10. (Statistical Mechanics)

A liquid is in equilibrium with its vapor at temperature and pressure: T_v; P_v. The surface between liquid and vapor is flat. The temperature of the vapor is increased to $T_v + \Delta T$ while keeping its pressure fixed. The liquid remains at temperature and pressure: T_v, P_v. Evaluate the net flux of gas to the liquid. You may treat the vapor as an ideal noble gas with atoms of mass m.

Solution: *Solution by Jonah Hyman (jthyman@g.ucla.edu)*

The logic in this problem requires several steps. We will therefore break the solution into subsections, identifiable by bolded headers.

Understanding the setup:
We ignore all interactions between the gas particles, and we ignore the effects of gravity. Here is a diagram of the setup:
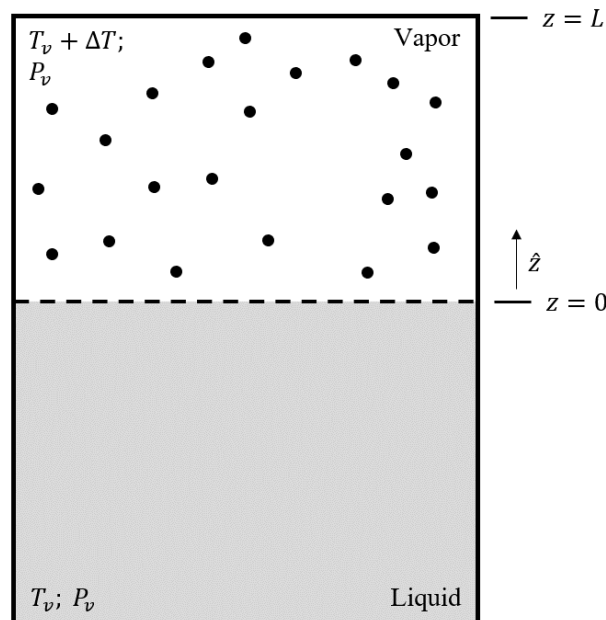
We are asked to find the *net* flux of gas to the liquid. The net flux of gas to the liquid is the difference between the flux of gas to the liquid and the flux of liquid to the gas:

$$\text{Net flux of gas to liquid} \Big|_{\text{liquid at } T_v, P_v}^{\text{gas at } T_v+\Delta T, P_v}$$

$$= \text{Flux from gas to liquid} \Big|_{\text{liquid at } T_v, P_v}^{\text{gas at } T_v+\Delta T, P_v} - \text{Flux from liquid to gas} \Big|_{\text{liquid at } T_v, P_v}^{\text{gas at } T_v+\Delta T, P_v} \quad (65)$$

Here, the term "flux from A to B" means the number of particles crossing the boundary from A to B per unit time per unit area of boundary, when the temperature and pressure of A are T and P, respectively.

***Relating total flux to a differential element of flux:***
We'll get to the "flux from liquid to gas" term later on. First, let's start by computing "flux from gas to liquid $\big|_{\text{gas at } T,P}$". This flux is easier to compute because it is easier to do statistical mechanics on a monatomic ideal gas than on a liquid.

Consider a patch of boundary between the gas and the liquid of surface area A, and consider a period of time Δt (to be more precise, these should be taken to be infinitesimal values). Then, by the definition of flux mentioned above,

$$\text{Flux from gas to liquid} = \frac{N_{\text{gas}\rightarrow\text{liquid}}(A, \Delta t)}{A\,\Delta t} \quad (66)$$

where $N_{\text{gas}\rightarrow\text{liquid}}(A, \Delta t)\big|_{T,P}$ is the number of particles crossing from the gas to the liquid through the patch of area A in the time period Δt, when the temperature and pressure of the gas are T and P respectively.

