

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Physics Department

8.044 Statistical Physics I

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**Solutions to Problem Set #4**

**Problem 1:** Thermal Equilibrium and the Concept of Temperature, I

a) Solve each of the two given equations for  $P''$ .

$$P'' = \frac{P(V - nb)}{V''} \qquad P'' = \frac{P'V'}{V''(1 - nB'/V')}$$

Equate these two and factor out  $1/V''$ .

$$P(V - nb) = \frac{P'V'}{1 - nB'/V'} = \begin{array}{l} \text{some constant,} \\ \text{call it } t \end{array}$$

Substitution of this result into the first equation gives  $P''V'' = t$ , allowing us to find the functional form for the temperature in each of the three systems.

$$P''V'' = t \qquad \text{for an ideal gas}$$

$$\frac{P'V'}{1 - nB'/V'} = t \qquad \text{for another non-ideal gas}$$

$$P(V - nb) = t \qquad \text{for one non-ideal gas}$$

b) To find the relation expressing thermal equilibrium between system A and system B we simply equate the two expressions for a common empiric temperature.

$$P(V - nb) = t = \frac{P'V'}{1 - nB'/V'}$$

$$\Rightarrow P(V - nb)(1 - nB'/V') - P'V' = 0$$

**Problem 2:** Thermal Equilibrium and the Concept of Temperature, II

a) Solve each equation for  $V$ .

$$V = \left(\frac{nR}{P}\right)\left(\frac{cH}{M}\right) \qquad V = \left(\frac{nR}{P}\right)\left(\Theta + \frac{c'H'}{M'}\right)$$

Equate these two and factor out  $nR/P$ .

$$\frac{cH}{M} = \Theta + \frac{c'H'}{M'} = \begin{array}{l} \text{some constant,} \\ \text{call it } h \end{array}$$

Substitution into the first equation gives  $PV/nR = h$ , so at equilibrium

$$\frac{PV}{nR} = \frac{cH}{M} = \Theta + \frac{c'H'}{M'}$$

b)  $PV/nR = h$  looks like the ideal gas law with  $h \rightarrow T$ , so call  $h \equiv T$  and thus find the following equations of state.

$$PV = nRT \quad \text{for an ideal gas}$$

$$M = c \frac{H}{T} \quad \text{for a Curie Law Paramagnet}$$

$$M' = c' \frac{H'}{T - \Theta} \quad \begin{array}{l} \text{Paramagnet with ordering} \\ \text{phase transition to a} \\ \text{ferromagnet at } t = \Theta \end{array}$$

### Problem 3: Work in a Simple Solid

Substitute the given model expression relating volume changes to changes in the pressure and the temperature,  $dV = -V\mathcal{K}_T dP + V\alpha dT$ , into the differential for work. As a simplification we are told to replace the actual volume  $V$  by its value at the starting point  $V_1$  in the coefficients entering the differential for the work. Of course the volume itself can not really remain constant, for in that case  $\delta W = -P dV = 0$ .

$$\delta W = -P dV = \mathcal{K}_T P V_1 dP - \alpha P V_1 dT$$

Along path “a”

$$\begin{aligned} W_{1 \rightarrow 2} &= \int_{\text{where } dP=0} \delta W + \int_{\text{where } dT=0} \delta W \\ &= -\alpha P_1 V_1 \int_1^2 dT + \mathcal{K}_T V_1 \int_1^2 P dP \\ &= \underline{\underline{-\alpha P_1 V_1 (T_2 - T_1) + \frac{1}{2} \mathcal{K}_T (P_2^2 - P_1^2) V_1}} \end{aligned}$$

Along path “b”

$$\begin{aligned}
 W_{1 \rightarrow 2} &= \int_{\text{where } dT=0} \not{d}W + \int_{\text{where } dP=0} \not{d}W \\
 &= \mathcal{K}_T V_1 \int_1^2 P dP - \alpha P_2 V_1 \int_1^2 dT \\
 &= \underline{\underline{\frac{1}{2} \mathcal{K}_T (P_2^2 - P_1^2) V_1 - \alpha P_2 V_1 (T_2 - T_1)}}
 \end{aligned}$$

Along “c”  $dT$  and  $dP$  are related at every point along the path,

$$dT = \frac{T_2 - T_1}{P_2 - P_1} dP,$$

so the expression for the differential of work can be written as

$$\begin{aligned}
 \not{d}W &= \mathcal{K}_T P V_1 dP - \alpha P V_1 \left( \frac{T_2 - T_1}{P_2 - P_1} \right) dP \\
 &= \left( \mathcal{K}_T V_1 - \alpha V_1 \frac{T_2 - T_1}{P_2 - P_1} \right) P dP
 \end{aligned}$$

Now we can carry out the integral along the path.

