

PHYS 617 - Statistical Mechanics
A Modern Course in Statistical Physics by *Linda E. Reichl*
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Homework 3

Problem 1

- (a) Show that the ratio of specific heats in a gas can be determined by the slope of an isentropic path through (P, V) space:

$$\frac{C_P}{C_V} = - \left(\frac{\partial \ln(P)}{\partial \ln(V)} \right)_S.$$

You may assume a multiplicity factor $\Omega(E, V) \propto E^{\alpha N} V^N$.

- (b) Show generally that a gas with an adiabatic equation of state

$$P = (\gamma - 1) \frac{E}{V}$$

obeys a polytropic equation of state under adiabatic transformations (i.e. when entropy is kept fixed):

$$P = K n^\gamma,$$

where $n = N/V$ is the number density. Again, you may assume the system has multiplicity $\Omega \propto E^{\alpha N} V^N$, as above.

Proof. (a) We have

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V \quad \text{and} \quad C_P = \left(\frac{\partial Q}{\partial T} \right)_P.$$

Assuming that $\Omega \propto E^{\alpha N} V^N$, then

$$\ln(\Omega) = \alpha N \ln(E) + N \ln(V).$$

From that, we can find the following

$$\begin{aligned} \beta &= \left(\frac{\partial \ln(\Omega)}{\partial E} \right)_V = \frac{\alpha N}{E} \implies E = \alpha N k_B T = \alpha P V, \\ \beta P &= \left(\frac{\partial \ln(\Omega)}{\partial v} \right)_E = \frac{N}{V} \implies P V = N k_B T \implies T = \frac{P V}{N k_B}. \end{aligned}$$

The entropy of our system is given by

$$S = k_B \ln(\Omega) = \alpha N k_B \ln(E) + N k_B \ln(V). \tag{1}$$

Computing the differentials, we have

$$\begin{aligned} dE &= T dS - P dV \\ dQ &= T dS = dE + P dV \\ \implies \frac{dQ}{dT} &= \frac{\partial E}{\partial T} + P \frac{\partial V}{\partial T} \end{aligned}$$

Computing the heat capacities, we have

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial E}{\partial T} \right)_V = \alpha N k_B$$

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = \left(\frac{\partial E}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P = \alpha N k_B + P \frac{N k_B}{P} = (\alpha + 1) N k_B$$

The change in entropy dS is given by

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial E} \right) dE + \left(\frac{\partial S}{\partial V} \right) dV \\ &= \frac{\alpha N k_B}{E} dE + \frac{N k_B}{V} dV \\ &= \frac{\alpha N k_B}{E} \left(\left(\frac{\partial E}{\partial V} \right) dV + \left(\frac{\partial E}{\partial P} \right) dP \right) + \frac{N k_B}{V} dV \\ &= \frac{\alpha N k_B}{\alpha P V} (\alpha P dV + \alpha V dP) + \frac{N k_B}{V} dV \\ &= \frac{\alpha N k_B}{V} dV + \frac{\alpha N k_B}{P} dP + \frac{N k_B}{V} dV \\ &= \frac{(\alpha + 1) N k_B}{V} dV + \frac{\alpha N k_B}{P} dP. \end{aligned}$$

Since we are moving on an isentropic path, then the change in entropy is zero. Hence

$$\begin{aligned} dS = 0 &= \frac{(\alpha + 1) N k_B}{V} dV + \frac{\alpha N k_B}{P} dP \\ \implies \frac{dP}{P} &= -\frac{\alpha + 1}{\alpha} \frac{dV}{V} \\ d \ln(P) &= -\frac{\alpha + 1}{\alpha} d \ln(V) \\ \frac{d \ln(P)}{d \ln(V)} &= -\frac{\alpha + 1}{\alpha} = -\frac{C_P}{C_V}. \end{aligned}$$

(b) We are given an equation of state

$$P = (\gamma - 1) \frac{E}{V}.$$

Assuming that $\Omega \propto E^{\alpha N} V^N$, then

$$\ln(\Omega) = \alpha N \ln(E) + N \ln(V).$$

and we have

$$\begin{aligned} \beta &= \left(\frac{\partial \ln(\Omega)}{\partial E} \right)_V = \frac{\alpha N}{E} \implies E = \alpha N k_B T = \alpha P V, \\ \beta P &= \left(\frac{\partial \ln(\Omega)}{\partial v} \right)_E = \frac{N}{V} \implies P V = N k_B T \implies P = n k_B T. \end{aligned}$$