To determine $N_{\text{gas}\rightarrow\text{liquid}}(A, \Delta t)$, consider the column of gas just above the patch of boundary of area A (blue rectangle in the diagram below). Then, consider a portion of this column a distance z above the boundary and of infinitesimal height dz (red rectangle in diagram below). Note that while we will call these "rectangles," they are really rectangular prisms of cross-sectional area A.
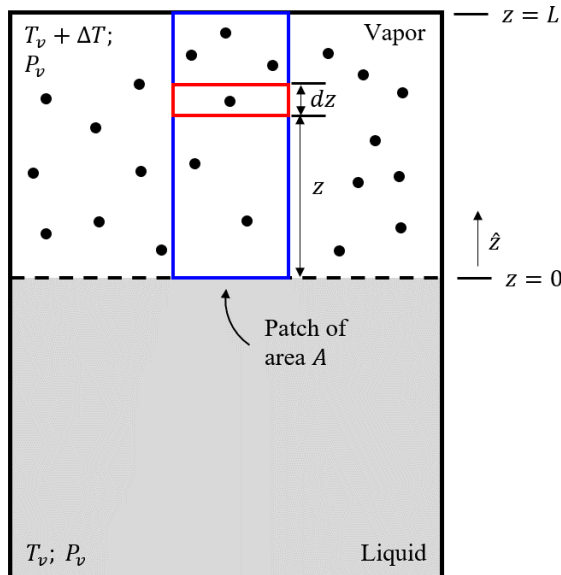

Let $dN_{\text{gas}\rightarrow\text{liquid}}(A, \Delta t, z)$ be the number of particles in the red rectangle, as measured at time $t = 0$, that cross the boundary from gas to liquid in the time Δt. Then, the number of particles in the entire column of area A (blue rectangle), as measured at time $t = 0$, that cross the boundary from gas to liquid in the time Δt is equal to the integral of dN for all possible distances z:

$$N'_{\text{gas}\rightarrow\text{liquid}}(A, \Delta t) = \int_{z=0}^{z=L} dN_{\text{gas}\rightarrow\text{liquid}}(A, \Delta t, z) \tag{67}$$

It turns out that the following two quantities are equivalent:

- $N_{\text{gas}\rightarrow\text{liquid}}$, the number of particles that cross from the gas to the liquid through the patch of area A in the time Δt (which is what we want to find), and

- $N'_{\text{gas}\rightarrow\text{liquid}}$, the number of particles that start in the column of area A (blue rectangle) and cross from the gas to the liquid in the time Δt (which is what we calculated in (67)).

The reason for this is that the setup is assumed invariant under translations in the xy-plane. Therefore, for every particle that starts *inside* the column of area A (blue rectangle) and crosses to the liquid *outside* the patch of area A, there is another particle that starts *outside* the column of area A (blue rectangle) and crosses to the liquid *inside* the patch of area A. Here is an example:
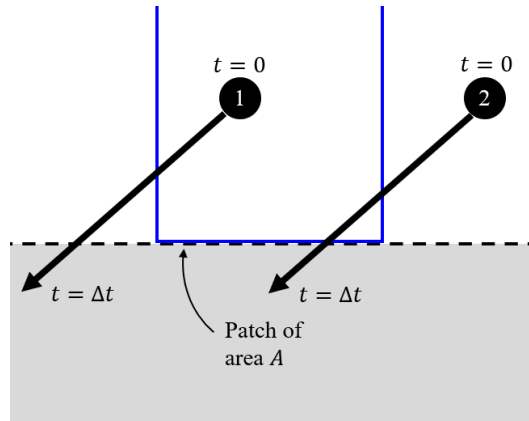
In this diagram, particle 1 is counted in our calculation of $N'_{\text{gas}\to\text{liquid}}$, since it starts inside the column of area A (blue rectangle), but it is not counted in our calculation of $N_{\text{gas}\to\text{liquid}}$, since it does not cross to the liquid through the patch of area A. Similarly, particle 2 is counted in our calculation of $N_{\text{gas}\to\text{liquid}}$, since it crosses to the liquid through the patch of area A, but it is not counted in our calculation of $N'_{\text{gas}\to\text{liquid}}$, since it starts outside the column of area A.

Even though $N_{\text{gas}\to\text{liquid}}$ and $N'_{\text{gas}\to\text{liquid}}$ count different particles, the *number* of particles counted is the same for both (particles 1 and 2 together contribute one particle to both quantities, though the particle counted is different). We can therefore use (67) as a formula for $N_{\text{gas}\to\text{liquid}}$:

$$N_{\text{gas}\to\text{liquid}}(A, \Delta t) = \int_{z=0}^{z=L} dN_{\text{gas}\to\text{liquid}}(A, \Delta t, z) \tag{68}$$

Plugging this into our formula for the flux (66), we get

$$\text{Flux from gas to liquid}\big|_{\text{gas at } T,P} = \frac{\int_{z=0}^{z=L} dN_{\text{gas}\to\text{liquid}}(A, \Delta t, z)\big|_{T,P}}{A\,\Delta t} \tag{69}$$

