

Homework 7 Solutions

Problem 1) Adsorption

a)

We will assume that the particles are identical. This means that there is only one micro-state state for the adsorbed particles (a.k.a. not two states for swapping the particles). If the gas particles have internal degrees of freedom we will assume that the same degrees of freedom are available in both the gas and adsorbed state so that those degrees of freedom can be integrated out without affecting the probability of being adsorbed. If we treat a single adsorption site as our system and work in the grand canonical ensemble

$$P_2 = \frac{e^{-\beta(\epsilon_2 - 2\mu)}}{1 + e^{-\beta(\epsilon_2 - 2\mu)}}$$

Note that I have understood the problem to mean that ϵ_2 represents the energy for both atoms rather than $2\epsilon_2$.

b)

Recall that the chemical potential of an ideal gas is

$$\mu = \tau \ln \left(\frac{N \lambda_\tau^3}{V} \right)$$

which we derived by both taking $(\partial F / \partial N)_\tau$ for a system where each independent particle can occupy $z_1 = V / \lambda_\tau^3$ different states. The dependence $\lambda_\tau = h / \sqrt{2\pi m \tau}$ came from explicitly counting the states in the box. We can use the ideal gas equation of state $PV = N\tau$

$$\mu = \tau \ln \left(P \frac{\lambda_\tau^3}{\tau} \right)$$

which makes our Boltzmann factor

$$e^{-\beta(\epsilon_2 - 2\mu)} = e^{-\beta\epsilon_2 + 2 \ln(P \lambda_\tau^3)} = P^2 e^{-\beta\epsilon_2 + 2 \ln(\beta \lambda_\tau^3)}$$

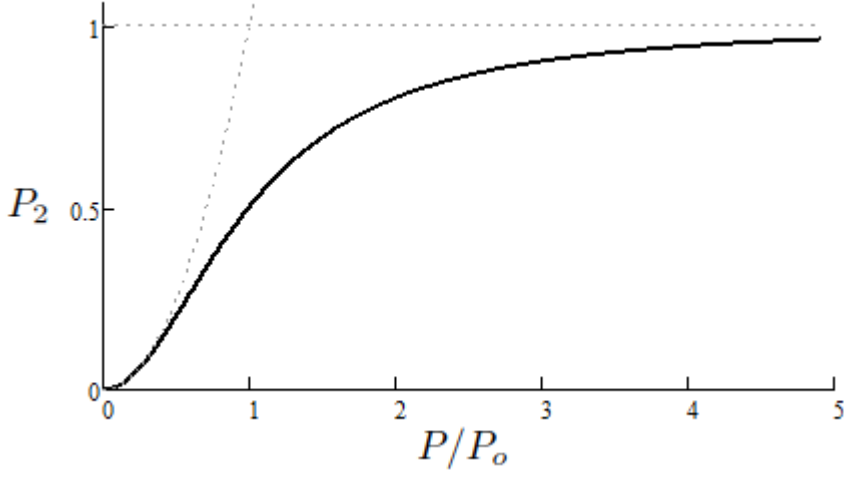
for convenience let's define $P_o = \frac{\tau}{\lambda_\tau^3} e^{\epsilon_2 / 2\tau}$ so that $e^{-\beta(\epsilon_2 - 2\mu)} = (P / P_o)^2$. This pressure, qualitatively is the pressure at which the site will be occupied half of the time. This makes the probability

$$P_2 = \frac{P^2}{P_o^2 + P^2}$$

c)

i)

The In the low pressure limit the probability grows as the square of P while. At high pressures it maxes out at P . At P_o it is 0.5.



where $P_o = \frac{\tau}{\lambda_\tau^3} e^{\epsilon_2/2\tau}$

ii)

