MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Physics Department

8.044 Statistical Physics I — Spring Term 2013

Solutions to Problem Set #6

Problem 1: Sound Waves in a Solid

We need to find $(\partial T/\partial P)_{\Delta Q=0}$. To do this we will use in sequence the first law, the energy derivative given in the statement of the problem, and the chain rule for partial derivatives.

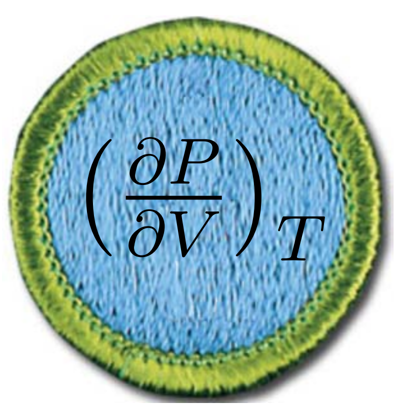
$$
\begin{aligned}
đQ &= dU - đW = dU + PdV \\
&= \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]}_{A} dV = 0 \\
A &= T\left(\frac{\partial P}{\partial T}\right)_V = T\,\frac{-1}{\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T} = T\,\frac{\left(\frac{\partial V}{\partial T}\right)_P}{-\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha T}{\kappa_T} \\
0 &= C_V\,dT + \frac{\alpha T}{\kappa_T}\,dV
\end{aligned}
$$

Now express dV in terms of dT and dP,

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = \alpha V_0\,dT - \kappa_T V_0\,dP$$

and substitute in to the adiabatic condition

$$
\begin{aligned}
0 &= C_V\,dT + \frac{\alpha T}{\kappa_T}\left(\alpha V_0\,dT - \kappa_T V_0\,dP\right) \\
\alpha T V_0\,dP &= \left(C_V + \frac{\alpha^2 T V_0}{\kappa_T}\right) dT \\
\frac{\Delta T}{\Delta P} &= \frac{\alpha T}{\left(\frac{C_V}{V_0}\right) + \left(\frac{\alpha^2 T}{\kappa_T}\right)}
\end{aligned}
$$



Problem 2: Energy of a Film

a) The best approach to take here is to find a general expression for C_A and then show that its derivative with respect to A is zero.

$$\begin{aligned}
C_A &\equiv \left.\frac{đQ}{dT}\right|_A \\
&= T\left(\frac{\partial S}{\partial T}\right)_A && \text{by the second law} \\
\left(\frac{\partial C_A}{\partial A}\right)_T &= T\frac{\partial^2 S}{\partial A \partial T} \\
&= T\frac{\partial}{\partial T}\left(\left(\frac{\partial S}{\partial A}\right)_T\right)_A && \text{interchanging order of the derivatives}
\end{aligned}$$

We use a Maxwell relation to find $(\partial S/\partial A)_T$. Note that S and $\mathcal{S}$ are different variables. I would normally construct a magic square to find the equivalent derivatives, but for clarity I will go through the more fundamental route here.

$$\begin{aligned}
dE &= T\,dS + \mathcal{S}\,dA \\
dF &= dE - d(TS) = -S\,dT + \mathcal{S}\,dA
\end{aligned}$$

Since F is a state function, the cross derivatives must be equal.

$$-\left(\frac{\partial S}{\partial A}\right)_T = \left(\frac{\partial \mathcal{S}}{\partial T}\right)_A = -\frac{Nk}{A-b}$$

Substitute this result into the expression for the derivative of the heat capacity.

$$\left(\frac{\partial C_A}{\partial A}\right)_T = T\frac{\partial}{\partial T}\left(\frac{Nk}{A-b}\right)_A = 0$$

This shows that the heat capacity at constant area does not depend on the area: $C_A(T, A) = C_A(T)$.

b) Now we find the exact differential for the energy and integrate up.

