

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

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

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  $\alpha$ ,  $\beta$ , and  $\gamma$ .

(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.

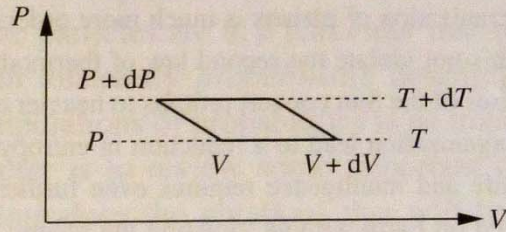
(d) By comparing the Gibbs free energies (or chemical potentials) in the two phases, obtain an expression for the energy gap  $\Delta$  in terms of  $\alpha$ ,  $\beta$ , and  $\gamma$ .

(e) In the presence of a magnetic field  $B$ , inclusion of magnetic work results in  $dE = TdS + BdM + \mu dN$ , 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  $B_0$ .

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.



- Express the work done,  $W$ , in the above cycle, in terms of  $dV$  and  $dP$ .
- Express the heat absorbed,  $Q$ , in expanding the gas *along an isotherm*, in terms of  $P$ ,  $dV$ , and an appropriate derivative of  $E(T, V)$ .
- Using the efficiency of the Carnot cycle, relate the above expressions for  $W$  and  $Q$  to  $T$  and  $dT$ .
- 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  $E(0, V) = 0$ .
- Find the relation describing the *adiabatic paths* in the above cycle.

### 11. Irreversible processes

- 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

$$\Delta S = \Delta S_1 + \Delta S_2 \geq \int_{T_1^0}^{T_f} \frac{dQ_1}{T_1} + \int_{T_2^0}^{T_f} \frac{dQ_2}{T_2} = \int \frac{T_1 - T_2}{T_1 T_2} dQ,$$

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  $S$ .*”

- 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

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

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  $G = E + PV - TS$ .*”