If we keep track of the temperature dependence of the Boltzmann factor is

$$\exp\left(-\frac{\epsilon_2}{\tau} + 2 \ln\left(\frac{P}{\tau} \frac{h^3}{(2\pi m\tau)^{3/2}}\right)\right)$$

$$\exp\left(-\frac{\epsilon_2}{\tau} + \ln\left(\frac{1}{\tau^5} \frac{P^2 h^6}{(2\pi m)^3}\right)\right)$$

or

$$\left(\frac{\tau}{\tau_0}\right)^5 \exp\left(-\frac{\epsilon_2}{\tau}\right)$$

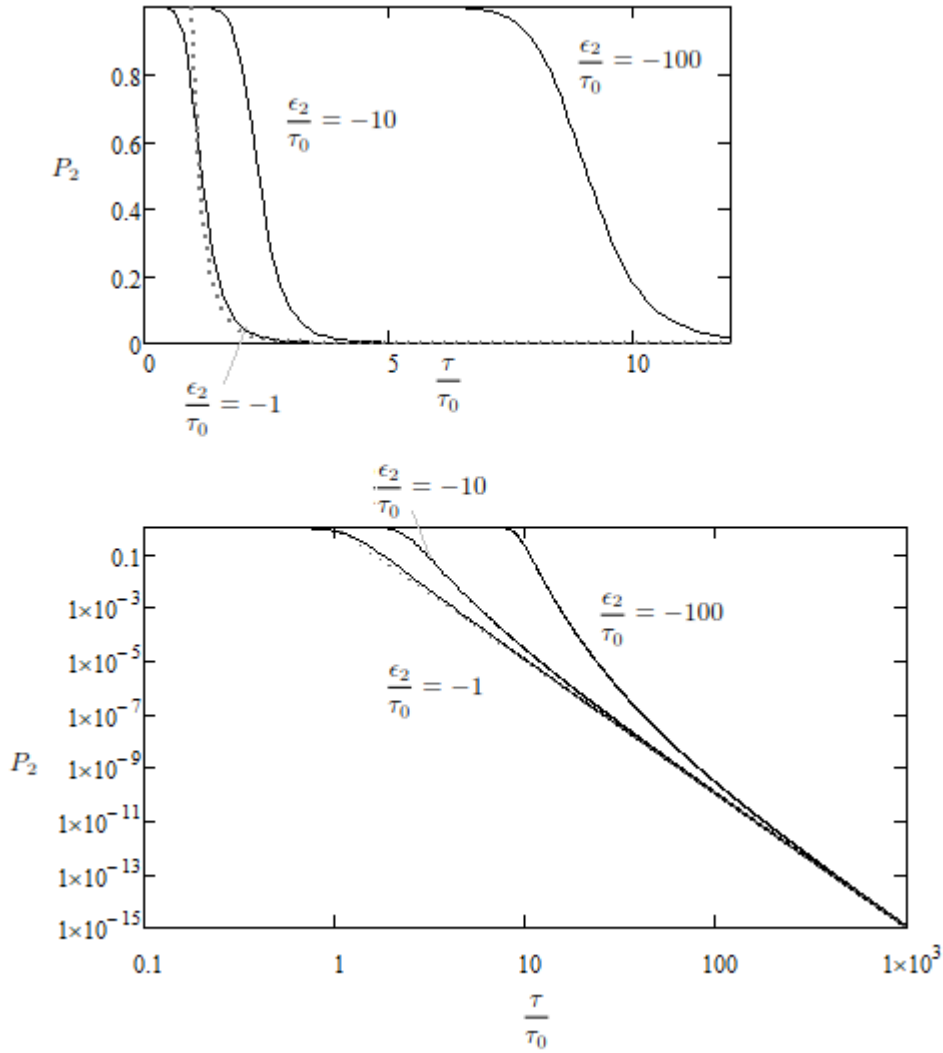
where

$$\tau_0 = \left(\frac{P^2 h^6}{(2\pi m)^3}\right)^{1/5}$$

So

$$P_2 = \frac{\left(\frac{\tau_0}{\tau}\right)^5 \exp\left(-\frac{\epsilon_2}{\tau}\right)}{1 + \left(\frac{\tau_0}{\tau}\right)^5 \exp\left(-\frac{\epsilon_2}{\tau}\right)}$$

For prospective hydrogen gas at one atmosphere $\tau_0/k_B \approx 2.9\text{K}$ which is well below where the ideal gas approximation works. Note that we are interested in $\epsilon_2 < 0$, (a.k.a. energetically for favorable binding). At low temperatures $P_2 \approx 1$ while at high temperatures it falls off as $(\tau_0/\tau)^5$ as can be seen by the comparison to the dotted line in the log-log plot. The crossover depends on both τ_0 and ϵ_2 .