$$
\begin{aligned}
dE &= T\,dS + \mathcal{S}\,dA \\
&= \underbrace{T\left(\frac{\partial S}{\partial T}\right)_A}_{C_A(T)} dT + \underbrace{\left(T\left(\frac{\partial S}{\partial A}\right)_T + \mathcal{S}\right)}_{-\frac{NkT}{A-b} + \mathcal{S} = 0} dA \\
&\Rightarrow \left(\frac{\partial E}{\partial A}\right)_T = 0 \\
E(T,A) &= E(T) \\
&= \underline{\int_0^T C_A(T')\,dT' + E(T=0)}
\end{aligned}
$$

Problem 3: Bose-Einstein Gas

a) In this problem, we just follow the directions.

$$
\begin{aligned}
dE &= T\,dS - P\,dV \\
&= \underbrace{T\left(\frac{\partial S}{\partial T}\right)_V}_{C_V} dT + \left(T\left(\frac{\partial S}{\partial V}\right)_T - P\right) dV \\
dF &= dE - d(TS) = -S\,dT - P\,dV \\
&\Rightarrow -\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V \\
\left(\frac{\partial P}{\partial T}\right)_V &= (5/2)aT^{3/2} + 3bT^2 = \left(\frac{\partial S}{\partial V}\right)_T \\
\left(T\left(\frac{\partial S}{\partial V}\right)_T - P\right) &= (5/2)aT^{5/2} + 3bT^3 - aT^{5/2} - bT^3 - cV^{-2} \\
&= (3/2)aT^{5/2} + 2bT^3 - cV^{-2}
\end{aligned}
$$

Collecting this all together gives

$$
\underline{dE = (dT^{3/2}V + eT^2V + fT^{1/2})dT + ((3/2)aT^{5/2} + 2bT^3 - cV^{-2})dV}
$$

b) Use the fact that the energy is a state function which requires that the cross derivatives must be equal.

$$\begin{aligned}
\frac{\partial}{\partial V}\left(\left(\frac{\partial E}{\partial T}\right)_V\right)_T &= \frac{\partial}{\partial T}\left(\left(\frac{\partial E}{\partial V}\right)_T\right)_V \\
dT^{3/2} + eT^2 &= (15/4)aT^{3/2} + 6bT^2 \\
&\Rightarrow \underline{d = (15/4)a, \quad e = 6b}
\end{aligned}$$

c) Use the results from b) to simplify the expression for dE in a).

$$dE = ((15/4)aT^{3/2}V + 6bT^2V + fT^{1/2})dT + ((3/2)aT^{5/2} + 2bT^3 - cV^{-2})dV$$

Integrate with respect to T first.

$$\begin{aligned}
E &= (3/2)aT^{5/2}V + 2bT^3V + (2/3)fT^{3/2} + \mathcal{F}(V) \\
\left(\frac{\partial E}{\partial V}\right)_T &= (3/2)aT^{5/2} + 2bT^3 + \mathcal{F}'(V) \qquad \text{from above} \\
&= (3/2)aT^{5/2} + 2bT^3 - cV^{-2} \qquad \text{from } dE \\
&\Rightarrow \mathcal{F}' = -cV^{-2}, \quad \mathcal{F} = cV^{-1} + K_E \\
E &= \underline{(3/2)aT^{5/2}V + 2bT^3V + (2/3)fT^{3/2} + cV^{-1} + K_E}
\end{aligned}$$

d) Proceed just as we did above for E.

$$\begin{aligned}
dS &= \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{C_V/T} dT + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\left(\frac{\partial P}{\partial T}\right)_V \text{ from a)}} dV \\
&= (dT^{1/2}V + eTV + fT^{-1/2})dT + ((5/2)aT^{3/2} + 3bT^2)dV
\end{aligned}$$

Integrate with respect to T first.

