From Kardar's *Statistical Physics of Particles* (2007).

Problem 1.7 (Filament). For an elastic filament it is found that, at a finite range in temperature, a displacement x requires a force

$$J = ax - bT + cTx,$$

where a, b, and c are constants. Furthermore, its heat capacity at constant displacement is proportional to temperature, that is, $C_x = A(x)T$.

(a) Use an appropriate Maxwell relation to calculate $\partial S/\partial x|_T$.

(b) Show that A has to in fact be independent of x, that is, $\mathrm{d}A/\mathrm{d}x = 0$.

(c) Give the expression for $S(T, x)$ assuming $S(0, 0) = S_0$.

(d) Calculate the heat capacity at constant tension, that is, $C_J = T\partial S/\partial T|_J$ as a function of T and J.

Solution. (a) From $dF = -SdT + Jdx + \mu dN$, we get the Maxwell relation

$$\frac{\partial^2 F}{\partial T \partial x} = \frac{\partial^2 F}{\partial x \partial T} \implies \left.\frac{\partial S}{\partial x}\right|_T = -\left.\frac{\partial J}{\partial T}\right|_x = b - cx.$$

(b) Note

$$C_x = \left.\frac{\partial Q}{\partial T}\right|_x = \left.\frac{\partial E}{\partial T}\right|_x.$$

Then,

$$\begin{aligned}
\left.\frac{\partial C_x}{\partial x}\right|_T &= \frac{\partial^2 E}{\partial T \partial x} \\
&= \left.\frac{\partial}{\partial T}\left(\left.\frac{\partial E}{\partial x}\right|_T\right)\right|_x \\
&= \left.\frac{\partial}{\partial T}\left(\left.\frac{\partial E}{\partial S}\right|_x \left.\frac{\partial S}{\partial x}\right|_T + \left.\frac{\partial E}{\partial x}\right|_S\right)\right|_T \\
&= \left.\frac{\partial(T(b - cx) + J)}{\partial T}\right|_x \\
&= \left.\frac{\partial(ax)}{\partial T}\right|_x \\
&= 0.
\end{aligned}$$

Notice also that

$$C_x = A(x)T \implies \left.\frac{\partial C_x}{\partial x}\right|_T = \frac{dA}{dx}T,$$

so

$$T\frac{dA}{dx} = 0 \implies \frac{dA}{dx} = 0.$$

(c) Since $\partial S/\partial x|_T = b - cx$, it follows that

$$S(T,x) = bx - \frac{c}{2}x^2 + f(T),$$

where $f(T)$ is a to-be-determined function. Then, since

$$\left.\frac{\partial S}{\partial T}\right|_x = \frac{1}{T}\left.\frac{\partial Q}{\partial T}\right|_x = \frac{C_x}{T} = A,$$

it follows that

$$\frac{df}{dT} = A \implies f(T) = AT + S_0,$$

so

$$S(T,x) = bx - \frac{c}{2}x^2 + AT + S_0.$$

(d) First,

$$C_J = T\left.\frac{\partial S}{\partial T}\right|_J = T\left[\left.\frac{\partial S}{\partial x}\right|_T \left.\frac{\partial x}{\partial T}\right|_J + \left.\frac{\partial S}{\partial T}\right|_x\right] = T\left[(b - cx)\left.\frac{\partial x}{\partial T}\right|_J + A\right].$$

Next, notice that we can invert

$$x = \frac{J + bT}{a + cT} \implies b - cx = b - c\left(\frac{J + bT}{a + cT}\right) = \frac{ab - cJ}{a + cT},$$

and also

$$\left.\frac{\partial x}{\partial T}\right|_J = \frac{b(a + cT) - c(J + bT)}{(a + cT)^2} = \frac{ab - cJ}{(a + cT)^2}.$$

Hence,

$$C_J(T,J) = T\left[\left(\frac{ab - cJ}{(a + cT)}\right)\left(\frac{ab - cJ}{(a + cT)^2}\right) + A\right] = \left[\frac{(ab - cJ)^2}{(a + cT)^3} + A\right]T. \quad \square$$

Problem 1.8 (Hard core gas). A gas obeys the equation of state $P(V - Nb) = Nk_BT$, and has a heat capacity C_V independent of temperature. (N is kept fixed in the following.)