Problem 2) Hemoglobin (from K&K 5.14)

Using the Boltzmann factor and explicitly dividing by the partition function

$$P_N = \frac{g(N) e^{-\beta N(\epsilon - \mu)}}{\sum_{N=0}^4 g(N) e^{-\beta N(\epsilon - \mu)}}$$

where $g(N)$ is the number of distinct ways of arranging the molecules in the sites. That is

$$g(N) = \frac{4!}{N!(4-N)!}$$

To make our expression simpler let's define

$$\phi' \equiv e^{-\beta(\epsilon - \mu)} = \phi / e^{\beta\epsilon}$$

a)

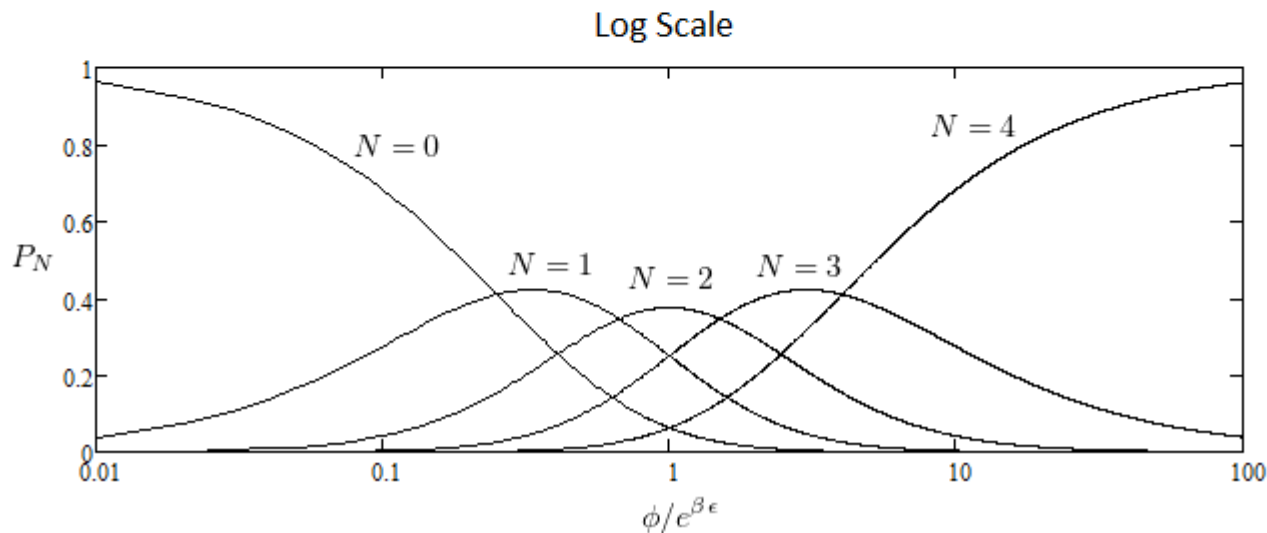
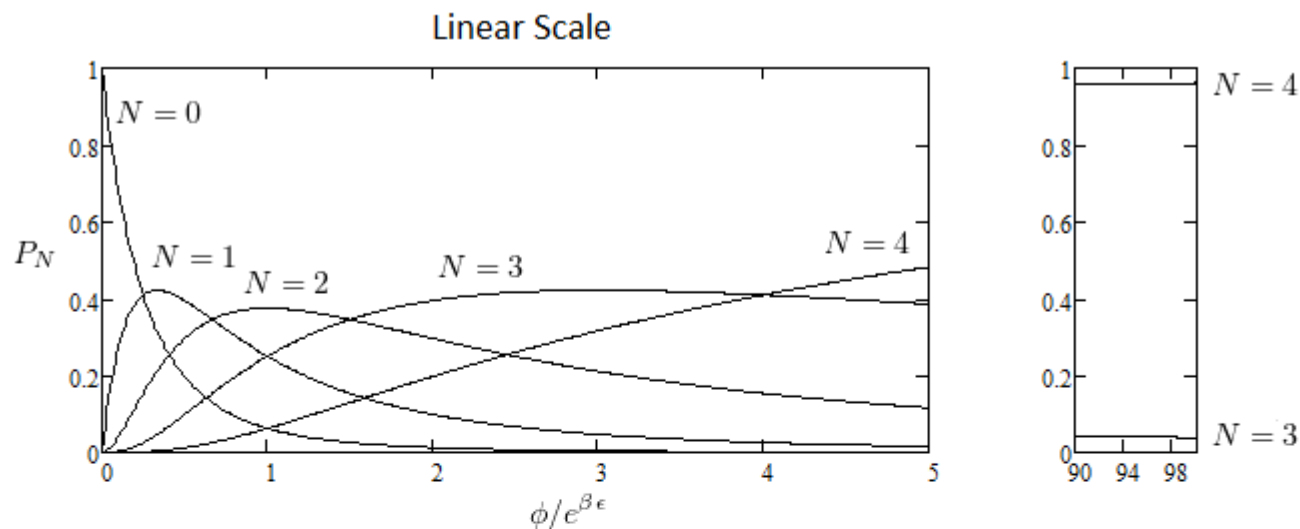
$$P_1 = \frac{4\phi'}{1 + 4\phi' + 6\phi'^2 + 4\phi'^3 + \phi'^4}$$