Relating the differential element of flux to the Maxwell velocity distribution:
Now we need to find $dN_{\text{gas}\to\text{liquid}}$, which is the number of particles in the red rectangle, as measured at time $t = 0$, that cross the boundary from gas to liquid in the time Δt. A particle in the red rectangle will cross the boundary from gas to liquid in the time Δt if the z-component of its velocity at time $t = 0$ is in the range $-\infty < v_z < -z/\Delta t$. In other words, the farther away the gas particle starts from the boundary, the faster it must be traveling to cross the boundary to the liquid in the time Δt. (The minus signs in the inequality occur because the boundary is in the $-\hat{\mathbf{z}}$ direction from the gas.)

We can write $dN_{\text{gas}\to\text{liquid}}$ in terms of the probability distribution for the z-components of the velocity of a particle. Let $p(v_z)dv_z$ be the probability of a gas particle's having velocity between v_z and $v_z + dv_z$, and let dN be the number of gas particles in the red rectangle at $t = 0$. From this, we can write

$$\underbrace{dN_{\text{gas}\to\text{liquid}}(A, \Delta t, z)}_{\substack{\text{number of particles in red rectangle} \\ \text{crossing boundary in time } \Delta t}} = \underbrace{dN}_{\substack{\text{number of particles} \\ \text{in red rectangle}}} \cdot \underbrace{\int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z\, p(v_z)}_{\substack{\text{probability of each particle} \\ \text{crossing boundary in time } \Delta t}} \tag{70}$$

To calculate dN, we assume that the gas is of uniform density. Therefore,

$$dN = \frac{A\,dz}{V} N \tag{71}$$

where $A\,dz$ is the volume of the red rectangle, V is the volume of the entire gas, and N is the number of gas particles in the entire gas. Using the ideal gas law $PV = NkT$, we can rewrite this in terms of the temperature T and pressure P of the gas:

$$dN = A\,dz\,\frac{P}{kT} \tag{72}$$

Plugging this into (70), we get

$$dN_{\text{gas}\to\text{liquid}}(A, \Delta t, z) = A\,dz\,\frac{P}{kT}\int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z\,p(v_z) \tag{73}$$

Finding the Maxwell velocity distribution—setup:
Now, we need to calculate $dv_z\,p(v_z)$, the probability of a gas particle's having velocity between v_z and $v_z + dv_z$. For this, we need to use the partition function. Recall that in the classical canonical distribution, the probability of the system being in a microstate r with energy E_r is weighted by the Boltzmann factor $e^{-\beta E_r}$, where $\beta \equiv 1/(kT)$. The normalization factor for this probability distribution is equal to $1/Z$, where Z is the partition function consisting of the sum of all these Boltzmann factors $Z \equiv \sum_r e^{-\beta E_r}$. Thus, the probability of the system being in a microstate r is

$$p_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{1}{Z}e^{-\beta E_r} \tag{74}$$

Now, let S be a set consisting of a number of microstates. The probability of the system's microstate being in set S is

$$p(r \in S) = \sum_{r \in S} p_r = \frac{1}{Z}\sum_{r \in S} e^{-\beta E_r} \tag{75}$$

In this case, we have a continuum of energy levels for the ideal gas, but the logic is the same: The set S is the set of all microstates with z-component of velocity between v_z and $v_z + dv_z$, and the partition function we need is the partition function for a single particle of a monatomic ideal gas.

We will need to use the phase-space formalism to ensure that we count everything correctly in the continuum limit:

Phase space:
Consider a particle in d-dimensional space. The particle's state can be defined by its position $\mathbf{x} = (x_1, \ldots, x_d)$, its momentum $\mathbf{p} = (p_1, \ldots, p_d)$, and any internal degrees of freedom (e.g. spin). Assume that there are g possible internal states for the particle.
The position and momentum of the particle constitute a point in $2d$-dimensional phase space: $(x_1, \ldots, x_d, p_1, \ldots, p_d)$.
To solve problems, discretize phase space by dividing it into $2d$-dimensional boxes. The volume of each box is h^d, where h is Planck's constant (which has units of position times momentum). The number of boxes in a phase-space volume $d^d p\,d^d x$ is the total volume divided by the volume of each box, or $\frac{d^d p\,d^d x}{h^d}$. Each box has g possible states, corresponding to the internal degrees of freedom of the particle. Therefore, the number of possible states in a phase-space volume $d^d p\,d^d x$ is

$$\text{Number of possible states in a phase-space volume } d^d p\,d^d x = g\frac{d^d p\,d^d x}{h^d} \tag{76}$$