From the equation of state, we have

$$P V = (\gamma - 1) E = \frac{1}{\gamma} E \implies \gamma = \frac{\alpha + 1}{\alpha}.$$

The change in entropy dS is given by

$$\begin{aligned}
 dS &= \left(\frac{\partial S}{\partial E} \right) dE + \left(\frac{\partial S}{\partial V} \right) dV \\
 &= \frac{\alpha N k_B}{E} dE + \frac{N k_B}{V} dV \\
 &= \frac{\alpha N k_B}{E} \left(\left(\frac{\partial E}{\partial V} \right) dV + \left(\frac{\partial E}{\partial P} \right) dP \right) + \frac{N k_B}{V} dV \\
 &= \frac{\alpha N k_B}{\alpha P V} (\alpha P dV + \alpha V dP) + \frac{N k_B}{V} dV \\
 &= \frac{\alpha N k_B}{V} dV + \frac{\alpha N k_B}{P} dP + \frac{N k_B}{V} dV \\
 &= \frac{(\alpha + 1) N k_B}{V} dV + \frac{\alpha N k_B}{P} dP.
 \end{aligned}$$

Under adiabatic transformations, we have $dS = 0$, hence

$$\begin{aligned}
 dS &= 0 \\
 \frac{dP}{P} &= -\frac{\alpha + 1}{\alpha} \frac{dV}{V} \\
 \ln(P) &= -\frac{\alpha + 1}{\alpha} \ln(V) + \text{constant} \\
 PV^{\frac{\alpha + 1}{\alpha}} &= \text{constant} \\
 P \left(\frac{N}{n} \right)^{\frac{\alpha + 1}{\alpha}} &= \text{constant} \\
 P &= K n^\gamma,
 \end{aligned}$$

where $K = \text{constant}$. ■

Problem 2

Let's think about the atmosphere. Atoms are bound by gravity, but they still seem to float some distance above Earth (rather than all staying on the ground, at minimum energy). We can figure out the distribution of atoms with height, using the magic of estimation.

- (a) First, assume a given mean free path λ for molecules (assuming a single species with mass m) and assume the atmosphere is some fixed temperature T . Estimate the diffusion constant ν in the atmosphere.
- (b) Atoms are always trying to fall in earth's gravity but they keep having collisions. Estimate the time Δt between collisions.
- (c) In the time Δt , gravity can give molecules a net drift velocity $v_d \sim -g\Delta t$, before the molecule is scattered and its velocity is totally random again. So, there is a downward flux of atoms given by $F = nv_d$, where n is the number density. This is cancelled by an equal and opposite diffusive flux (computed from homework 1, remember?). In equilibrium, these fluxes cancel (so that $\dot{n} = 0$); set the fluxes to cancel and use this fact to compute $n(z)$, the number density in the atmosphere, as a function of z . (call n_0 the number density at the base of the Earth). Assume g is a constant (not dependent on z).

Proof. (a) The diffusion equation is given by

$$\frac{\partial \rho}{\partial t} = \nu \frac{\partial^2 \rho}{\partial x^2}.$$

We can say, by dimensional analysis, that

$$\frac{1}{\Delta t} \sim \frac{\nu}{\lambda^2} \implies \nu \sim \lambda v_0,$$

where $v_0 \equiv \frac{\lambda}{\Delta t}$.

We define the density as $\rho = \frac{M}{V} = \frac{Nm}{V}$. Since energy is conserved, then the kinetic energy of a group of particles is equal to their free energy. We have

$$\begin{aligned} \frac{Nm v_0^2}{2} &= \frac{5}{2} N k_B T \\ m v_0^2 &= 5 k_B T \\ v_0 &= \sqrt{\frac{5 k_B T}{m}} \\ v_0 &\sim \sqrt{\frac{k_B T}{m}} \\ \implies \nu &\sim \lambda v_0 \sim \lambda \sqrt{\frac{k_B T}{m}}. \end{aligned}$$

(b) From before, we have

$$\Delta t \sim \frac{\lambda}{v_0} \sim \lambda \sqrt{\frac{m}{k_B T}}.$$

(c) We are given a drift velocity $v_d \sim -g\Delta t$ and a downward flux of atoms $F = nv_d$, where n is the number density.