At values $\phi \ll e^{\beta\epsilon}$ this will increase linearly. It will peak and then be exponentially suppressed at $\phi \gg e^{\beta\epsilon}$.

b)

$$P_1 = \frac{\phi'^4}{1 + 4\phi' + 6\phi'^2 + 4\phi'^3 + \phi'^4}$$

At values $\phi \ll e^{\beta\epsilon}$ this will increase as a quartic. It will approach one as $\phi \gg e^{\beta\epsilon}$.



Problem 3) Symmetry of filled and vacant orbitals (K&K 6.2)

The probability of an orbital δ above the Fermi level being occupied is

$$f(\mu + \delta) = \frac{e^{-\beta\delta}}{1 + e^{-\beta\delta}}$$

and δ below as

$$f(\mu - \delta) = \frac{e^{\beta\delta}}{1 + e^{\beta\delta}}$$

we add them

$$\begin{aligned} f(\mu + \delta) + f(\mu - \delta) &= \frac{e^{-\beta\delta}}{1 + e^{-\beta\delta}} + \frac{e^{\beta\delta}}{1 + e^{\beta\delta}} \\ &= \frac{e^{\beta\delta} + 1 + e^{-\beta\delta} + 1}{(1 + e^{\beta\delta})(1 + e^{-\beta\delta})} \\ &= 1 \end{aligned}$$

so

$$f(\mu + \delta) = 1 - f(\mu - \delta)$$

as expected

Problem 4) Convective isentropic equilibrium of the atmosphere (K&K 6.11)

a)

Consider a small volume element of air of area A and height dz . It's weight of $\rho g A dz$ is supported by a force from a difference in pressure between it's top and bottom $A dp$.

$$\frac{dp}{dz} = g\rho = -gm \frac{N}{V}$$

using the equation of state for an ideal gas

$$\frac{dp}{dz} = -gm \frac{p}{\tau} \quad (1)$$

Note that τ changes with altitude so we can't integrate this yet. To see how τ changes we assume that the atmosphere is in convective equilibrium

$$pV^\gamma = \text{const.} \quad (2)$$

using the equation of state again

$$p \left(\frac{N\tau}{p} \right)^\gamma = \text{const.}$$

As we are using this equation to relate p and τ of a fixed number of molecules at different heights we may absorb N into the constant

$$p^{1-\gamma} \tau^\gamma = \text{const.} \quad (3)$$

$$p = \tau^{\frac{\gamma}{\gamma-1}} \text{const.} \quad (4)$$

$$dp = \frac{\gamma}{\gamma-1} \tau^{\frac{1}{\gamma-1}} d\tau \quad (5)$$

Plugging 4 and 5 into equation 1 we have

$$\frac{\gamma}{\gamma-1} \tau^{\frac{1}{\gamma-1}} \frac{d\tau}{dz} = gm \frac{\tau^{\frac{\gamma}{\gamma-1}}}{\tau}$$

$$\frac{d\tau}{dz} = -gm \frac{\gamma-1}{\gamma}$$

or

$$\frac{dT}{dz} = -\frac{gm}{k_B} \frac{\gamma-1}{\gamma}$$

where the right hand side is a constant (as long γ is roughly independent of temperature) as expected.