Finding the Maxwell velocity distribution—calculating the ideal gas partition function:
Using the phase-space formalism for classical noninteracting point particles, the partition function for a single particle in a monatomic ideal gas is

$$Z_1 = \int \frac{d^3 p\,d^3 x}{h^3}e^{-\beta E} \quad \text{where } \beta \equiv \frac{1}{kT} \tag{77}$$

The energy of a single particle is its nonrelativistic kinetic energy:

$$E = \frac{p^2}{2m} \tag{78}$$

Plugging this in and carrying out the spatial integral for the partition function, we get

$$
\begin{aligned}
Z_1 &= \int \frac{d^3p\, d^3x}{h^3} e^{-\beta\left(\frac{p^2}{2m}\right)} \\
&= \int \frac{d^3p\, d^3x}{h^3} e^{-\beta p^2/(2m)} \\
&= \frac{V}{h^3} \int d^3p\, e^{-\beta p^2/(2m)} \quad \text{since} \int d^3x = V \\
&= \frac{V}{h^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z\, e^{-\beta(p_x^2 + p_y^2 + p_z^2)/(2m)]} \\
&= \frac{V}{h^3} \left[\int_{-\infty}^{\infty} dp_x\, e^{-\beta p_x^2/(2m)} \right] \left[\int_{-\infty}^{\infty} dp_y\, e^{-\beta p_y^2/(2m)} \right] \left[\int_{-\infty}^{\infty} dp_z\, e^{-\beta p_z^2/(2m)} \right]
\end{aligned}
\tag{79}
$$

Each of these three integrals is the same Gaussian integral, which can be calculated by a change of coordinates $u \equiv (\beta/(2m))^{1/2}\, p = (2mkT)^{-1/2}\, p$:

$$
\begin{aligned}
\int_{-\infty}^{\infty} dp\, e^{-\beta p^2/(2m)} &= (2mkT)^{1/2} \int_{-\infty}^{\infty} du\, e^{-u^2} \\
&= (2\pi mkT)^{1/2} \quad \text{using the result} \int_{-\infty}^{\infty} du\, e^{-u^2} = \pi^{1/2}
\end{aligned}
\tag{80}
$$

Plugging this back into (79), we get

$$
\begin{aligned}
Z_1 &= \frac{V}{h^3} (2mkT)^{3/2} \\
&= V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \\
Z_1 &= \frac{V}{\lambda^3} \quad \text{for} \quad \lambda \equiv \left(\frac{h^2}{2\pi mkT} \right)^{1/2}
\end{aligned}
\tag{81}
$$

The quantity λ is called the thermal wavelength.

Finding the Maxwell velocity distribution—calculating the probability:

Now, we are ready to find the equivalent of (75) for the case at hand. Remember that S is the set of all microstates with z-component of velocity between v_z and $v_z + dv_z$. Therefore, using the phase-space formalism, the equivalent of the sum (75) for the continuous case is

$$\sum_{r \in S} e^{-\beta E_r} \approx dp_z \int \frac{dp_x\, dp_y\, d^3x}{h^3} e^{-\beta E} \tag{82}$$

Notice that we are taking the integral of dp_x, dp_y, and d^3x, since the x- and y-components of the momentum and the position of the particle are independent of the z-component of the particle. (The integral is analogous to the sum in the discrete case. We need to integrate over momentum rather than velocity because the phase-space boxes of volume h^3 are in units of momentum, not velocity.) Therefore, dividing by the partition function for a single particle of the ideal gas Z_1, the probability

distribution we need is given by the equivalent of (75), which is

$$
\begin{aligned}
p(v_z)\, dv_z &= \frac{1}{Z_1} dp_z \int \frac{dp_x\, dp_y\, d^3x}{h^3} e^{-\beta E} \\
&= \frac{1}{Z_1} m\, dv_z \int \frac{dp_x\, dp_y\, d^3x}{h^3} e^{-\beta E} \quad \text{since } dp_i = m\, dv_i \\
&= \frac{1}{Z_1} m\, dv_z \int \frac{dp_x\, dp_y\, d^3x}{h^3} e^{-\beta(p_x^2+p_y^2+p_z^2)/(2m)} \quad \text{since } E = \frac{p^2}{2m} \\
&= \frac{1}{Z_1} \frac{mV}{h^3} dv_z \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y\, e^{-\beta(p_x^2+p_y^2+p_z^2)/(2m)} \quad \text{taking the integral } \int d^3x = V \\
&= \frac{1}{Z_1} \frac{mV}{h^3} e^{-\beta p_z^2/(2m)} dv_z \left[\int_{-\infty}^{\infty} dp_x\, e^{-\beta p_x^2/(2m)} \right] \left[\int_{-\infty}^{\infty} dp_y\, e^{-\beta p_y^2/(2m)} \right]
\end{aligned}
\tag{83}
$$

