Problem 1: Equation of State for a Ferromagnet

a) We are looking for the magnetization as a function of the field and the temperature, $M(H, T)$, so we form the differential of $M$ as follows.

$$dM = \left( \frac{\partial M}{\partial H} \right)_T \, dH + \left( \frac{\partial M}{\partial T} \right)_H \, dT$$

We are given the two coefficients in the expansion, but must make sure that their cross derivatives are equal as is required for an exact differential.

$$\frac{\partial}{\partial T} \left( \frac{\partial M}{\partial H} \right)_T = \frac{1}{T_c} \frac{a}{(1 - T/T_c)^2}$$

$$\frac{\partial}{\partial H} \left( \frac{\partial M}{\partial T} \right)_H = \frac{1}{T_c} \frac{f'(H)}{(1 - T/T_c)^2}$$

The equality of these two expressions requires that $f'(H) = a$. Integration gives $f(H) = aH + c$ but we are told that $f(0) = 0$ so we know that $c = 0$. Thus

$$f(H) = aH$$

b) Now we must integrate the exact differential to find the state function $M(H, T)$.

$$M(H, T) = \int \left( \frac{\partial M}{\partial T} \right)_H \, dT + g(H)$$

$$= \frac{f(H)}{1 - T/T_c} + M_0(1 - T/T_c)^{3/2} + g(H)$$

$$\left( \frac{\partial M}{\partial H} \right)_T = \frac{f'(H)}{(1 - T/T_c)} + g'(H) \quad \text{by calculation from above}$$

$$= \frac{a}{1 - T/T_c} + 3bH^2 \quad \text{as given}$$

Now we set about finding an expression for $g(H)$.

$$g'(H) = 3bH^2$$

$$g(H) = bH^3 + K$$

$$M(H = 0, T = T_c) = 0 \implies K = 0$$
Now putting all the pieces together gives

\[
M(H, T) = M_0(1 - T/T_c)^{1/2} + \frac{aH}{(1 - T/T_c)} + bH^3
\]

**Problem 2: Heat Capacity at Constant Pressure in a Simple Fluid**

Start with the first law of thermodynamics.

\[
\dot{Q} = dU + P \, dV
\]

The relation for \( C_P \) we are looking for involves \( (\partial U/\partial T)_P \) so it is natural to try to do our expansion in terms of the variables \( T \) and \( P \). We expand both \( dU \) and \( dV \) in terms of \( dT \) and \( dP \).

\[
dU = \left( \frac{\partial U}{\partial T} \right)_P \, dT + \left( \frac{\partial U}{\partial P} \right)_T \, dP
\]

\[
dV = \left( \frac{\partial V}{\partial T} \right)_P \, dT + \left( \frac{\partial V}{\partial P} \right)_T \, dP
\]

\[
\dot{Q} = \left( \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P \right) \, dT + \left( \left( \frac{\partial U}{\partial P} \right)_T + P \left( \frac{\partial V}{\partial P} \right)_T \right) \, dP
\]

Since we need the derivative at constant \( P \) the second term in the above expression will drop out.

\[
C_P = \frac{\dot{Q}}{dT} \bigg|_P
\]

\[
= \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P
\]

\[
= \left( \frac{\partial U}{\partial T} \right)_P + \alpha VP
\]

**Problem 3: Heat Supplied to a Gas**

To find \( C_P \) we proceed as follows. Rearrange the first law to isolate \( \dot{Q} \).

\[
\dot{Q} = dU + P \, dV
\]

Expand the differential of the energy in terms of \( dT \) and \( dV \).

\[
dU = \left( \frac{\partial U}{\partial T} \right)_V \, dT + \left( \frac{\partial U}{\partial V} \right)_T \, dV
\]
Substitute into the expression for $dQ$.

$$dQ = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T + P \right) dV$$

Form the derivative with respect to $T$ by dividing by $dT$ and specifying the path as one of constant $P$.

$$\left. \frac{dQ}{dT} \right|_P \equiv C_P = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T + P \right) \left( \frac{\partial V}{\partial T} \right)_P$$

Now use the given information $(\partial U/\partial V)_T = 0$, $PV = NkT$, and $C_V = (5/2)Nk$ in the equation above to find that

$$C_P = (7/2)Nk.$$

a) It is easy to find the heat along the two rectangular paths by integration.

