



Problem Set 05

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Quantum Statistics

1. Show that Liouville's theorem,

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$$

is equivalent to the statement

$$\frac{d\rho}{dt} = 0.$$

What is the physical interpretation of this ? [**Hint:** $\rho = \rho(q, p, t)$]

2. Given the time evolution of the density operator

$$\hat{\rho}(t) = e^{-i\hat{H}t/\hbar} \hat{\rho}(0) e^{i\hat{H}t/\hbar}$$

show that it leads to quantum version of Liouville's theorem

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} + [\hat{\rho}, \hat{H}] = 0$$

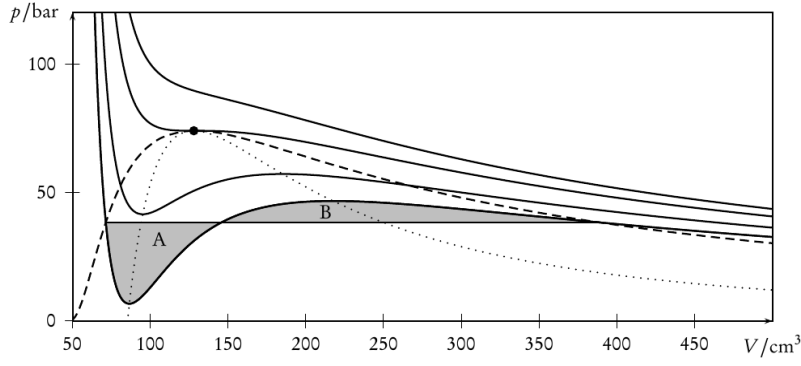
provided, Hamiltonian does not depend on time *explicitly*.

3. Calculate the average energy of a free quantum mechanical particle following the density matrix formalism in canonical ensemble. [**Hint:** $\langle \hat{f} \rangle = \text{Tr}(\hat{\rho} \hat{f})$; $\hat{\rho} = e^{-\beta \hat{H}}/Z$.]

Phenomenology of real gases

1. In modelling the interaction between the molecules of a real gas, can the attractive part of the potential be taken as Coulomb potential ($\sim 1/r$) ? [**Hint:** Check the evaluation of $A(T) = \int_0^\infty d^3r (e^{-\beta U(r)} - 1)$.]
2. **Effective volume in a real gas:** In our derivation of equation of state for a real gas, the effective excluded volume per molecule should be $v_{\text{eff}} = \frac{4}{3}\pi r_0^3 = 2b$, where r_0 is the distance of closest approach between two molecules. However, we got the volume correction per molecule as $(v - b)$. How can we explain this apparent discrepancy ? [**Hint:** $\int d^3N q \sim (V - v_{\text{eff}})(V - 2v_{\text{eff}})(V - 3v_{\text{eff}}) \dots (V - Nv_{\text{eff}})$ and use $v_{\text{eff}} \ll V/N$.]
3. Show that the critical parameters of van der Waals gas satisfy,

$$P_c V_c = \frac{3}{8} k_B T_c.$$



Slika 1: Isotherms of a real gas. The dashed curve is called the liquid-gas co-existence curve. Under this curve the liquid and gas phases co-exist in equilibrium.

4. **Virial Expansion:** A real gas can be also be modelled as corrections to ideal gas law via power series expansion in terms of number density. In particular,

$$\frac{P}{k_B T} = \left(\frac{N}{V}\right) + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + \dots$$

where, $B_i(T)$ are called Virial coefficients. Calculate the second Virial coefficient $B_2(T)$ for van der Waals equation at critical temperature.

5. **The law of corresponding states:** In van der Waals equation of state, the parameters a and b are the characteristics of the gas. Show that the van der Waals equation of state can be expressed as,

$$\left(P_r + \frac{3}{v_r^2}\right)\left(v_r - \frac{1}{3}\right) = \frac{8}{3}T_r,$$

where, $P_r = P/P_c$, $v_r = v/v_c$ and $T_r = T/T_c$ are called reduced variables. The critical parameters for different gases are different, however, their phase diagram plotted using reduced variables are expected to be the same.

6. Show that the isothermal compressibility of a van der Waals gas at critical volume is given by,

$$k_T|_{v=v_c} = \frac{4b}{3k_B}(T - T_c)^{-1}.$$

7. Show that the condition for co-existence of liquid and gas phases implies that the grey regions **A** and **B** in Fig. 1 have equal area.
8. Show that the continuity of Gibbs free energy $G = U - TS + PV$ across the co-existence curve between liquid-gas phases leads to,

$$\frac{dP}{dT} = \frac{L}{T(V_{\text{gas}} - V_{\text{liquid}})}$$

where, the quantity $L = T\Delta S$ is defined as the latent heat released in phase transition. The above equations is known as **Clausius-Clapeyron equation**.

9. According to Ehrenfest, in an n^{th} order phase transition, the n^{th} derivative of a thermodynamic potential is discontinuous. Argue that the liquid-gas transition is an example of first order phase transition.