b)

If we take $\gamma = 7/5$, $g = 9.81 \text{m/s}^2$, and $m = 2 \times 14.0067 \text{g/mol}$ we find that

$$\frac{dT}{dz} \approx -9.4 \frac{^\circ\text{C}}{\text{km}}$$

c)

We may multiply both sides of 2 by $(mN)^{-\gamma}$ and then absorb them into the constant on the right hand side.

$$p \left(\frac{V}{mN} \right)^\gamma = \text{const.}$$

or

$$p \propto \rho^\gamma$$

To see why we can absorb m and N into the constant, consider the flexible balloon increasing a volume of air. The equation $pV^\gamma = \text{const.}$ relates how pressure changes the volume of this balloon. As no particles enter or leave the balloon, m and N are constant.

Problem 5) Ideal Gas Calculations (K&K 6.14)

a)

The energy of an ideal gas is only a function of its temperature (by the equipartition theorem) so if we keep the temperature the same the energy will not change. This means that the heat entering the gas during isothermal expansion must equal the work done by the gas.

$$\begin{aligned}
Q &= \int_{V_o}^{V_f} p dV \\
&= \int_{V_o}^{V_f} \frac{N\tau}{V} dV \\
&= N\tau \ln(V_f/V_o) \\
&= 300\text{K} (1\text{mol}) \left(8.315 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \ln(2) \\
&\approx 1.73 \times 10^3 \text{J}
\end{aligned}$$

Because isentropic is the same as adiabatic reversible, no heat enters the system during that step.

b)

During the isentropic expansion the gas obeys $pV^\gamma = \text{const.}$ Using the ideal gas law $pV = N\tau$ we have

$$\left(\frac{N\tau}{V} \right) V^\gamma = \text{const.}$$

$$\tau \propto V^{1-\gamma}$$

$$T_f = T_o \left(\frac{V_f}{V_o} \right)^{1-\gamma}$$

For a monatomic gas, which has 3 degrees of freedom, $\gamma = 5/3$ so that

$$300\text{K} (2)^{1-\frac{5}{3}} \approx 189\text{K}$$

c)

The increase in entropy is the same as the entropy that would have entered the system

$$dS = \frac{dQ}{T}$$

using our result from part a) we have

$$\begin{aligned}
\Delta S &= (1\text{mol}) \left(8.315 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \ln(2) \\
&\approx 5.763 \frac{\text{J}}{\text{K}}
\end{aligned}$$

Alternatively we note that each particle has twice as many possible states afterwards so the change in entropy is

$$\Delta\sigma = (6.02 \times 10^{23}) \ln(2)$$

which is the same thing up to Boltzmann's constant.

Problem 6) Compressibility and density of states

a)

Roughly speaking $(\partial n / \partial \mu)_\tau$ is how tighter the particles pack if you shove them in harder.

The pressure of a gas is related to its chemical potential; both measure how much particles want to leave the system. The compressibility measures (the inverse of) how much the pressure goes up when a gas is compressed into a smaller volume. A gas being compressed from volume $V + \Delta V$ into the volume V is the same as adding particles that were in ΔV into V . Hence, we see that the compressibility is related to the thermodynamic density of states which is (the inverse of) how much the chemical potential goes up when you put more particles into a smaller volume.

The answer to this part is inherently subjective. If you think yours was graded incorrectly please explain your thinking to me and I'll re-evaluate. Quinn.

b)

In general when we have a differential volume of matter that is in thermal (τ set by the reservoir), mechanical (p set by the reservoir), and chemical (μ set by the reservoir) equilibrium with its surroundings. We need to know **three** of the set $\{\mu, \tau, n, p\}$ in order to predict the fourth.