$$\Delta Q(acb) = \int_a^b C_V dT + \int_c^b C_P dT$$

$$= \int_{P_a}^{P_b} C_V \frac{V_1}{Nk} dP + \int_{V_1}^{V_2} C_P \frac{P_2}{Nk} dV$$

$$= \frac{(19/2)NkT_1}{NkT_1}$$

$$\Delta Q(adb) = \int_a^d C_P dT + \int_c^d C_V dT$$

$$= \int_{V_1}^{V_2} C_P \frac{P_1}{Nk} dV + \int_{P_1}^{P_2} C_V \frac{V_2}{Nk} dP$$

$$= \frac{(17/2)NkT_1}{NkT_1}$$

Before we compute the heat along the diagonal path, it is useful to find the difference in internal energy between $b$ and $a$. Since the internal energy is a state function, it does not matter what path we use to find it. We already know the heat input $\Delta Q$ along the path $adb$ and the work $\Delta W$ is easy to find.

$$\Delta W(adb) = \int -P dV = -\int_{V_a}^{V_d} P_1 dV = -NkT_1$$

Then the path-independent result for $\Delta U$ can be computed along this particular path.

$$\Delta U = \Delta Q + \Delta W = (17/2 - 2/2)NkT_1 = (15/2)NkT_1$$
The work along the diagonal path $ab$ can be calculated by integration using the $V$ dependence of $P$: $P = (P_1/V_1)V$.

$$
\Delta W(ab) = - \int_a^b P \, dV = -(P_1/V_1) \int_{V_1}^{V_2} V \, dV
$$

$$
= -(1/2)(P_1/V_1)(V_2^2 - V_1^2) = -(3/2)P_1V_1 = -(3/2)NkT_1
$$

Finally we can compute the heat supplied along the diagonal path.

$$
\Delta Q = \Delta U - \Delta W = 9NkT_1
$$

b) Examine the constraint along the diagonal path $ab$.

$$
\delta Q = dU + P \, dV
$$

$$
= \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T + P \right) dV
$$

$$
C_{ab} \equiv \left. \frac{\delta Q}{dT} \right|_{ab} = C_V + \left. \frac{dV}{dT} \right|_{ab}
$$

Along the path $ab$

$$
P = \frac{P_1}{V_1}V = \frac{NkT}{V} \Rightarrow V^2 = \frac{V_1}{P_1}NkT.
$$

So along $ab$ we can construct an expression relating $dV$ to $dT$ by taking the derivative of this expression.

$$
2V \, dV = \frac{V_1}{P_1}Nk \, dT
$$

$$
\Rightarrow \left( \frac{\partial V}{\partial T} \right)_{ab} = \frac{V_1 \, Nk}{P_1 \, 2V}
$$

Finally

$$
C_{ab} = C_V + \frac{V_1}{P_1} \, Nk \frac{P}{V} = C_V + (1/2)Nk = 3Nk.
$$
As a check we can integrate this heat capacity along the path.

\[
\Delta Q(ab) = \int_a^b C_{ab} \, dT = 3Nk(T_b - T_a) = 9NkT_1
\]

This is identical to the result we found above in part a).

Comment: \(C_V = (5/2)Nk\) is an approximation to a diatomic gas where the rotational degrees of freedom are contributing to \(C_V\) but the vibrational degrees of freedom are not (they are frozen out; we will understand why later in the course). If we had used the monatomic result \(C_V = (3/2)Nk\) we would have found \(C_P = (5/2)Nk\), \(\Delta Q(acb) = (13/2)NkT_1\), \(\Delta Q(adb) = (11/2)NkT_1\), \(\Delta U = (9/2)NkT_1\), \(\Delta Q(ab) = 6NkT_1\), and \(C_{ab} = 2Nk\).

