

Physics 136, Caltech: Applications of Classical Physics — Fall Term, 2006
Assignment 4

Reading

Chapter 4 of Blanford and Thorne. You can find some notes of mine on the renormalization group at <http://www.its.caltech.edu/mcc/Ph127/b/Lecture10.pdf>.

Problems (due in class, 1pm Wednesday October 25)

Numbers refer to exercises in Blanford and Thorne, as posted on website.

A. Exercise 4.1: *Pressure Measuring Device*

Since the answer Eq. (4.5) might seem more fundamental than the starting point, maybe a better way to word the questions is to show that the constant P introduced as the multiplier of the volume in the “supercanonical” distribution Eq. (3.20) or the Gibbs ensemble distribution Eq. (3.23) is given by Eq. (4.5) and so we identify it as the pressure.

B. Do either of the following:

1. Exercise 4.3: *Enthalpy Representation for Thermodynamics* (Part (e) should refer to Exercise 1.24)
2. *Thermodynamic manipulations:* Consider the cooling produced by various schemes of expanding a *non-ideal gas*. We want to relate the cooling rate to familiar thermodynamic quantities.

- (a) A gas is confined in one fraction (of volume V) of a container isolated from the surroundings, with the other fraction (of volume ΔV) containing a vacuum. It is now allowed to expand into the whole container. We want to calculate the change in temperature ΔT for small ΔV

$$\frac{\Delta T}{\Delta V} \simeq \frac{dT}{dV}. \quad (1)$$

Identify what should be held constant in this derivative, and hence show

$$\frac{\Delta T}{\Delta V} \simeq -\frac{T^2}{C_V} \frac{\partial}{\partial T} \left(\frac{P}{T} \right)_V \quad (2)$$

where $P = P(T, V)$ is the equation of state for the gas, and C_V is the specific heat at constant volume.

- (b) A thermally isolated gas is expanded reversibly from volume V to $V + \Delta V$ (i.e., by slowly allowing a piston to expand driven by the pressure of the gas). Again identify what is held constant, and show that in this case

$$\frac{\Delta T}{\Delta V} \simeq -\frac{T}{C_V} \left(\frac{\partial P}{\partial T} \right)_V. \quad (3)$$

- (c) A gas is forced through a porous plug reversibly and thermally isolated from the surroundings. The pressure on one side of the plug is P and on the other side is $P + \Delta P$. Argue that in this case the enthalpy per particle $h = H/N$ is constant and so the temperature change is

$$\frac{\Delta T}{\Delta P} \simeq \left(\frac{\partial T}{\partial P} \right)_h = \frac{V}{C_P} (T\alpha_P - 1), \quad (4)$$

with C_P the specific heat at constant pressure and α_P the constant-pressure coefficient of expansion.

Hint: The scheme is to use the reciprocity identity (see Box 4.1 in the text)

$$\left(\frac{\partial T}{\partial V}\right)_X = -\frac{\left(\frac{\partial X}{\partial V}\right)_T}{\left(\frac{\partial X}{\partial T}\right)_V} \quad (5)$$

(or the similar one for the pressure derivative) and then to manipulate the derivatives appearing on the right hand side starting from the thermodynamic identity

$$dX = \dots, \quad (6)$$

and/or use Maxwell identities. In these expressions X is the thermodynamic potential that is constant in the expansion.