In most materials the density is uniform so that

$$\left(\frac{\partial N}{\partial V}\right)_{p,\tau} = \frac{N}{V}$$

When this is the case we may divide the system up into smaller systems which are all the same. Consider one such small volume in the middle of the original system. This small volume isn't directly affected by the location of the distant walls of the container. This means that $p = (\partial F / \partial V)_{\tau,N}$ doesn't directly affect this smaller volume but only affects it indirectly via μ . We may use the equation of state to relate μ, τ , and n for this small volume. This means that we only need **two** variables in order to get the others.

c)

i)

From above arguments

$$\left(\frac{\partial n}{\partial \mu}\right)_\tau = \left(\frac{\partial n}{\partial \mu}\right)_{\tau,N}$$

Using the chain rule for compressing the material we have

$$\begin{aligned} \left(\frac{\partial n}{\partial \mu}\right)_\tau &= \left(\frac{\partial n}{\partial V}\right)_{\tau,N} \left(\frac{\partial V}{\partial \mu}\right)_{\tau,N} \\ &= \left(\frac{\partial (N/V)}{\partial V}\right)_{\tau,N} \left(\frac{\partial V}{\partial \mu}\right)_{\tau,N} \\ &= -\frac{N}{V^2} \left(\frac{\partial V}{\partial \mu}\right)_{\tau,N} \\ &= -\frac{n}{V} \left(\frac{\partial V}{\partial \mu}\right)_{\tau,N} \end{aligned}$$

ii)

$$dF = -pdV - \sigma d\tau + \mu dN$$

$$\left(\frac{\partial}{\partial N}\right)_{\tau,V} \left(\frac{\partial}{\partial V}\right)_{\tau,N} F = \left(\frac{\partial}{\partial V}\right)_{\tau,N} \left(\frac{\partial}{\partial N}\right)_{\tau,V} F$$

$$\left(\frac{\partial}{\partial N}\right)_{\tau,V}(-p) = \left(\frac{\partial}{\partial V}\right)_{\tau,N}(\mu)$$

$$-\left(\frac{\partial N}{\partial p}\right)_{\tau,V} = \left(\frac{\partial V}{\partial \mu}\right)_{\tau,N}$$

iii)

By definition

$$\kappa_\tau = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_{\tau,N}$$

Noting that we have N constant and we want V constant instead we try the cyclic relation

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

And, as noted in part b)

$$\left(\frac{\partial N}{\partial V}\right)_{\tau,p} = \frac{N}{V}$$

so

$$\left(\frac{\partial V}{\partial p}\right)_{\tau,N} = -\frac{V}{N} \left(\frac{\partial N}{\partial p}\right)_{\tau,V}$$

substituting this into the definition of κ_τ

$$\kappa_\tau = \frac{1}{N} \left(\frac{\partial N}{\partial p}\right)_{\tau,V}$$

by the definition of n we have

$$\kappa_\tau n V = \left(\frac{\partial N}{\partial p}\right)_{\tau,V}$$

iv)

Combining iii) and ii) we have

$$\kappa_\tau n V = -\left(\frac{\partial V}{\partial \mu}\right)_{\tau,N}$$

now combining with i) we have

$$\left(\frac{\partial n}{\partial \mu}\right)_\tau = \kappa_\tau n^2 \tag{6}$$

Problem 7) Number Fluctuations and compressibility

a)

We define the Gibbs sum as the sum over all numbers of particles and states of the Boltzmann factor

$$\mathcal{Z} = \sum_{n,a.s.} e^{-\beta(E - N\mu)}$$

taking derivatives and multiply by temperature we can get

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln(\mathcal{Z})$$

$$\langle N^2 \rangle = \frac{1}{\beta^2} \frac{1}{\mathcal{Z}} \frac{\partial^2}{\partial \mu^2} \mathcal{Z}$$

With the variation defined as $(\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2$ we see that

$$(\Delta N)^2 = \frac{1}{\beta^2} \left(\frac{1}{\mathcal{Z}} \frac{\partial^2}{\partial \mu^2} \mathcal{Z} - \left(\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \mu} \mathcal{Z} \right)^2 \right) \quad (7)$$

This can be simplified to

$$(\Delta N)^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \ln(\mathcal{Z})$$

b)