**Problem 4:** Equation of State and Heat Capacity of a Liquid Surface

a) Here we follow the standard procedure for integrating an exact differential. Since the partial derivatives involve \(A\) and \(T\) and the expressions for them are given in terms of \(A\) and \(T\), it is natural to choose these as the independent variables (even if the question did not specifically ask for \(S(A, T)\)).

\[
dS(A, T) = \left( \frac{\partial S}{\partial T} \right)_A dT + \left( \frac{\partial S}{\partial A} \right)_T dA
\]

\[
S(A, T) = \int \left( \frac{\partial S}{\partial T} \right)_A dT + f(A)
\]

\[
= \int \frac{1}{\left( \frac{\partial T}{\partial S} \right)_A} dT + f(A)
\]

\[
= - \int \frac{Nk}{A-b} dT + f(A)
\]

\[
= - \frac{NkT}{A-b} + f(A)
\]

Now we go about finding an expression for the unknown function \(f(A)\).

\[
\left( \frac{\partial S}{\partial A} \right)_T = \frac{NkT}{(A-b)^2} + f'(A) \quad \text{by differentation}
\]

\[
= \frac{NkT}{(A-b)^2} - \frac{2aN^2}{A^3} \quad \text{given}
\]
Equating the last two lines gives an expression for \( f'(A) \).

\[
f'(A) = -\frac{2aN^2}{A^3}
\]

\[
f(A) = \frac{aN^2}{A^2} + c
\]

\[
\lim_{N \to 0} S = \frac{c}{c} = S_0
\]

Putting it all together gives the final result.

\[
S(A,T) = -\frac{NkT}{A - b} + \frac{aN^2}{A^2} + S_0
\]

b) Begin by expanding the differential of the internal energy in terms of the chosen independent variables.

\[
dU = \left( \frac{\partial U}{\partial T} \right)_A dT + \left( \frac{\partial U}{\partial A} \right)_T dA
\]

Next write the first law in terms of the differential of work appropriate to a two dimensional film and then substitute in the above expansion for the energy differential.

\[
\Delta Q = dU - dW
\]

\[
\Delta Q = dU - S dA
\]

\[
\Delta Q = \left( \frac{\partial U}{\partial T} \right)_A dT + \left( \left( \frac{\partial U}{\partial A} \right)_T - S \right) dA
\]

\[
\frac{\Delta Q}{dT} = \left( \frac{\partial U}{\partial T} \right)_A + \left( \left( \frac{\partial U}{\partial A} \right)_T - S \right) \frac{dA}{dT}
\]

The constant area heat capacity is easy since constant area means \( dA = 0 \).

\[
\left. \frac{\Delta Q}{dT} \right|_A \equiv C_A = \left( \frac{\partial U}{\partial T} \right)_A
\]

In finding \( C_S \) we must be careful to specify the constraint (or path) associated with the derivative of the area with respect to temperature in the generic expression found above.

\[
\left. \frac{\Delta Q}{dT} \right|_S \equiv C_S = \left( \frac{\partial U}{\partial T} \right)_A + \left( \left( \frac{\partial U}{\partial A} \right)_T - S \right) \left( \frac{\partial A}{\partial T} \right)_S
\]
The last partial derivative in the above line is not among the ones we are told to use in the final expression, so we use the chain rule to convert it to the partial derivatives requested.

\[ C_S = C_A - \left( \frac{\partial U}{\partial A} \right)_T - \mathcal{S} \left( \frac{\partial T}{\partial S} \right)_A \frac{\partial S}{\partial A} \]

**Problem 5:** Thermodynamics of a Curie Law Paramagnet

All the manipulations we perform here for a simple magnetic system mirror those we carried out in lecture for a simple hydrostatic system.

a) Heat capacities for the generic magnet.

\[ dU = \left( \frac{\partial U}{\partial T} \right)_M dT + \left( \frac{\partial U}{\partial M} \right)_T dM \]

first law

\[ \delta Q = dU - \delta W = dU - H dM \]

substitution

\[ C_M \equiv \left. \frac{\delta Q}{dT} \right|_M = \left( \frac{\partial U}{\partial T} \right)_M \]

from line above

\[ C_H \equiv \left. \frac{\delta Q}{dT} \right|_H = \left( \frac{\partial U}{\partial T} \right)_M + \left( \left( \frac{\partial U}{\partial M} \right)_T - H \right) \left( \frac{\partial M}{\partial T} \right)_H \]

from \( \delta Q \)

\[ C_H - C_M = \left( \left( \frac{\partial U}{\partial M} \right)_T - H \right) \left( \frac{\partial M}{\partial T} \right)_H \]

by rearrangement

Now substitute into the general expansion of \( dU \) to arrive at

\[ dU(T, M) = C_M(T, M) dT + \left[ \frac{C_H(T, M) - C_M(T, M)}{\left( \frac{\partial M}{\partial T} \right)_H} + H(T, M) \right] dM \]
b) Now find the results specific to the Curie law paramagnet.

