B}\langle K\rangle = \frac{4}{3}T.$$

(e) From part (b), we know that the flux of escaping particles is $n\sqrt{k_BT/2\pi m}$. It follows that for this case,

$$\frac{(24\cdot 10^{-3})(6.02\cdot 10^{23})/201}{(0.1\cdot 10^{-6})(30\cdot 24\cdot 3600)} = n\sqrt{\frac{(1.38\cdot 10^{-23})(273)}{2\pi(0.201/(6.02\cdot 10^{23}))}}$$

$$\implies n = 6.54\cdot 10^{18}\ \frac{\text{particles}}{\text{m}^3}$$

$$\implies P = nk_BT = (6.54\cdot 10^{18})(1.38\cdot 10^{-23})(273) = 0.0247\text{ Pa.}\qquad\square$$