These Gaussian integrals are the same as those in (80). We can plug in the result for the Gaussian integral and simplify to get our answer in terms of the thermal wavelength λ:

$$
\begin{aligned}
p(v_z)\, dv_z &= \frac{1}{Z_1} \frac{mV}{h^3} e^{-\beta p_z^2/(2m)}\, dv_z\, (2\pi m k T) \\
&= \frac{1}{Z_1} \frac{mV}{h} \left(\frac{2\pi m k T}{h^2} \right) e^{-\beta p_z^2/(2m)}\, dv_z \\
&= \frac{1}{Z_1} \frac{mV}{h} \frac{1}{\lambda^2} e^{-\beta p_z^2/(2m)}\, dv_z \quad \text{for} \quad \lambda \equiv \left(\frac{h^2}{2\pi m k T} \right)^{1/2} \\
&= \frac{1}{Z_1} \frac{mV}{h} \frac{1}{\lambda^2} e^{-m v_z^2/(2kT)}\, dv_z \quad \text{using } p_z = m v_z \text{ and } \beta = 1/(kT)
\end{aligned}
\tag{84}
$$

Plugging in our result for the partition function (81), we get

$$
\begin{aligned}
p(v_z)\, dv_z &= \frac{\lambda^3}{V} \frac{mV}{h} \frac{1}{\lambda^2} e^{-m v_z^2/(2kT)}\, dv_z \\
&= \frac{\lambda m}{h} e^{-m v_z^2/(2kT)}\, dv_z \\
&= \left(\frac{m}{2\pi k T} \right)^{1/2} e^{-m v_z^2/(2kT)}\, dv_z \quad \text{since } \lambda \equiv \left(\frac{h^2}{2\pi m k T} \right)^{1/2}
\end{aligned}
\tag{85}
$$

Evaluating the flux integral:
We now have all the ingredients we need to explicitly set up the flux integral given in (69):

$$
\begin{aligned}
\text{Flux from gas to liquid}\big|_{T,P} &= \frac{\int_{z=0}^{z=L} dN_{\text{gas}\to\text{liquid}}(A, \Delta t, z)\big|_{T,P}}{A\, \Delta t} \\
&= \frac{\int_{z=0}^{z=L} A\, dz\, \frac{P}{kT} \int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z\, p(v_z)}{A\, \Delta t} \quad \text{by (73)} \\
&= \frac{1}{\Delta t} \frac{P}{kT} \int_{z=0}^{z=L} dz \int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z\, p(v_z) \\
&= \frac{1}{\Delta t} \frac{P}{kT} \left(\frac{m}{2\pi k T} \right)^{1/2} \int_{z=0}^{z=L} dz \int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z\, e^{-m v_z^2/(2kT)} \quad \text{by (85)}
\end{aligned}
\tag{86}
$$

The v_z integral is not analytically solvable, since its upper limit is $-z/\Delta t$ (and not 0 or ∞). The good news is that the set of both integrals is analytically solvable via integration by parts. Define

$$
I(z) \equiv \int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z\, e^{-m v_z^2/(2kT)}
\tag{87}
$$

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Then, the integral that we are interested in is

$$\int_{z=0}^{z=L} dz \int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z \, e^{-mv_z^2/(2kT)} = \int_{z=0}^{z=L} dz \, I(z)$$