\[ C_M = bT, \quad \left( \frac{\partial U}{\partial M} \right)_T = 0 \quad \text{given} \]

\[ dU = \left( \frac{\partial U}{\partial T} \right)_M dT + \left( \frac{\partial U}{\partial M} \right)_0 dM \quad \text{expansion} \]

\[ U(T, M) = \int_0^T bT' dT' = (1/2)bT^2 + f(M) \quad \text{integration} \]

\[ \left( \frac{\partial U}{\partial M} \right)_T = f'(M) = 0 \text{ (given)} \Rightarrow f(M) = \text{ constant} = U(T = 0) \]

\[ 0 \text{ by assumption} \]

\[ U(T) = (1/2)bT^2 + U(T = 0) \]

\[ \left( \frac{\partial M}{\partial T} \right)_H = \frac{\partial}{\partial T} \left( \frac{aH}{T} \right)_H = -\frac{aH}{T^2} \quad \text{from eq. of state} \]

\[ C_H - C_M = (0 - H)(-\frac{aH}{T^2}) = \frac{aH^2}{T^2} = \frac{M^2}{a} \quad \text{from a)} \]

\[ C_H(T, M) = bT + \frac{M^2}{a} \]
c) Here we practice working with an alternative pair of independent variables.

\[ dU = \left( \frac{\partial U}{\partial H} \right)_M dH + \left( \frac{\partial U}{\partial M} \right)_H dM \]  
expansion

\[ \phi Q = \frac{dU}{dT} = \frac{dU}{dH} M + \left( \frac{\partial U}{\partial M} - H \right) dM \]  
first law and substitution

\[ C_M \equiv \left( \frac{\partial Q}{\partial T} \right)_M = \left( \frac{\partial U}{\partial H} \right)_M \left( \frac{\partial H}{\partial T} \right)_M \]  
dividing the above by \( dT \)

\[ \left( \frac{\partial H}{\partial T} \right)_M = \frac{-1}{\left( \frac{\partial T}{\partial M} \right)_H \left( \frac{\partial M}{\partial H} \right)_T} = -\left( \frac{\partial M}{\partial T} \right)_H \chi_T \]  
chain rule

\[ C_M = -\frac{1}{\chi_T} \left( \frac{\partial U}{\partial H} \right)_M \left( \frac{\partial M}{\partial T} \right)_H \]  
substitution

\[ \left( \frac{\partial U}{\partial H} \right)_M = -\frac{C_M \chi_T}{\left( \frac{\partial M}{\partial T} \right)_H} \]  
rearrangement of above

\[ C_H \equiv \left. \frac{\partial Q}{\partial T} \right|_H = \left( \frac{\partial U}{\partial M} \right)_H - H \left( \frac{\partial M}{\partial T} \right)_H \]  
from \( \phi Q \) expression

\[ \left( \frac{\partial U}{\partial M} \right)_H = \frac{C_H}{\left( \frac{\partial M}{\partial T} \right)_H} + H \]  
rearrangement of above

Now substitute into the general expansion of \( dU(H, M) \) to arrive at

\[ dU(H, M) = \frac{C_M(H, M) \chi_T(H, M)}{\left( \frac{\partial M}{\partial T} \right)_H} dH + \left( \frac{C_H(H, M)}{\left( \frac{\partial M}{\partial T} \right)_H} + H \right) dM \]

Note that the coefficient of the \( dM \) term in the expansion of \( dU(H, M) \) found here is different from the coefficient of the \( dM \) term in the expansion of \( dU(T, M) \) found in part a).
d) Now we use the equation of state associated with a Curie law paramagnet.