The number density

$$n = \frac{\langle N \rangle}{V} = \frac{1}{V\beta} \frac{\partial}{\partial \mu} \ln(\mathcal{Z})$$

and it's derivative

$$\begin{aligned} \left(\frac{d\langle n \rangle}{d\mu} \right)_{\tau, V} &= \frac{1}{V} \left(\frac{d\langle N \rangle}{d\mu} \right)_{\tau, V} \\ &= \frac{1}{V} \frac{d}{d\mu} \left(\frac{1}{\beta} \frac{d}{d\mu} \ln(\mathcal{Z}) \right) \\ &= \frac{1}{V\beta} \frac{d}{d\mu} \left(\frac{1}{\mathcal{Z}} \frac{d}{d\mu} \mathcal{Z} \right) \\ &= \frac{1}{V\beta} \left(\frac{1}{\mathcal{Z}} \frac{d^2}{d\mu^2} \mathcal{Z} - \frac{1}{\mathcal{Z}^2} \left(\frac{d}{d\mu} \mathcal{Z} \right)^2 \right) \end{aligned}$$

comparing to 7 we have

$$\begin{aligned} (\Delta N)^2 &= \frac{V\beta}{\beta^2} \left(\frac{d\langle n \rangle}{d\mu} \right)_{\tau, V} \\ \Delta N &= \sqrt{\frac{V}{\beta} \left(\frac{d\langle n \rangle}{d\mu} \right)_{\tau, V}} \end{aligned}$$

c)

Noting that both β and $(d\langle n \rangle / d\mu)_{\tau, V}$ are intensive quantities we see that ΔN scales as \sqrt{V} . In other words

$$\frac{\Delta N}{N} = \frac{1}{\sqrt{N}} \sqrt{\frac{1}{\beta n} \left(\frac{d\langle n \rangle}{d\mu} \right)_{\tau, V}}$$

where the second square root is a proportionality constant independent of the size of the system. The relative fluctuations $\Delta N/N$ will approach zero as $1/\sqrt{N}$ as N gets large.

d)

Using equation 6

$$\begin{aligned} \left(\frac{\partial n}{\partial \mu} \right)_{\tau} &= \kappa_{\tau} n^2 \\ \frac{\Delta N}{N} &= \frac{1}{\sqrt{N}} \sqrt{\frac{\kappa_{\tau} n}{\beta}} \end{aligned} \quad (8)$$

or

$$\frac{\Delta N}{N} = \sqrt{\frac{\tau \kappa_{\tau}}{V}}$$

e)

By definition

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

for an ideal gas $pV = N\tau$ so

$$\kappa_\tau = -\frac{N\tau}{V} \left(\frac{\partial}{\partial p} p^{-1} \right)_{\tau, V}$$

$$\kappa_\tau = \frac{N\tau}{Vp^2}$$

$$\kappa_\tau = \frac{1}{p}$$

plugging this into 8 and using the equation of state $p = n\tau$ the number fluctuation simplifies to

$$\frac{\Delta N}{N} = \frac{1}{\sqrt{N}}$$

Note that this is a general result for systems of non-interacting particles, not just the ideal gas.

Problem 8) Sound Waves

a)

Let's apply $F = ma$ to the differential volume element of gas pictured

$$-A\Delta x \frac{\partial p}{\partial x} = \rho A\Delta x \frac{\partial}{\partial t^2} \xi$$

Where ρ is the density (I don't include variations in ρ in this equation as $\Delta\rho \ll \rho$). This simplifies to

$$-\frac{\partial p}{\partial x} = \rho \frac{\partial}{\partial t^2} \xi \quad (9)$$

Now let's express the relative change in volume

$$\frac{\Delta V}{V} = \frac{A\Delta\xi}{A\Delta x}$$

Because Δx is assumed to be small we can linearize it $\Delta\xi = \Delta x \frac{\partial \xi}{\partial x}$ to give

$$\frac{\Delta V}{V} = \frac{\partial \xi}{\partial x} \quad (10)$$

Now we take the definition of adiabatic compressibility (as described in the problem statement the compression is adiabatic so this will give us the relationship between dV and dp that we will use. We don't need to keep writing that σ is held constant.)

$$dp = -\frac{1}{\kappa_\sigma V} dV$$

if the changes in pressure/volume are small enough that $\kappa_p V$ are roughly constant (this is the small amplitude limit on the sound waves)

$$\Delta p = -\frac{1}{\kappa_\sigma V} \Delta V \quad (11)$$

Combining equations 11 and 10 we have

$$-\kappa_\sigma \Delta p = \frac{\partial \xi}{\partial x} \quad (12)$$

In order to get this into equation 9 we take $\partial/\partial x$ of 9 and recall that the order of differentiation doesn't matter

$$-\frac{\partial^2 p}{\partial x^2} = \rho \frac{\partial}{\partial t^2} \frac{\partial \xi}{\partial x}$$

$$\frac{\partial^2 p}{\partial x^2} = \rho \kappa_\sigma \frac{\partial}{\partial t^2} \Delta p$$