C. Do one of the following two exercises:

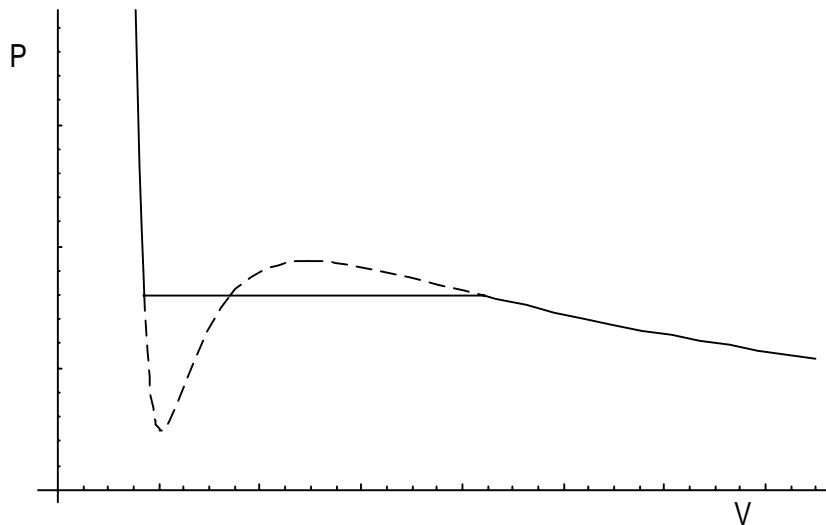
1. Exercise 4.6 *Saha Equation for Ionization Equilibrium* (I sketched this one in class in a non-relativistic formulation; you should work it for the relativistic formulation as posed in the question)
2. Exercise 4.5 *Electron-Positron Equilibrium at “Low” Temperatures*

D. Do either:

1. Exercise 4.4 *Latent Heat and Clausius Clapeyron Equation*, or
2. Exercise 4.9 *One Dimensional Ising Lattice*

E. *Liquid-Gas Transition in a Van der Waals Gas*

The figure shows a PV isotherm calculated for the Van der Waals approximation modelling a non-ideal gas. The Van der Waals equation gives the smooth curve. However stability arguments tell us that for the physical isotherm the dashed part of the curve must be replaced by the horizontal (constant pressure) line at some pressure P_M . But where to draw the line?



The expression for the Helmholtz free-energy of the Van der Waals gas is

$$F(T, V, N) = F_{ideal}(T, V, N) - Nk_B T \ln(1 - Nb/V) - N^2 a/V. \quad (7)$$

with F_{ideal} the ideal gas expression. The second term is the change in entropy because of the volume excluded by the repulsive cores of the atoms and the third term is the change in energy from the attractive interaction at larger separations.

- (a) Show that this leads to the Van der Waals equation of state

$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = Nk_B T. \quad (8)$$

- (b) Show that below some critical temperature T_{crit} the isotherm has the form shown in the figure, with a minimum and a maximum for $P(V)$, and three solutions for $V(P)$ over a range of pressures. Find T_{crit} .
- (c) Consider the following argument for the *convexity* of the Helmholtz free energy $F(V)$ as a function of volume (for some fixed number of particles N and temperature T). A macroscopic system is in contact with a heat bath at temperature T . A movable partition is now added to divide the system into two identical halves, each of volume V . Show that the condition for the stability of the uniform state towards relocating the partition requires

$$F(V + \Delta V) + F(V - \Delta V) \geq F(V) \quad (9)$$

for any ΔV (not necessarily small). Interpret this condition geometrically for the curve $F(V)$. For infinitesimal ΔV this leads to a condition on the second derivative. Derive this condition and interpret it in terms of familiar thermodynamic variables. (Note: the second derivative may not be defined everywhere, and we then return to the more general expression.)

- (d) Sketch the volume dependence of the Helmholtz free energy $F(V)$ for the a Van der Waals isotherm below the critical temperature. You may use Eq. (7) and a plotting program, or sketch the curve from the given $P - V$ figure and the relationship between $F(V)$ and $P(V)$. Now add to your sketch the physical curve for $F(V)$ satisfying the convexity requirement. Note that the constant- P portion of the physical $P - V$ isotherm corresponds to a straight line portion of $F(V)$.
- (e) Describe the physical state of the system for each portion of the physical isotherm?
- (f) The convexity requirement fixes where to draw the flat portion of the PV isotherm. To derive this it is useful to make a Legendre transformation to the Gibbs free energy $G(P, T, N) = F + PV$. Use the “slope-intercept” interpretation of this transformation (i.e. $-P$ is the slope of the tangent to $F(V)$ at V) and $G(P)$ is the intercept of the tangent on the F axis) to sketch $G(P)$ for the both the Van der Waals and the physical $F(V)$ curves. Use the form of $G(P)$ and the thermodynamic identity for G to derive the Maxwell “equal-area” construction for P_M (namely, P_M is chosen so that the area of the dashed curve above the P_M line is equal in magnitude to the area of the dashed curve under the line).