Using integration by parts to simplify, we get

$$\int_{z=0}^{z=L} dz \int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z \, e^{-mv_z^2/(2kT)} = \int_{z=0}^{z=L} dz \left[(zI(z))' - zI'(z) \right]$$

$$= [zI(z)]_{z=0}^{z=L} - \int_{z=0}^{z=L} dz \, z \, I'(z) \tag{88}$$

First, let's evaluate the boundary term $[zI(z)]_{z=0}^{z=L}$:

$$[zI(z)]_{z=0}^{z=L} = L \cdot I(L) - 0 \cdot I(0)$$

$$= L \int_{v_z=-\infty}^{v_z=-L/\Delta t} dv_z \, e^{-mv_z^2/(2kT)}$$

Recall that L is the total height of the gas. We will now assume that the gas is large enough that we can take $L \to \infty$. This is justified because as the distance z from the liquid-gas boundary increases, the probability that a particle has enough velocity to cross the boundary within a time Δt drops precipitously. As $L \to \infty$, the expression above for $[zI(z)]_{z=0}^{z=L}$ goes to zero, so the boundary term cancels. That leaves us with the second term in (88), which is (taking $L \to \infty$ here too)

$$\int_{z=0}^{z=L} dz \int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z \, e^{-mv_z^2/(2kT)} \approx - \int_{z=0}^{z=\infty} dz \, z \, I'(z) \tag{89}$$

By the second fundamental theorem of calculus and the chain rule, the derivative $I'(z)$ is equal to

$$I'(z) = \frac{d}{dz} \left(\int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z \, e^{-mv_z^2/(2kT)} \right)$$

$$= -\frac{1}{\Delta t} \left[e^{-mv_z^2/(2kT)} \right]_{v_z=-z/\Delta t}$$

$$= -\frac{1}{\Delta t} \exp\left(-\frac{mz^2}{2kT(\Delta t)^2} \right) \tag{90}$$

Plugging this into (89), we find that we can now evaluate the remaining integral:

$$\int_{z=0}^{z=L} dz \int_{v_z=-\infty}^{v_z=-z/\Delta t} dv_z \, e^{-mv_z^2/(2kT)} \approx -\frac{1}{\Delta t} \int_{z=0}^{z=\infty} dz \, z \exp\left(-\frac{mz^2}{2kT(\Delta t)^2} \right)$$

$$= \frac{1}{\Delta t} \left(\frac{kT(\Delta t)^2}{m} \right) \int_{u=0}^{u=\infty} du \, e^{-u} \quad \text{using } u \equiv \left(\frac{m}{2kT(\Delta t)^2} \right) z^2$$

$$= \frac{1}{\Delta t} \left(\frac{kT(\Delta t)^2}{m} \right) \left[-e^{-u} \right]_{u=0}^{u=\infty}$$

$$= \frac{kT\Delta t}{m} \tag{91}$$

Plugging this back into (86), we get our final answer for the flux from the gas to the liquid:

$$\text{Flux from gas to liquid}\Big|_{\text{gas at } T,P} = \frac{1}{\Delta t} \frac{P}{kT} \left(\frac{m}{2\pi kT} \right)^{1/2} \left(\frac{kT\Delta t}{m} \right)$$

$$= \frac{P}{(2\pi mkT)^{1/2}} \tag{92}$$

Solving for the net flux—detailed balance:
Recall our first equation for the net flux from the gas to the liquid (**??**):

$$\text{Net flux of gas to liquid} \left.\right|^{\text{gas at } T_v + \Delta T,\, P_v}_{\text{liquid at } T_v,\, P_v}$$

$$= \text{Flux from gas to liquid} \left.\right|^{\text{gas at } T_v + \Delta T,\, P_v}_{\text{liquid at } T_v,\, P_v} - \text{Flux from liquid to gas} \left.\right|^{\text{gas at } T_v + \Delta T,\, P_v}_{\text{liquid at } T_v,\, P_v}$$

We have already solved for the first term on the right side, the flux from the gas to the liquid:

$$\text{Flux from gas to liquid} \left.\right|^{\text{gas at } T_v + \Delta T,\, P_v}_{\text{liquid at } T_v,\, P_v} = \frac{P_v}{(2\pi m k (T_v + \Delta T))^{1/2}} \tag{93}$$

But what about the second term, the flux from the liquid to the gas? We don't know enough about liquids to calculate it directly. Instead, we need to use the property of "detailed balance":

> **Detailed balance:**
> Consider two systems, labeled 1 and 2, and suppose that particles can move between the two systems. Consider a microscopic process by which a particle moves from system 1 to system 2. Then, if systems 1 and 2 are in equilibrium, the rates of the forward and reverse versions of this microscopic process are equal.

Note that in the setup of this problem, the liquid and the gas are *not* in equilibrium. If they were, then there would be no net flux of particles from the gas to the liquid. Despite this, we can calculate the flux from the liquid to the gas by relating this setup to a different setup, in which the liquid and the gas are at equilibrium.