Now substituting in 12 and noting that the derivative of Δp is the same as the derivative of p we have

$$\frac{1}{\rho \kappa_\sigma} \frac{\partial^2 p}{\partial x^2} = \frac{\partial p}{\partial t^2} \quad (13)$$

b)

We showed in class that an ideal gas under reversible adiabatic compression satisfies

$$pV^\gamma = \text{const.} \quad (14)$$

where $\gamma = C_p/C_V$. We will show this again here, though it is not necessary for a complete solution. Adiabatic compression is defined as no heat flow. We can achieve a small adiabatic compression by combining a small constant pressure compression (a.k.a. cooling) followed by a constant volume heating that puts back in exactly as much heat that come out during the compression. The two heat capacities are defined as

$$C_p = \left(\frac{dQ}{dT} \right)_p, \quad \text{and} \quad C_V = \left(\frac{dQ}{dT} \right)_V$$

using the ideal gas law $pV = Nk_B T$

$$C_p = \frac{Nk_B}{p} \left(\frac{dQ}{dV} \right)_p, \quad \text{and} \quad C_V = \frac{Nk_B}{V} \left(\frac{dQ}{dp} \right)_V$$

To have a net heat flow of zero we have $(dQ)_P = -(dQ)_V$ which gives us

$$pC_p dV = -VC_V dp$$

$$\frac{C_p}{V} dV = -\frac{C_V}{p} dp$$

integrating both sides we have

$$\ln(V) C_P = -\ln(p) C_V + \text{const.}$$

Equation 14 follows as expected.

Now we would like to use equation 14 to find κ_σ . Differentiating it we find

$$V^\gamma dp + \gamma V^{\gamma-1} p dV = 0$$

$$-dp + \gamma V^{-1} p dV$$

$$-\frac{1}{V} \frac{dV}{dp} = \kappa_\sigma = \frac{1}{\gamma p} \quad (15)$$

c)

i)

From the wave equation 13 we have the velocity

$$u = \frac{1}{\sqrt{\rho \kappa_\sigma}}$$

Inserting the mas density $\rho = mN/V$ and equation 15 we have

$$u = \sqrt{\frac{VP\gamma}{mN}}$$

using the ideal gas law $PV = N\tau$

$$u = \sqrt{\frac{\tau\gamma}{m}} \quad (16)$$

ii)

To get the distribution for the x-component of the velocity write the Boltzmann factor (we can integrate out the other degrees of freedom as they are independent)

$$P_{v_x} \propto e^{-\beta E} = e^{-\beta m v^2 / 2}$$

the correct normalization is

$$P_{v_x} = \sqrt{\frac{\beta m}{2\pi}} e^{-\beta m v^2 / 2}$$

$$v_{x,rms} = \sqrt{\int dv_x P_{v_x} v_x^2}$$

we could do this integral or simply recall that the standard deviation of a normal distribution is its rms which is

$$v_{x,rms} = \frac{1}{\sqrt{\beta m}}$$

from equation 16 we have

$$u = v_{x,rms} \sqrt{\gamma} \tag{17}$$

d.

i)

When $T = 300\text{K}$ and $m = 28\text{g/mol}$ for nitrogen we have $v_{x,rms} \approx 298\text{m/s}$.

ii)

At room temperature there are three translation degrees of freedom and two rotational. By the equipartition theorem we have $C_V = \frac{5}{2} N k_B$. When heating at constant pressure an ideal gas does work on the surroundings to a tune of $p dV = N k_B T$ adding $N k_B$ to the heat capacity, $C_p = \frac{7}{2} N k_B$. Hence $\gamma = \frac{7}{5}$.

iii)

From equation 17 we have

$$u \approx 453\text{m/s}$$

The actual speed of sound in air is about 347m/s which is lower than our estimate because there is a significant amount of oxygen in the air as well which is heavier and therefore slower.