

## 5500 Problem Set 2

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### Question I.

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Return to HW1 P4. What is the chemical potential of blackbody radiation, an ideal gas of “photons” in thermal equilibrium?

We can use Gibbs free energy:

$$G = U - TS + pV$$

From homework 1 question 4 we have:

$$\begin{aligned}\frac{U}{V} &= 3p \\ pV &= \frac{U}{3} \\ G &= \frac{4}{3}U - TS\end{aligned}$$

We also have the relation:

$$\mu = \frac{G}{N}$$

All we need to find is  $S$ :

$$\begin{aligned}S &= \int dS \\ &= \int \frac{dU}{T} + \frac{p}{T} dV \\ U &= aVT^4 \\ dU &= aT^4 dV + 4aVT^3 dT \\ S &= \int \int aT^3 dV + 4aVT dT + \frac{1}{3}aT dV \\ &= \int \frac{4}{3}aT^3 + 4aVT^2 dT \\ &= \int d\left(\frac{4}{3}aVT^3\right) \\ S &= \frac{4}{3}aVT^3 \\ &= \frac{4}{3}U\end{aligned}$$

Putting it all together we have

$$\begin{aligned} G &= \frac{4}{3}U - \frac{4}{3}U \\ &= 0 \end{aligned}$$

From this we get the chemical potential  $\mu = 0$

## Question II.

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Show that  $C_p/C_V = \kappa_T/\kappa_S$ .

The heat capacities at constant volume and constant pressure are defined as such:

$$\begin{aligned} C_V &= \left( \frac{\partial Q}{\partial T} \right)_V \\ &= T \left( \frac{\partial S}{\partial T} \right)_V \\ C_p &= T \left( \frac{\partial S}{\partial T} \right)_p \\ &= \left( \frac{\partial H}{\partial T} \right)_p \end{aligned}$$

We also define the compressibilities to be

$$\begin{aligned} \kappa_T &= -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \\ \kappa_S &= -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S \end{aligned}$$

With some abuse of the triple product rule we get

$$\begin{aligned} \frac{C_p}{C_V} &= \frac{\kappa_T}{\kappa_S} \\ \frac{\left( \frac{\partial T}{\partial V} \right)_S \left( \frac{\partial V}{\partial S} \right)_T}{\left( \frac{\partial T}{\partial P} \right)_S \left( \frac{\partial P}{\partial S} \right)_T} &= \frac{\left( \frac{\partial P}{\partial S} \right)_V \left( \frac{\partial S}{\partial V} \right)_P}{\left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_P} \end{aligned}$$

If we now abuse some Maxwell relations we find this becomes

$$\frac{\left( \frac{\partial P}{\partial S} \right)_V \left( \frac{\partial S}{\partial V} \right)_P}{\left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial V} \right)_P} = \frac{\left( \frac{\partial P}{\partial S} \right)_V \left( \frac{\partial T}{\partial P} \right)_V}{\left( \frac{\partial V}{\partial S} \right)_P \left( \frac{\partial T}{\partial V} \right)_P}$$

Which, when rearranged, are equivalent.

## Question III.

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- (a) Suppose that in a gas-liquid phase transition the latent heat is a once-and-for-all constant, that the volume of the liquid is negligible compared to the volume of the gas, and that the gas may be assumed ideal. Find the liquid-gas coexistence curve.

Let us solve the Clausius-Clapeyron relation where  $\Delta V = v_{gas} = NkT/p$  and  $\Delta q$  is a constant equal to the latent heat.

$$\begin{aligned}\frac{dp}{dT} &= \frac{\Delta q}{Nk} \frac{p}{T^2} \\ \frac{dp}{p} &= \frac{\Delta q}{Nk} \frac{dT}{T^2} \\ \ln(p - p_0) &= \frac{\Delta q}{Nk} \frac{-1}{2T}\end{aligned}$$

The solution of this has the functional form  $p(T) \propto e^{\frac{\alpha}{T}}$  where  $\alpha = \frac{\Delta q}{Nk}$ .

- (b) Find vapor pressure data for water as a function of temperature from, say, <https://webbook.nist.gov/chemistry/fluid>.

How good is the functional form found in part (a)? The latent heat at the usual boiling point of water is  $2.26 \times 10^6$  J/kg.

The functional form in part a has behavior dominated by the large latent heat at low temperatures and goes like  $e^{1/x}$  at higher temperatures, which is demonstrated by this curve.

#### Question IV.

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Local-density approximation. When a gas is subject to an external potential energy (per particle)  $\Phi(\vec{r})$ , it may happen that the potential varies little over the length scale over which the gas can find an equilibrium, and so the gas may be taken to behave locally as if there were no confining potential at all. It simply has some equilibrium properties that vary as a function of position. Assume in this question that the temperature is a constant across the gas. There is no point in keeping track of the exact temperature dependences.

- (a) Sketch a local equilibrium argument showing that the equilibrium condition is  $\mu(\vec{r}) + \Phi(\vec{r}) = \text{constant}$ . HINT: The external potential creates forces on the molecules, so this really is a question of mechanical equilibrium between the forces from (the gradient of the) pressure and from the potential.

See Figure 1. The state is in equilibrium where the sum of the gradients is zero, so the sum of the potentials is a constant.

- (b) Find the chemical potential for an ideal gas. In a form of what is known as Gibbs paradox, you may meet with thermodynamic quantities that are neither extensive nor intensive. As is discussed later, the cure is to subtract  $kN \ln N$  from entropy; do it if you want to, but do not get hung up on this.

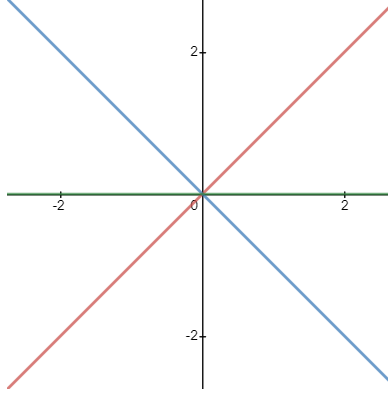


Figure 1: For Problem 4a. The orange and blue represent example potentials and the green represents a sum of the two. The state is in equilibrium where the sum of the gradients is zero, so the sum of the potentials is a constant.

We know from the Gibbs free energy that

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V}$$

We also know that the entropy of an ideal gas is

$$S = Nk \left[ \ln \left( \frac{V}{N} \left( \frac{2\pi m U}{3N\hbar^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

So we get

$$\mu = -kT \ln \left( \frac{V}{N} \left( \frac{2\pi m U}{3N\hbar^2} \right)^{3/2} \right)$$

- (c) Suppose the atmosphere is made of molecules of mass  $m$ , and is at constant temperature (not even close...). How would the pressure vary as a function of height?

This changes only the  $U$  in the expression for entropy which now becomes

$$S = Nk \left[ \ln \left( \frac{V}{N} \left( \frac{2\pi m (U - Nmgz)}{3N\hbar^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

and gives us the simple addition to the chemical potential

$$\mu = -kT \ln \left( \frac{V}{N} \left( \frac{2\pi m U}{3N\hbar^2} \right)^{3/2} \right) + mgz$$