Theoretical Statistical Physics

Solution to Exercise Sheet 5

1 Ideal gas work (3 points)

Within the kinetic model of an ideal gas, show that the work done to the gas when changing the volume is $-p\,\mathrm{d}V$.

Kinetic theory traces the macroscopic phenomenon of pressure on a surface back to a constant bombardment by microscopic particles, each of which obeys Newton's laws of motion. Upon impact, a tiny amount of momentum is transferred onto the surface. The resulting average force can be calculated explicitly by considering a simple toy model, a cubic box of length L containing N particles, each of mass m. We assume that a particle travelling with momentum v_x in the x-direction bounces off a wall perfectly elastically so that it returns with velocity $-v_x$. The resulting momentum transfer is $\Delta p_x = 2m\,v_x$. Since the particle is trapped in a box, it will again hit the *same* wall after $\Delta t = 2L/v_x$. The force due to this single particle is thus

$$F_p = \frac{\Delta p_x}{\Delta t} = \frac{m\,v_x^2}{L}. \tag{1}$$

Summing up the contributions from all N particles in the container, the total average force is

$$F = \frac{N\,m\,\langle v_x^2\rangle}{L}. \tag{2}$$

$\langle v_x^2\rangle$ is the square of the velocity in x-direction averaged over all particles. The x-direction is in no way distinguished from y or z, meaning $\langle v_x^2\rangle = \langle v^2\rangle/3$. Thus the differential work required to impress one of the container's walls by a distance $\mathrm{d}x$ is

$$\delta W = -F\,\mathrm{d}x = -\frac{N\,m\,\langle v^2\rangle}{3L}\,\mathrm{d}x = -\frac{2N\,\langle E_{\mathrm{kin}}\rangle}{3L^3}\,L^2\,\mathrm{d}x = -\frac{2N\,\langle E_{\mathrm{kin}}\rangle}{3V}\,\mathrm{d}V. \tag{3}$$

The sign above stems from the fact that if $\mathrm{d}V < 0$, we need to exert a force to squeeze the box, thereby increasing its energy, whereas for $\mathrm{d}V > 0$, the system itself is doing the work, thus decreasing its energy. Inserting $\langle E_{\mathrm{kin}}\rangle = \frac{3}{2}k_{\mathrm{B}}\,T$ and the ideal gas law $p\,V = N\,k_{\mathrm{B}}\,T$, we get

$$\delta W = -\frac{N\,k_{\mathrm{B}}\,T}{V}\,\mathrm{d}V = -p\,\mathrm{d}V. \tag{4}$$

2 Density of states (2 points)

Consider a system of N identical, uncoupled quantum mechanical oscillators. Compute the number of states at a given total energy of the system.

A quantum harmonic oscillator features the well-known ladder of equidistant energy states

$$E_n = \big(n + \tfrac{1}{2}\big)\hbar\omega, \qquad \text{with } n \in \mathbb{N}_0. \tag{5}$$

For N identical oscillators, we can thus immediately write down the ground state energy as $E_{\mathrm{min}} = \frac{N}{2}\,\hbar\omega$. Since this energy is attained only by a single state $n_i = 0\ \forall\, i \in \{1,\dots,N\}$, the number of microstates with energy E_{min} is $\Omega(E_{\mathrm{min}}) = 1$.

At the first excited level $E_{\text{min}} + \hbar\omega$, we have one energy quantum to allocate. We could use it to excite any of the N oscillators, so the number of states increases to

$$\Omega(E_{\text{min}} + \hbar\omega) = N. \tag{6}$$

At $E_{\text{min}} + 2\hbar\omega$, we have 2 quanta to distribute. Either we give both quanta to one oscillator for which there are again N possibilities, or to two different oscillators, resulting in $N(N-1)$ possibilities. However, order doesn't matter since first giving a quantum to oscillator i followed by exciting oscillator j results in the same state as doing it the other way round. We therefore have to halve the number of states resulting from the second configuration. In total, this gives

$$\Omega(E_{\text{min}} + 2\hbar\omega) = N + \frac{N}{2}(N-1) = \frac{N}{2}(N+1). \tag{7}$$

The counting problem we are dealing with is simply that of how many ways we can distribute m identical quanta amongst N oscillators? The answer is provided by the binomial coefficient,

$$\Omega_m = \Omega(E_m) = \binom{N+m-1}{m} = \frac{(N+m-1)!}{m!\,(N-1)!}, \tag{8}$$

where $E_m = E_{\text{min}} + m\,\hbar\omega = \left(\frac{N}{2} + m\right)\hbar\omega$. For $m \in \{0,1,2,3,4\}$, we thus get the following numbers of states.