(a) Find the Maxwell relation involving $\partial S/\partial V|_{T,N}$.

(b) By calculating $dE(T,V)$, show that E is a function of T (and N) only.

(c) Show that $\gamma \equiv C_P/C_V = 1 + Nk_B/C_V$ (independent of T and V).

(d) By writing an expression for $E(P,V)$, or otherwise, show that an adiabatic change satisfies the equation $P(V - Nb)^\gamma = \text{constant}$.

Solution. (a) We want to work with $F = -SdT - PdV + \mu dN$. Then the Maxwell relation is

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \implies \left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N}.$$

For a gas, this becomes

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \frac{Nk_B}{V - Nb}.$$

(b) Assuming N is fixed,

$$\begin{aligned}
dE(T,V) &= \left.\frac{\partial E}{\partial T}\right|_V dT + \left.\frac{\partial E}{\partial V}\right|_T dV \\
&= C_V dT + \left[\left.\frac{\partial E}{\partial S}\right|_V \left.\frac{\partial S}{\partial V}\right|_T + \left.\frac{\partial E}{\partial V}\right|_S \right] dV \\
&= C_V dT + \left[T\left(\frac{Nk_B}{V-Nb}\right) - P \right] dV \\
&= C_V dT + (P - P)\, dV \\
&= C_V dT,
\end{aligned}$$

so $\partial E/\partial V|_T = 0$, and it follows that $E = E(T,N)$.

(c) Note that

$$C_P = \left.\frac{\partial Q}{\partial T}\right|_P = \left.\frac{dE + PdV}{dT}\right|_P = \left.\frac{\partial E}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P.$$

Since $E = E(T,N)$ from the previous part, we get that $\partial E/\partial T|_P = \partial E/\partial T|_V = C_V$, so

$$\gamma \equiv \frac{C_P}{C_V} = \frac{C_V + P\frac{\partial V}{\partial T}|_P}{C_V} = 1 + \frac{P}{C_V}\left(\frac{Nk_B}{P}\right) = 1 + \frac{Nk_B}{C_V}.$$

(d) For an adiabatic change, we have $dQ = 0$, so $dE = -PdV$. From the equation of state and the previous part, we can also find that

$$dE = C_V dT = \frac{C_V}{Nk_B} d(P(V - Nb)) = \frac{C_V}{Nk_B}\left[dP(V - Nb) + PdV\right].$$

Thus, we get that

$$-PdV = \frac{C_V}{Nk_B}\left[(V - Nb)dP + PdV\right]$$

$$\implies (V - Nb)dP = -P\left(\frac{Nk_B}{C_V} + 1\right)dV = -\gamma PdV$$

$$\implies \frac{dP}{P} = -\frac{\gamma dV}{V - Nb}.$$

Integrating then yields

$$\ln P = -\gamma \ln(V - Nb) + c$$
$$\implies P = (V - Nb)^{-\gamma} + e^c = P(V - Nb)^{\gamma} = e^c = \text{constant},$$

where c is a constant of integration. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\square$

Problem 1.9 (Superconducting transition)**.** Many metals become superconductors at low temperatures T, and magnetic fields B. The heat capacities of the two phases at zero magnetic field are approximately given by

$$\begin{cases} C_s(T) = V\alpha T^3 & \text{in the superconducting phase} \\ C_n(T) = V\left[\beta T^3 + \gamma T\right] & \text{in the normal phase} \end{cases},$$

where V is the volume, and $\{\alpha, \beta, \gamma\}$ are constants. (There is no appreciable change in volume at this transition, and mechanical work can be ignored throughout this problem.)

(a) Calculate the entropies $S_s(T)$ and $S_n(T)$ of the two phases at zero field, using the third law of thermodynamics.

(b) Experiments indicate that there is no latent heat ($L = 0$) for the transition between the normal and superconducting phases at zero field. Use this information to obtain the transition temperature T_c, as a function of α, β, and γ.

(c) At zero temperature, the electrons in the superconductor form bound Cooper pairs. As a result, the internal energy of the superconductor is reduced by an amount $V\Delta$, that is, $E_n(T = 0) = E_0$ and $E_s(T = 0) = E_0 - V\Delta$ for the metal and superconductor, respectively. Calculate the internal energies of both phases at finite temperatures.