\[
\chi_T \equiv \left( \frac{\partial M}{\partial H} \right)_T = \frac{\partial}{\partial H} \left( \frac{aH}{T^2} \right)_T = \frac{a}{T}
\]

\[
\left( \frac{\partial M}{\partial T} \right)_H = -\frac{aH}{T^2}
\]

\[
dU(H,M) = \left( -\frac{bT}{-\frac{aH}{T^2}} \right) dH + \left( \frac{bT + a\frac{H^2}{T^2}}{-\frac{aH}{T^2}} + H \right) dM
\]

\[
= \frac{bT^2}{H} dH - \frac{bT^2}{M} dM
\]

\[
= \frac{ba^2 H}{M^2} dH - \frac{ba^2 H^2}{M^3} dM \quad \text{by eliminating } T
\]

\[
U(H,M) = \frac{ba^2 H^2}{2 M^2} + f(M) \quad \text{integration}
\]

\[
\left( \frac{\partial U}{\partial M} \right)_H = -\frac{ba^2 H^2}{M^3} + f'(M)
\]

Comparison with the coefficient of \(dM\) in the differential form \(dU(H,M)\) above shows that \(f'(M) = 0\) which, when integrated, gives \(f = \text{constant}\). Thus we can write

\[
U(H,M) = \frac{ba^2 H^2}{2 M^2} + \text{constant}
\]

There is no reason to carry around a constant term in the internal energy which never responds to any change in the independent variables, so we are free to set the constant equal to zero.

\[
U(H,M) = \frac{ba^2 H^2}{2 M^2}
\]

By using the equation of state, \(M = aH/T\), we see that this reduces to the same result obtained in b), that is \(U = (b/2)T^2\).
e) We are looking for the adiabatic constraint on $dT$ and $dM$.

$$dQ = \left( \frac{\partial U}{\partial T} \right)_M dT + \left( \frac{\partial U}{\partial M} \right)_T dM = 0$$

for an adiabatic path

$$C_M dT = - \left( \left( \frac{\partial U}{\partial M} \right)_T - H \right) dM$$

by rearrangement

$$\Rightarrow \frac{dT}{dM} \bigg|_{\Delta Q=0} = - \left( \frac{\left( \frac{\partial U}{\partial M} \right)_T - H}{C_M} \right)$$

This gives the slope of an adiabatic path for any magnetic system.

f) Next we specialize to the case of a Curie law paramagnet.

$$\left( \frac{\partial U}{\partial M} \right)_T = 0, \quad C_M = bT$$

Curie law paramagnet

$$\frac{dT}{dM} \bigg|_{\Delta Q=0} = - \frac{(0-H)}{bT} = \frac{H}{bT} = \frac{M}{ab}$$

using the general result from e)

$$dT = \frac{1}{ab} M dM$$

after rearrangement

$$(T - T_0) = \frac{1}{2ab} (M^2 - M_0^2)$$

integration

$$(T - T_0) = \frac{1}{2ab} (M - M_0)(M + M_0)$$
g) An isothermal path in the $H M$ plane is easy to picture from the given equation of state, $M = a H / T$. It is a straight line going through the origin with slope $(\partial M / \partial H)_T = a / T$. This is shown in the figure accompanying the statement of the problem. In part f) we found the relation which must hold between $dT$ and $dM$ along an adiabatic path: $dT = (1 / ab) M dM$. In order to explore an adiabatic path in the $H M$ plane we must express $dT$ in terms of $dM$ and $dH$.

\[
T = \frac{a H}{M} \quad \text{equation of state}
\]

\[
dT = \frac{a}{M} dH - \frac{a H}{M^2} dM \quad \text{differential of above}
\]

Substitute this general expression for $dT$ into the adiabatic path derivative and separate the $dH$ and $dM$ terms.

\[
(1 / ab) M dM = \frac{a}{M} dH - \frac{a H}{M^2} dM
\]

\[
dH = \left( \frac{1}{a^2 b} M^2 + \frac{H}{M} \right) dM = \left( \frac{M^2}{a^2 b} + \frac{T}{a} \right) dM = \frac{T}{a} \left( 1 + \frac{M^2}{abT} \right) dM
\]

This allows us to find the slope of an adiabatic line in the $H M$ plane in terms of the quantity $a / T$ which is the slope of an isotherm.

\[
\left. \frac{dM}{dH} \right|_{\Delta Q = 0} = \frac{a}{T} \left( \frac{1}{1 + \frac{M^2}{abT}} \right) < \frac{a}{T}
\]

Note that the slope of the adiabatic path is less than that of the isothermal path going through the same point.