

PHY 831: Statistical Mechanics

Homework 1

Due Friday September 17th, 2021

1. In this problem, you will prove the equivalence of the ideal gas temperature scale Θ and the thermodynamic temperature scale T defined in class via Carnot engine efficiencies. To do this, consider a Carnot cycle that utilizes an ideal gas as its working substance. It might help to refresh your memory and look at a PV diagram of an ideal gas Carnot cycle, such as Fig. 1 on the Wikipedia page for the Carnot cycle. You can assume that $PV = Nk_B\Theta$, and that $E = E(\Theta)$, but with no assumptions made on the functional form.
 - (a) Explicitly calculate the heat exchanges Q_H and Q_C as a function of Θ_H , Θ_C , and the volume expansion factors.
 - (b) Calculate the volume expansion factor in an adiabatic process as a function of Θ .
 - (c) Show that $\eta = W/Q_H = 1 - Q_C/Q_H = 1 - \Theta_C/\Theta_H$, thereby proving that the ideal gas temperature scale Θ is the same as the thermodynamic scale T introduced in our class discussion of Carnot engines.
2. In class, we used Joule's experiment of the free expansion of an ideal gas in an adiabatically isolated container to argue that $E = E(T)$ ¹. Here we will reach the same conclusion using a more theoretical approach.
 - (a) Use the 1st Law to show that one can express the differential dQ as

$$dQ = C_V dT + \left[\left(\frac{\partial E}{\partial V} \right)_{T,N} + P \right] dV$$

- (b) Use the 2nd Law to convert this into an expression for dS . Then use that dS is an exact differential (hint: a quick check of Wikipedia might be useful if you don't recall the mathematical condition for a differential to be "exact"), together with the definition $C_V = \left(\frac{\partial E}{\partial T} \right)_{V,N}$ to derive

$$\left(\frac{\partial E}{\partial V} \right)_{T,N} = T \left(\frac{\partial P}{\partial T} \right)_{V,N} - P$$

- (c) Lastly, use the ideal gas equation $PV = Nk_B T$ to show that $E = E(T, N)$.

¹To be more precise, we really should write $E = E(T, N)$. But for problems where there are no chemical reactions going on or multiple coexisting phases, we can be sloppy about writing the explicit N dependence.

3. Derive the Maxwell relations

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

and

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

4. A substance has the following properties:

- (a) At constant temperature T_0 the work done by it expanding from V_0 to V is

$$W = T_0 \ln \frac{V}{V_0} \quad (1)$$

- (b) The entropy of the substance is give by

$$S = \frac{V}{V_0} \left(\frac{T}{T_0}\right)^a \quad (2)$$

where V_0 , T_0 , and a are fixed constants.

- (a) Calculate the Helmholtz free energy (relative to the Helmholtz free energy at (V_0, T_0)).
- (b) Find the equation of state.
- (c) Find the work done by an arbitrary expansion at an arbitrary constant temperature.