m	0	1	2	3	4
Ω_m	1	N	$\frac{N}{2}(N+1)$	$\frac{N}{6}(N+1)(N+2)$	$\frac{N}{24}(N+1)(N+2)(N+3)$

Now that we have the number of states at a given energy, it is a trivial matter to derive the entropy S_m of N oscillators with total energy E_m. Using Stirlings approximation for large factorials, $\ln(n!) = n\,\ln(n) - n + \mathcal{O}(\ln n)$, we get

$$\begin{aligned}
S_m = k_\text{B}\,\ln(\Omega_m) &= k_\text{B}\Big(\ln[(N+m-1)!] - \ln(m!) - \ln[(N-1)!]\Big) \\
&\approx k_\text{B}\Big((N+m-1)\ln(N+m-1) - m\ln(m) - (N-1)\ln(N-1)\Big) \\
&\approx k_\text{B}\Big((N+m)\ln(N+m) - m\ln(m) - N\ln(N)\Big) \\
&= k_\text{B}\Big(N\ln\big(\tfrac{N+m}{N}\big) + m\ln\big(\tfrac{N+m}{m}\big)\Big).
\end{aligned} \tag{9}$$

3 Stationary distribution (2 points)

Consider the Boltzmann equation with external force $\boldsymbol{F}(\boldsymbol{x}) = -\boldsymbol{\nabla}_x V(\boldsymbol{x})$. Find the stationary distribution $f_0(\boldsymbol{x}, \boldsymbol{p})$.

The Boltzmann equation describes the dynamical evolution of phase space densities for systems with a large number of constituents such as a gas. It is an integro-differential equation whose significance derives from its ability to describe out-of-equilibrium processes. It reads[1]

$$\Big(\frac{\partial}{\partial t} + \frac{\boldsymbol{p}}{m}\cdot\boldsymbol{\nabla}_x + \boldsymbol{F}\cdot\boldsymbol{\nabla}_p\Big) f(\boldsymbol{x},\boldsymbol{p},t) = \int \mathrm{d}^3k\,\mathrm{d}^3p'\,\mathrm{d}^3k'\,|\langle\boldsymbol{p}',\boldsymbol{k}'|T|\boldsymbol{p},\boldsymbol{k}\rangle|^2\,\big[f_{p'}\,f_{k'} - f_p f_k\big]. \tag{10}$$

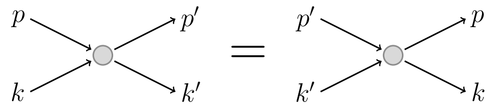
The above formulation already incorporates the Stosszahlansatz, also known as molecular chaos, which assumes that the collision term results solely from two-body collisions between particles that are uncorrelated prior to the collision.[2] This was the key assumption by Boltzmann, as it

[1] Boltzmann assumed that the influence of the external force $\boldsymbol{F}$ on the collision rate is negligible to derive (10).
[2] Molecular chaos can also intuitively be interpreted as the assumption that velocity and position of a constituent particle are uncorrelated.

allows to write the collision term as a momentum-space integral in which the two-particle correlator $F(\boldsymbol{x},\boldsymbol{p},\boldsymbol{k},t)$ factorizes into two one-particle distribution functions $f(\boldsymbol{x},\boldsymbol{p},t)\,f(\boldsymbol{x},\boldsymbol{k},t)$. The term $\big[f_{p'}\,f_{k'} - f_p f_k\big]$ in (10) is a shorthand notation for $\big[f(\boldsymbol{x},\boldsymbol{p}',t)\,f(\boldsymbol{x},\boldsymbol{k}',t) - f(\boldsymbol{x},\boldsymbol{p},t) f(\boldsymbol{x},\boldsymbol{k},t)\big]$. For a stationary system, the Boltzmann equation greatly simplifies in two ways. On the one hand, the particle distribution loses its explicit time-dependence, $f(\boldsymbol{x},\boldsymbol{p},\not{t})$. On the other hand, stationarity implies that the Boltzmann H-function must be time-independent, since its time-dependence derives exclusively from $f(\boldsymbol{x},\boldsymbol{p},t)$,

$$H(t) = \int \mathrm{d}^3 x \int \mathrm{d}^3 p\, f(\boldsymbol{x},\boldsymbol{p},t) \ln[f(\boldsymbol{x},\boldsymbol{p},t)]. \tag{11}$$