$$\begin{aligned}
 W_{1 \rightarrow 2} &= \left( \mathcal{K}_T V_1 - \alpha V_1 \frac{T_2 - T_1}{P_2 - P_1} \right) \underbrace{\int_1^2 P dP}_{\frac{1}{2}(P_2^2 - P_1^2) = \frac{1}{2}(P_1 + P_2)(P_2 - P_1)} \\
 &= \underline{\underline{\frac{1}{2} \mathcal{K}_T (P_2^2 - P_1^2) V_1 - \frac{1}{2} \alpha (P_1 + P_2) (T_2 - T_1) V_1}}
 \end{aligned}$$

Note that the work done along each path is different due to the different contributions from the  $\alpha$  (thermal expansion) term. Path “b” requires the least work; path “a” requires the most.

**Problem 4: Work in a Non-Ideal Gas**

Often it is best to work with the given differential in the work term if at all possible, rather than expanding the differential in terms of the other variables as was done in Problem 3. The form of the differential,  $\delta W = -P dV$ , indicates that we should try to find  $P$  as a function of  $V$  so that the integration can be carried out simply.

$$(P + \frac{a}{V^2})(V - b) = NkT \quad \Rightarrow \quad P = \frac{NkT}{V - b} - \frac{a}{V^2}$$

Now we can carry out the integration to find the total work done along the path.

$$\begin{aligned} W_{1 \rightarrow 2} &= \int_1^2 \left[ -\frac{NkT}{V - b} + \frac{a}{V^2} \right] dV \\ &= NkT \left[ -\ln(V - b) \right]_1^2 + \left[ -\frac{a}{V} \right]_1^2 \\ &= -NkT \ln\left(\frac{V_2 - b}{V_1 - b}\right) - \left(\frac{a}{V_2} - \frac{a}{V_1}\right) \\ &= \underline{NkT \ln\left(\frac{V_1 - b}{V_2 - b}\right) - \left(\frac{a}{V_2} - \frac{a}{V_1}\right)} \end{aligned}$$

We are given that  $V_2 < V_1$ . The equation of state used in the problem is known as the Van der Waals equation. In it the parameter  $b$  is thought of as a small correction to the total volume  $V$  due to the volume taken up by the other atoms and  $a/V^2$  is a small correction to the pressure due to the weak attraction between the atoms at large distances (the Van der Waals attraction). Thus in the above expression the logarithm term is positive and the term after the minus sign is also positive.

**Problem 5: Work and the Radiation Field**

The differential of work is  $\delta W = -P dV$  as in the previous problem and one immediately thinks about trying to express  $P$  in terms of  $V$  in order to simplify the integral. However, along path “a” this is not necessary: along one part  $dV = 0$  and along the other the temperature, and hence the pressure, is a constant.

$$\begin{aligned} W_{1 \rightarrow 2} &= \int_1^2 \underbrace{T \text{ constant}}_0 P dV - \int_1^2 \underbrace{V \text{ constant}}_0 P dV \\ &= -\frac{1}{3}\sigma T_1^4 \int_1^2 dV = -\frac{1}{3}\sigma T_1^4 (V_2 - V_1) \\ &= \underline{\frac{1}{3}\sigma T_1^4 V_2 \left(\frac{V_1}{V_2} - 1\right)} \end{aligned}$$

Since the figure in the problem indicates that  $V_1 > V_2$ , the underlined result is positive.

Along path “b” there are no shortcuts and we must prepare to carry out the integral. Since  $\delta W$  is expressed in terms of  $dV$ , we convert the  $T$  dependence of  $P$  into a function of  $V$ .

$$VT^3 = \text{a constant} \equiv V_1 T_1^3$$

$$T = \left(\frac{V_1}{V}\right)^{1/3} T_1$$

$$T^4 = T_1^4 \left(\frac{V_1}{V}\right)^{4/3} = T_1^4 \left(\frac{V}{V_1}\right)^{-4/3}$$

Now we can carry out the integral over the path to obtain the total work done.

$$\begin{aligned} W_{1 \rightarrow 2} &= - \int_1^2 P dV = -\frac{1}{3}\sigma \int_1^2 T^4(V) dV \\ &= -\frac{1}{3}\sigma T_1^4 \int_1^2 \left(\frac{V}{V_1}\right)^{-4/3} dV \\ &= -\frac{1}{3}\sigma T_1^4 V_1 \left[ -\frac{1}{1/3} \left(\frac{V}{V_1}\right)^{-1/3} \right]_1^2 \\ &= \sigma T_1^4 V_1 \left( \left(\frac{V_2}{V_1}\right)^{-1/3} - 1 \right) \\ &= \underline{\sigma T_1^4 V_1 \left( \left(\frac{V_1}{V_2}\right)^{1/3} - 1 \right)} \end{aligned}$$

Since  $V_1 > V_2$ , this quantity is also positive.