In equilibrium, we have another flux $J = \nu \frac{\partial n}{\partial z}$. The change in the number density as a function of

vertical height is the difference between both fluxes and should be zero. Then

$$\begin{aligned}\frac{\partial n}{\partial z} &= J - F = 0 \\ \Rightarrow \nu \frac{\partial n}{\partial z} - n v_d &= 0 \\ \nu \frac{\partial n}{\partial z} + n g \Delta t &= 0 \\ \frac{dn}{n} &= -\frac{g \Delta t}{\nu} dz \\ \ln \left(\frac{n}{n_0} \right) &= -\frac{mg}{k_B T} z \\ n(z) &= n_0 e^{-\frac{mgz}{k_B T}}.\end{aligned}$$

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Problem 3

- (a) Show that you can attain the results of problem (2c) by assuming that the chemical potential gets an external component

$$\mu = \mu_0(n, T) + \mu_{\text{ext}}(z),$$

where

$$\mu_{\text{ext}}(z) = mgz,$$

and assuming $\mu = \text{constant}$ in the atmosphere. Why would we add such a term to the chemical potential and why would we assume that μ is a constant throughout the atmosphere?

- (b) The atmosphere is roughly a 4-to-1 mixture Nitrogen and Oxygen. By what factor does the ratio n_{N_2}/n_{O_2} change when I go 10 km above the ground? You can assume the atmosphere has $T = 300$ Kelvin.

Proof. (a) The multiplicity of this system is given by

$$\Omega(E, V, N) = f(N) E^{\frac{3N}{2}} V^N,$$

where

$$f(N) = \left(\frac{2\pi m}{h^2} \right)^{\frac{3N}{2}} \frac{1}{N! \left(\frac{3N}{2} \right)!}.$$

Then, by taking the logarithm and deriving with respect to N , keeping E and V constant, we get the chemical potential given by

$$\beta \mu_0 = \left(\frac{\partial \ln(\Omega)}{\partial N} \right)_{E, V} = k_B T \ln(n),$$

where $n = \frac{N}{V}$ is the number density.

We have that

$$\begin{aligned}\mu &= \mu_0(n, T) + \mu_{\text{ext}}(z) \\ &= k_B T \ln(n) + f(T) + mgz \\ &= \text{const.}\end{aligned}$$

Since the chemical potential is constant throughout the atmosphere, then

$$\begin{aligned}\frac{d\mu}{dz} &= 0 \\ \frac{k_B T}{n} \frac{dn}{dz} + mg &= 0 \\ \frac{dn}{n} &= \frac{mg}{k_B T} dz \\ n(z) &= n_0 e^{\frac{mgz}{k_B T}}.\end{aligned}$$

(b) Given that the atmosphere is roughly a 4-to-1 mixture of Nitrogen and Oxygen, then

$$n_{\text{N}_2}(0) = 4n_{\text{O}_2}(0),$$

where $m_{\text{N}_2} = 28$ amu and $m_{\text{O}_2} = 32$ amu. Then

$$\begin{aligned}n_{\text{N}_2}(z) &= n_{\text{N}_2}(0) e^{-\frac{m_{\text{N}_2} gz}{k_B T}}, \\ n_{\text{O}_2}(z) &= n_{\text{O}_2}(0) e^{-\frac{m_{\text{O}_2} gz}{k_B T}}.\end{aligned}$$

Taking the ratio, we have

$$\frac{n_{\text{N}_2}(z)}{n_{\text{O}_2}(z)} = 4e^{-\frac{gz}{k_B T}(m_{\text{N}_2} - m_{\text{O}_2})}.$$

Going up 10 km, we get a change of

$$\frac{n_{\text{N}_2}(10)}{n_{\text{O}_2}(10)} = 4e^{-\frac{(9.81)(10)}{(1.38 \times 10^{-23})(300)}(28-32)1.67 \times 10^{-23}} = 4e^{\frac{4(9.81)(1.67)}{(1.38)(30)}} = 19.475.$$

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