The flux of particles from the liquid to the gas depends only on the properties of the liquid (because this quantity depends only on how many liquid particles cross the boundary to the gas in a period of time). Therefore,

$$\text{Flux from liquid to gas} \left.\right|^{\text{gas at } T_v + \Delta T,\, P_v}_{\text{liquid at } T_v,\, P_v} = \text{Flux from liquid to gas} \left.\right|^{\text{gas at } T_v,\, P_v}_{\text{liquid at } T_v,\, P_v}$$

The right-hand side of this equation represents a setup in which the liquid and gas are at equilibrium (same temperature and pressure). Therefore, we can apply detailed balance: The rate of the process "a particle moves from the liquid to the gas" is equal to the rate of the process "a particle moves from the gas to the liquid." This implies that

$$\text{Flux from liquid to gas} \left.\right|^{\text{gas at } T_v,\, P_v}_{\text{liquid at } T_v,\, P_v} = \text{Flux from gas to liquid} \left.\right|^{\text{gas at } T_v,\, P_v}_{\text{liquid at } T_v,\, P_v}$$

But we have already calculated this flux in (**??**):

$$\text{Flux from gas to liquid} \left.\right|^{\text{gas at } T_v,\, P_v}_{\text{liquid at } T_v,\, P_v} = \frac{P_v}{(2\pi m k T_v)^{1/2}}$$

Putting the last three equations together, we get our answer for the flux from the liquid to the gas:

$$\text{Flux from liquid to gas} \left.\right|^{\text{gas at } T_v + \Delta T,\, P_v}_{\text{liquid at } T_v,\, P_v} = \frac{P_v}{(2\pi m k T_v)^{1/2}} \tag{94}$$

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Putting together (93) and (94), we get our final expression for the net flux from the gas to the liquid in the non-equilibrium setup of the problem:

$$\text{Net flux of gas to liquid} \left.\right|_{\text{liquid at } T_v, P_v}^{\text{gas at } T_v + \Delta T, P_v} = \frac{P_v}{(2\pi m k (T_v + \Delta T))^{1/2}} - \frac{P_v}{(2\pi m k T_v)^{1/2}}$$

$$= \frac{P_v}{(2\pi m k T_v)^{1/2}} \left[\frac{T_v^{1/2}}{(T_v + \Delta T)^{1/2}} - 1 \right]$$

$$\boxed{\text{Net flux of gas to liquid} \left.\right|_{\text{liquid at } T_v, P_v}^{\text{gas at } T_v + \Delta T, P_v} = \frac{P_v}{(2\pi m k T_v)^{1/2}} \left[\left(1 + \left(\frac{\Delta T}{T_v} \right) \right)^{-1/2} - 1 \right]} \qquad (95)$$

If we further assume that $\Delta T \ll T_v$, we can take a lowest-order Taylor expansion of this result:

$$\text{Net flux of gas to liquid} \left.\right|_{\text{liquid at } T_v, P_v}^{\text{gas at } T_v + \Delta T, P_v} = \frac{P_v}{(2\pi m k T_v)^{1/2}} \left[\left(1 - \frac{1}{2} \frac{\Delta T}{T_v} + \dots \right) - 1 \right]$$

$$\boxed{\text{Net flux of gas to liquid} \left.\right|_{\text{liquid at } T_v, P_v}^{\text{gas at } T_v + \Delta T, P_v} = -\frac{1}{2} \frac{P_v}{(2\pi m k T_v)^{1/2}} \frac{\Delta T}{T_v} \quad \text{for} \quad \Delta T \ll T_v} \qquad (96)$$

Note that, somewhat counterintuitively, increasing the temperature of the gas makes particles flow from the liquid to the gas (net flux of gas to liquid is negative), rather than the other way round. The reason for this is that the temperature increase is done at constant pressure. Since pressure and temperature are related by $PV = NkT$, increasing the temperature at constant pressure necessarily decreases the density of the gas N/V. This causes the the net flux to be from the liquid to the gas, rather than from the gas to the liquid.

Phew! This problem of finding the flux of a gas through a hole is called the "effusion problem." It is somewhat amazing that, just using microscopic information about the canonical ensemble, we can calculate quite a bit of macroscopic information about fluxes. If you want another example of an effusion problem, look at 2013 Q8.