$$\begin{aligned}
S &= \underbrace{(2/3)dVT^{3/2}}_{(5/2)aVT^{3/2}} + \underbrace{(1/2)eVT^2}_{3bVT^2} + 2fT^{1/2} + \mathcal{G}(V) \\
\left(\frac{\partial S}{\partial V}\right)_T &= (5/2)aT^{3/2} + 3bT^2 + \mathcal{G}'(V) \qquad \text{from above} \\
&= (5/2)aT^{3/2} + 3bT^2 \qquad \text{from } dS \\
&\Rightarrow \mathcal{G}'(V) = 0, \quad \mathcal{G}(V) = K_S \\
S(T,V) &= \underline{(5/2)aVT^{3/2} + 3bVT^2 + 2fT^{1/2} + K_S}
\end{aligned}$$

Problem 4: Paramagnet

a) This is virtually identical in approach to problem 2.

$$\begin{aligned}
C_M &\equiv \left.\frac{đQ}{dT}\right|_M \\
&= T\left(\frac{\partial S}{\partial T}\right)_M \qquad \text{by the second law} \\
\left(\frac{\partial C_M}{\partial M}\right)_T &= T\frac{\partial^2 S}{\partial M \partial T} \\
&= T\frac{\partial}{\partial T}\left(\left(\frac{\partial S}{\partial M}\right)_T\right)_M \qquad \text{interchanging order of the derivatives}
\end{aligned}$$

We will need $H(T,M)$ for what follows.

$$M = \frac{A}{T - T_0}H \quad \Rightarrow \quad H = \frac{M}{A}(T - T_0)$$

We use a Maxwell relation to find $(\partial S/\partial M)_T$.

$$\begin{aligned}
dE &= T\,dS + H\,dM \\
dF &= dE - d(TS) = -S\,dT + H\,dM
\end{aligned}$$

Since F is a state function, the cross derivatives must be equal.

$$-\left(\frac{\partial S}{\partial M}\right)_T = \left(\frac{\partial H}{\partial T}\right)_M = \frac{M}{A}$$

Substitute this result into the expression for the derivative of the heat capacity.

$$\left(\frac{\partial C_M}{\partial M}\right)_T = T\frac{\partial}{\partial T}\left(-\frac{M}{A}\right)_M = 0$$

This shows that the heat capacity at constant magnetization does not depend on the magnetization: $\underline{C_M(T,M) = C_M(T)}$.

b)

$$\begin{aligned}
dE &= T\,dS + H\,dM \\
&= \underbrace{T\left(\frac{\partial S}{\partial T}\right)_M}_{C_M(T)} dT + \underbrace{\left(T\left(\frac{\partial S}{\partial M}\right)_T + H\right)}_{-MT/A + H = -MT_0/A} dM
\end{aligned}$$

Do the T integration first.

$$\begin{aligned}
E(T,M) &= \int_0^T C_M(T')\,dT' + f(M) \\
\left(\frac{\partial E}{\partial M}\right)_T &= f'(M) && \text{from above} \\
&= -\frac{MT_0}{A} && \text{from } dE \\
&\Rightarrow f(M) = -\frac{M^2T_0}{2A} + K_E \\
E(T,M) &= \underline{\int_0^T C_M(T')\,dT' - \frac{M^2T_0}{2A} + K_E}
\end{aligned}$$

c)

$$\begin{aligned}
dS &= \underbrace{\left(\frac{\partial S}{\partial T}\right)_M}_{C_M(T)/T} dT + \underbrace{\left(\frac{\partial S}{\partial M}\right)_T}_{-M/A \text{ from a)}} dM \\
S(T,M) &= \int_0^T \frac{C_M(T')}{T'}\,dT' + g(M)
\end{aligned}$$

$$
\begin{aligned}
\left(\frac{\partial S}{\partial M}\right)_T &= g'(M) && \text{from above} \\
&= -\frac{M}{A} && \text{from } dS \\
&\Rightarrow\ g(M) = -\frac{M^2}{2A} + K_S \\
S(T,M) &= \underline{\int_0^T \frac{C_M(T')}{T'}\,dT' - \frac{M^2}{2A} + K_S}
\end{aligned}
$$

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