(d) By comparing the Gibbs free energies (or chemical potentials) in the two phases, obtain an expression for the energy gap Δ in terms of α, β, and γ.

(e) In the presence of a magnetic field B, inclusion of magnetic work results in $\mathrm{d}E = T\mathrm{d}S + B\mathrm{d}M + \mu\mathrm{d}N$, where M is the magnetization. The superconducting phase is a perfect diamagnet, expelling the magnetic field from its interior, such that $M_s = -VB/(4\pi)$ in appropriate units. The normal metal can be regarded as approximately non-magnetic, with $M_n = 0$. Use this information, in conjunction with previous results, to show that the superconducting phase becomes normal for magnetic fields larger than

$$B_c(T) = B_0\left(1 - \frac{T^2}{T_c^2}\right),$$

giving an expression for B_0. (*Remark:* You can assume that the magnetic part of the thermodynamic potentials (the part that involves M and B) does not depend on the temperature and/or entropy and can be added to the temperature/entropy-dependent thermodynamic potentials, computed at zero field.)

Solution. (a) At zero field, by the third law, we know that

$$S_s(T) = \int_0^T \frac{C_s(T')}{T'}\, dT' = V\alpha \int_0^T T'^2\, dT' = \frac{V\alpha T^3}{3},$$

and

$$S_n(T) = \int_0^T \frac{V\left(\beta T'^3 + \gamma T'\right)}{T'}\, dT' = \frac{V\beta T^3}{3} + V\gamma T.$$

(b) Since there is no latent heat at the transition, it follows that

$$S_s(T_c) = S_n(T_c)$$

$$\implies \frac{1}{3}V\alpha T_c^3 = \frac{1}{3}V\beta T_c^3 + V\gamma T_c$$

$$\implies T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}}.$$

(c) Since we are ignoring mechanical work, it follows that $dE = C\, dT$, so

$$E_n(T) = E_0 + \int_0^T V\left(\beta T'^3 + \gamma T'\right)\, dT' = E_0 + \frac{1}{4}V\beta T^4 + \frac{1}{2}V\gamma T^2,$$

and

$$E_s(T) = E_0 - V\Delta + \int_0^T V\alpha T'^3\, dT' = E_0 - V\Delta + \frac{1}{4}V\alpha T^4.$$

(d) Since we are ignoring mechanical work, the Gibbs free energy is simply given by $G = E - TS$. Using the previously calculated energies and entropies, we see that

$$G_s(T) = E_0 - V\Delta + \frac{1}{4}V\alpha T^4 - \frac{1}{3}V\alpha T^4 = E_0 - V\Delta - \frac{1}{12}V\alpha T^4,$$

$$G_n(T) = E_0 + \frac{1}{4}V\beta T^4 + \frac{1}{2}V\gamma T^2 - \frac{1}{3}V\beta T^4 - V\gamma T^2 = E_0 - \frac{1}{12}V\beta T^4 - \frac{1}{2}V\gamma T^2.$$

At the critical temperature, the free energies will be equal, so

$$G_s(T_c) = G_n(T_c)$$

$$\implies E_0 - V\Delta - \frac{1}{12}V\alpha T_c^4 = E_0 - \frac{1}{12}V\beta T_c^4 - \frac{1}{2}V\gamma T_c^2$$

$$\implies \Delta = \frac{1}{12}(\beta - \alpha)T_c^4 + \frac{1}{2}\gamma T_c^2.$$

Thus,

$$\Delta = \frac{1}{12}(\beta - \alpha)\left(\frac{3\gamma}{\alpha - \beta}\right)^2 + \frac{1}{2}\gamma\left(\frac{3\gamma}{\alpha - \beta}\right) = \frac{3\gamma^2}{2(\alpha - \beta)} - \frac{3\gamma^2}{4(\alpha - \beta)} = \frac{3\gamma^2}{4(\alpha - \beta)}.$$

(e) To compute the critical temperature, we can first compute the energies with the magnetic contribution, then compute the Gibbs free energy and find where it is equal for both phases.