A stationary H results in a condition known as detailed balance (see lecture notes from November 22), in which the number of particles leaving a certain mode due to a given scattering process is exactly equal to the number of particles entering that mode by the reverse process. Conceptually:



Under these circumstances, the loss and gain terms $f_p f_k$ and $f_{p'}\,f_{k'}$ in (10) exactly cancel, meaning the r.h.s. of the Boltzmann equation vanishes. We are left with

$$\begin{aligned}\frac{\boldsymbol{p}}{m}\cdot\boldsymbol{\nabla}_x\, f_0(\boldsymbol{x},\boldsymbol{p}) &= -\boldsymbol{F}(\boldsymbol{x})\cdot\boldsymbol{\nabla}_p\, f_0(\boldsymbol{x},\boldsymbol{p})\\ &= \boldsymbol{\nabla}_x\, V(\boldsymbol{x})\cdot\boldsymbol{\nabla}_p\, f_0(\boldsymbol{x},\boldsymbol{p}).\end{aligned} \tag{12}$$

This partial differential equation is solved by the ansatz

$$f_0(\boldsymbol{x},\boldsymbol{p}) = \alpha\,\exp\!\left(\frac{\beta}{2\,m}(\boldsymbol{p}-\boldsymbol{p}_0)^2 + \gamma\,V(\boldsymbol{x})\right) + \delta. \tag{13}$$

Reinserting (13) into (12) gives

$$\frac{\boldsymbol{p}}{m}\cdot\gamma\,\boldsymbol{\nabla}_x\, V(\boldsymbol{x}) = \boldsymbol{\nabla}_x\, V(\boldsymbol{x})\cdot\frac{\beta}{m}\,(\boldsymbol{p}-\boldsymbol{p}_0), \tag{14}$$

from which we infer $\beta = \gamma$ and $\boldsymbol{p}_0 = 0$. Moreover, normalizability of the phase space density requires $\delta = 0$. Thus, $f_0(\boldsymbol{x},\boldsymbol{p}) = \alpha\, e^{\beta\left(\frac{\boldsymbol{p}^2}{2\,m}+V(\boldsymbol{x})\right)}$. For

$$\alpha = \left(\frac{m}{2\pi\,k_\mathrm{B}\,T}\right)^{\frac{d}{2}}\left(\int \mathrm{d}^d x\, e^{\beta\,V(\boldsymbol{x})}\right)^{-\frac{d}{2}}, \qquad \beta = -\frac{1}{k_\mathrm{B}\,T}, \tag{15}$$

this is precisely the Maxwell-Boltzmann distribution in d dimensions.

4 Pressure on a wall (3 points)

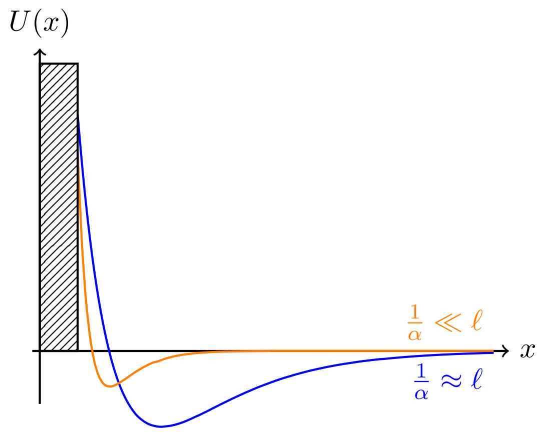
Compute the pressure of an ideal gas in three dimensions upon a wall at $x = 0$ that attracts molecules at large distance and repels them at smaller distance. Let the force be given by the potential

$$U(x) = -A\,e^{-\alpha x} + B\,e^{-2\alpha x}, \tag{16}$$

with $A, B > 0$. Consider separately the cases where the range of the force is

a) small compared to the mean free path ℓ, and

b) comparable to it.