To compute the energies, for the normal state, since $M_n = 0$, we get that $E_n(T, B) = E_n(T)$. For the superconducting state, since $M = -VB/4\pi \implies B = -4\pi M/V$, it follows that at for the superconducting state,

$$E_s(B, T) = E(0, T) + \int_0^{-VB/4\pi} -\frac{4\pi M}{V}dM = E(0, T) - \frac{VB^2}{8\pi}.$$

We are assuming that the entropies are independent of B, and $\Delta = \gamma T_c^2/4$, so it follows that the Gibbs free energies given by $G = E - TS - BM$ are then

$$G_s(B, T) = G_s(0, T) - \frac{VB^2}{8\pi} - B\left(-\frac{VB}{4\pi}\right) = E_0 - \frac{1}{4}V\gamma T_c^2 - \frac{1}{12}V\alpha T^4 + \frac{VB^2}{8\pi}$$

$$G_n(B, T) = G_n(0, T) = E_0 - \frac{1}{12}V\beta T^4 - \frac{1}{2}V\gamma T^2.$$

At a given T and at the critical $B_c(T)$, the free energies will be equal, so

$$E_0 - \frac{1}{4}V\gamma T_c^2 - \frac{1}{12}V\alpha T^4 + \frac{VB_c^2}{8\pi} = E_0 - \frac{1}{12}V\beta T^4 - \frac{1}{2}V\gamma T^2$$

$$\implies \frac{B_c^2}{8\pi} = \frac{1}{4}\gamma T_c^2 - \frac{1}{2}\gamma T^2 \frac{1}{12}(\alpha - \beta)T^4$$

$$= \frac{\alpha - \beta}{12}\left[T_c^4 - 2T_c^2 T^2 + T^4\right] = \frac{\alpha - \beta}{12}\left(T_c^2 - T^2\right)^2$$

$$\implies B_c = \sqrt{\frac{2\pi(\alpha - \beta)}{3}}(T_c^2 - T^2) = \sqrt{2\pi\gamma}T_c\left(1 - \frac{T^2}{T_c^2}\right).$$
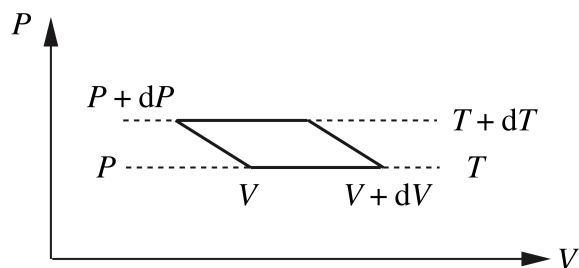
Thus, we see that

$$B_c(T) = B_0\left(1 - \frac{T^2}{T_c^2}\right),$$

where

$$B_0 = \sqrt{2\pi\gamma}T_c = \sqrt{8\pi\Delta} = \sqrt{\frac{6\pi\gamma^2}{\alpha - \beta}}. \qquad \square$$

Problem 1.10 (Photon gas Carnot cycle)**.** The aim of this problem is to obtain the black-body radiation relation, $E(T, V) \propto VT^4$, starting from the equation of state, by performing an infinitesimal Carnot cycle on the photon gas.

(a) Express the work done, W, in the above cycle, in terms of dV and dP.

(b) Express the heat absorbed, Q, in expanding the gas *along an isotherm*, in terms of P, dV, and an appropriate derivative of $E(T, V)$.

(c) Using the efficiency of the Carnot cycle, relate the above expressions for W and Q to T and dT.

(d) Observations indicate that the pressure of the photon gas is given by $P = AT^4$, where $A = \pi^2 k_B^4 / 45(\hbar c)^3$ is a constant. Use this information to obtain $E(T, V)$, assuming $E(T, 0) = 0$.

(e) Find the relation describing the *adiabatic paths* in the above cycle.

Solution. (a) The work done is simply the area enclosed by the cycle, which is given by $W = dV\, dP$.

(b) First, notice

$$dE(T, V) = \left.\frac{\partial E}{\partial T}\right|_V dT + \left.\frac{\partial E}{\partial V}\right|_T dV.$$

When expanding along an isotherm, $dT = 0$, so $dE = \partial E/\partial V|_T dV$. Then, $dE = Q - PdV$, so

$$Q - PdV = \left.\frac{\partial E}{\partial V}\right|_T dV \implies Q = \left(P + \left.\frac{\partial E}{\partial V}\right|_T\right) dV.$$

(c) The efficiency of the Carnot cycle is given by

$$\eta = \frac{T_H - T_C}{T_H} = \frac{dT}{T} = \frac{W}{Q} = \frac{dV\, dP}{(P + \partial E/\partial V|_T)\, dV} = \frac{dP}{P + \partial E/\partial V|_T},$$

where we have used $T_H \approx T$.

(d) Since $P = AT^4$ with $dP = 4AT^3 dT$, it follows that

$$\frac{1}{T} = \frac{4AT^3}{AT^4 + \partial E/\partial V|_T},$$

so
$$\left.\frac{\partial E}{\partial V}\right|_T = 3AT^4.$$

Then,
$$E(T,V) = E(T,0) + \int_0^V 3AT^4 \, dV = E(T,0) + 3AVT^4.$$

Assuming $E(T,0) = 0$, this means that
$$E(T,V) = 3AVT^4 = \frac{\pi^2 k_B^2 V T^4}{15(\hbar c)^3}.$$

(e) Along an adiabatic path, we have that $dE = W = -PdV = -AT^4 dV$. From the previous part, we also know that $dE = 3AT^4 dV + 12AVT^3 dT$. Thus,

$$-AT^4 = 3AT^4 dV + 12AVT^3 dT$$
$$\implies \frac{dV}{V} + 3\frac{dT}{T} = 0$$
$$\implies \ln V + 3\ln T = \text{constant}$$
$$\implies VT^3 = \text{constant}.$$

Since $T = (P/A)^{1/4}$, we get that

$$VP^{3/4} = \text{constant}. \qquad \square$$

Problem 1.11 (Irreversible processes). (a) Consider two substances, initially at temperatures T_1^0 and T_2^0, coming to equilibrium at a final temperature T_f through heat exchange. By relating the direction of heat flow to the temperature difference, show that the change in the total entropy, which can be written as

$$\Delta S = \Delta S_1 + \Delta S_2 \geq \int_{T_1^0}^{T_f} \frac{đQ_1}{T_1} + \int_{T_2^0}^{T_f} \frac{đQ_2}{T_2} = \int \frac{T_1 - T_2}{T_1 T_2} đQ,$$

must be positive. This is an example of the more general condition that "*in a closed system, equilibrium is characterized by the maximum value of entropy S.*"

(b) Now consider a gas with adjustable volume V, and diathermal walls, embedded in a heat bath of constant temperature T, *and* fixed pressure P. The change in the entropy of the bath is given by

$$\Delta S_{\text{bath}} = \frac{\Delta W_{\text{bath}}}{T} = -\frac{\Delta Q_{\text{gas}}}{T} = -\frac{1}{T}\left(\Delta E_{\text{gas}} + P\Delta V_{\text{gas}}\right).$$

By considering the change in entropy of the combined system establish that "*the equilibrium of a gas at fixed T and P is characterized by the minimum of the Gibbs free energy $G = E + PV - TS$.*"

Solution. (a) Let $dQ = dQ_2$, so $dQ_1 = -dQ$. Then, we get that

$$\Delta S \geq -\int_{T_1^0}^{T_f} \frac{dQ}{T_1} + \int_{T_2^0}^{T_f} \frac{dQ}{T_2} = \int_{\{T_1^0, T_2^0\}}^{T_f} \frac{T_1 - T_2}{T_1 T_2} \, dQ$$

by Clausius' theorem. Then, by the second law, we know that $dQ = dQ_2$ must have the same sign as $T_1 - T_2$, so it follows that $(T_1 - T_2)dQ \geq 0 \implies \Delta S \geq 0$.

(b) By Clausius' theorem, we know that

$$\Delta S_{\text{total}} = \Delta S_{\text{bath}} + \Delta S_{\text{gas}} \geq 0.$$

Thus,

$$\Delta S_{\text{gas}} - \frac{1}{T} \left(\Delta E_{\text{gas}} + P \Delta V_{\text{gas}} \right) \geq 0$$
$$\implies -T \Delta S_{\text{gas}} + \Delta E_{\text{gas}} + P \Delta V_{\text{gas}} \leq 0$$
$$\implies \Delta \left(E_{\text{gas}} + T S_{\text{gas}} + P V_{\text{gas}} \right) = \Delta G_{\text{gas}} \leq 0.$$

Thus, any spontaneous process decreases G_{gas}, so at equilibrium for a gas at fixed T, P, it follows that G_{gas} is minimized. $\square$