The energy of a particle in the vicinity of the wall where $U(x) \neq 0$ is

$$E(x, \dot{\boldsymbol{x}}) = \frac{m}{2}\,\dot{\boldsymbol{x}}^2 + U(x). \tag{17}$$

Energy must be conserved during collisions with the wall. Since the potential depends only on x (rather than $\boldsymbol{x}$), the transverse energy $E_t = \frac{m}{2}(\dot{y}^2 + \dot{z}^2)$ is separately conserved from the normal contribution

$$E_n = E - E_t = \frac{m}{2}\,\dot{x}^2 + U(x). \tag{18}$$

We can solve the latter for the velocity in x-direction,

$$\dot{x}(x) = \pm\sqrt{\tfrac{2}{m}\big[E_n - U(x)\big]}. \tag{19}$$

The pressure on the wall is determined by the total momentum transfer from all particle collisions. If a single particle encounters the wall at time t_0, its change in momentum is

$$\begin{aligned} \Delta p_x &= p_x(t_0 + \tau) - p_x(t_0 - \tau) \\ &= m\big[\dot{x}(t_0 + \tau) - \dot{x}(t_0 - \tau)\big], \end{aligned} \tag{20}$$

where $\tau = \ell/\bar{v}_x$ is the characteristic scattering time inversely proportional to the average velocity in x-direction $\bar{v}_x = \sqrt{2E_n/m}$.

a) In the weak scattering case where the range of the force $1/\alpha$ is much smaller than the mean free path ℓ, the velocity $\dot{x}(t_0 \pm \tau) \approx \dot{x}(\ell)$ in (20) will be evaluated at a distance ℓ from the wall. This is because $x(t_0) = 0$ and the particle moves towards/away from the wall with $\bar{v}_x$ carrying it to a distance of approximately $\bar{v}_x\tau = \ell$ within the scattering time τ. At $x \approx \ell$, the potential becomes negligible. Inserting (19) into (20) for $U(\ell) \approx 0$ gives

$$\Delta p_{x,a} = 2\sqrt{2m\,E_n} \tag{21}$$

b) In the strong scattering case, the scattering time $\tau = \ell/\bar{v}_x$ is much shorter and the mean free path decreases, becoming of the order of the range of the force $\frac{1}{\alpha} \approx \ell$. To compute the momentum transfer, the velocity will now be evaluated at a shorter distance ℓ from the wall where the potential still exerts a significant attraction on the particle, $F_x = -\partial_x U(\ell) < 0$. This increases the momentum transfer onto the wall and thus the pressure,

$$\Delta p_{x,b} = 2\sqrt{2m\,\big[E_n - U(x)\big]} \overset{\text{assuming } B \gg A}{\approx} 2\sqrt{2m\,\big(E_n + A\,e^{-\alpha x}\big)} > 2\sqrt{2m\,E_n} = \Delta p_{x,a}. \tag{22}$$

To get a more quantitative result, rather than this rough approximation, we can separate variables in (19) to get

$$\frac{\mathrm{d}x}{\pm\sqrt{\frac{2}{m}\big[E_n - U(x)\big]}} = \mathrm{d}t. \tag{23}$$

The solution to this differential equation is

$$x(t) = \frac{1}{\alpha} \ln\left[\xi \cosh[\alpha \bar{v}_x (t - t_0)] - \frac{A}{2E_n}\right], \qquad \text{where } \xi = \left(\frac{B}{E_n} + \frac{A^2}{4E_n^2}\right)^{\frac{1}{2}}. \tag{24}$$

Differentiating (24) w.r.t. time results in the velocity

$$\dot{x}(t) = \frac{\sinh[\alpha \bar{v}_x (t - t_0)]}{\cosh[\alpha \bar{v}_x (t - t_0)] - \frac{A}{2E_n \xi}} \bar{v}_x, \tag{25}$$

and the momentum transfer

$$\begin{aligned} \Delta p_{x,b} &= m\big[\dot{x}(t_0 + \tau) - \dot{x}(t_0 - \tau)\big] \\ &= m\,\bar{v}_x \left[\frac{\sinh[\alpha \bar{v}_x \tau]}{\cosh[\alpha \bar{v}_x \tau] - \frac{A}{2E_n \xi}} - \frac{\sinh[-\alpha \bar{v}_x \tau]}{\cosh[-\alpha \bar{v}_x \tau] - \frac{A}{2E_n \xi}}\right] \\ &= \Delta p_{x,a} \frac{\sinh[\alpha \bar{v}_x \tau]}{\cosh[\alpha \bar{v}_x \tau] - \frac{A}{2E_n \xi}}, \end{aligned} \tag{26}$$

where we used $\sinh(-x) = -\sinh(x)$ and $\cosh(-x) = \cosh(x)$. Since $\alpha \bar{v}_x \tau = \alpha \ell \approx 1$, we can approximate this as

$$\Delta p_{x,b} = \Delta p_{x,a} \left(1 + \frac{A}{E_n \xi} e^{-\alpha \bar{v}_x \tau}\right). \tag{27}$$

Again, this is larger than the momentum transfer we obtained in the weak scattering case, resulting in an increased pressure on the wall.