1. *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.

• Finite temperature entropies are obtained by integrating $dS = đQ/T$, starting from $S(T = 0) = 0$. Using the heat capacities to obtain the heat inputs, we find

$$\begin{cases} C_s = V\alpha T^3 = T\dfrac{dS_s}{dT}, & \Longrightarrow \quad S_s = V\dfrac{\alpha T^3}{3}, \\ C_n = V\left[\beta T^3 + \gamma T\right] = T\dfrac{dS_n}{dT}, & \Longrightarrow \quad S_n = V\left[\dfrac{\beta T^3}{3} + \gamma T\right] \end{cases}.$$

(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.

• The Latent hear for the transition is related to the difference in entropies, and thus

$$L = T_c\left(S_n(T_c) - S_s(T_c)\right) = 0.$$

Using the entropies calculated in the previous part, we obtain

$$\frac{\alpha T_c^3}{3} = \frac{\beta T_c^3}{3} + \gamma T_c, \quad \Longrightarrow \quad T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}}.$$

(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 $V\Delta$, i.e. $E_n(T = 0) = E_0$ 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.

• Since $dE = TdS + BdM + \mu dN$, for $dN = 0$, and $B = 0$, we have $dE = TdS = CdT$. Integrating the given expressions for heat capacity, and starting with the internal energies E_0 and $E_0 - V\Delta$ at $T = 0$, yields

$$\begin{cases} E_s(T) = E_0 + V\left[-\Delta + \dfrac{\alpha}{4}T^4\right] \\ E_n(T) = E_0 + V\left[\dfrac{\beta}{4}T^4 + \dfrac{\gamma}{2}T^2\right] \end{cases}.$$

(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.

• The Gibbs free energy $G = E - TS - BM = \mu N$ can be calculated for $B = 0$ in each phase, using the results obtained before, as

$$\begin{cases} G_s(T) = E_0 + V\left[-\Delta + \dfrac{\alpha}{4}T^4\right] - TV\dfrac{\alpha}{3}T^3 = E_0 - V\left[\Delta + \dfrac{\alpha}{12}T^4\right] \\ G_n(T) = E_0 + V\left[\dfrac{\beta}{4}T^4 + \dfrac{\gamma}{2}T^2\right] - TV\left[\dfrac{\beta}{3}T^3 + \gamma T\right] = E_0 - V\left[\dfrac{\beta}{12}T^4 + \dfrac{\gamma}{2}T^2\right] \end{cases}.$$

At the transition point, the chemical potentials (and hence the Gibbs free energies) must be equal, leading to

$$\Delta + \frac{\alpha}{12}T_c^4 = \frac{\beta}{12}T_c^4 + \frac{\gamma}{2}T_c^2, \quad \Longrightarrow \quad \Delta = \frac{\gamma}{2}T_c^2 - \frac{\alpha - \beta}{12}T_c^4.$$

Using the value of $T_c = \sqrt{3\gamma/(\alpha - \beta)}$, we obtain

$$\Delta = \frac{3}{4}\frac{\gamma^2}{\alpha - \beta}.$$

(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.

• Since $dG = -SdT - MdB + \mu dN$, we have to add the integral of $-MdB$ to the Gibbs free energies calculated in the previous section for $B = 0$. There is no change in the metallic phase since $M_n = 0$, while in the superconducting phase there is an additional contribution of $-\int M_s dB = (V/4\pi)\int BdB = (V/8\pi)B^2$. Hence the Gibbs free energies at finite field are

$$\begin{cases} G_s(T,B) = E_0 - V\left[\Delta + \dfrac{\alpha}{12}T^4\right] + V\dfrac{B^2}{8\pi} \\ G_n(T,B) = E_0 - V\left[\dfrac{\beta}{12}T^4 + \dfrac{\gamma}{2}T^2\right] \end{cases}.$$

Equating the Gibbs free energies gives a critical magnetic field

$$\begin{aligned} \frac{B_c^2}{8\pi} &= \Delta - \frac{\gamma}{2}T^2 + \frac{\alpha-\beta}{12}T^4 = \frac{3}{4}\frac{\gamma^2}{\alpha-\beta} - \frac{\gamma}{2}T^2 + \frac{\alpha-\beta}{12}T^4 \\ &= \frac{\alpha-\beta}{12}\left[\left(\frac{3\gamma}{\alpha-\beta}\right)^2 - \frac{6\gamma T^2}{\alpha-\beta} + T^4\right] = \frac{\alpha-\beta}{12}\left(T_c^2 - T^2\right)^2, \end{aligned}$$

where we have used the values of Δ and T_c obtained before. Taking the square root of the above expression gives

$$B_c = B_0\left(1 - \frac{T^2}{T_c^2}\right), \quad \text{where} \quad B_0 = \sqrt{\frac{2\pi(\alpha-\beta)}{3}}T_c^2 = \sqrt{\frac{6\pi\gamma^2}{\alpha-\beta}} = T_c\sqrt{2\pi\gamma}.$$

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2. *Probabilities:* Particles of type A or B are chosen independently with probabilities p_A and p_B.

(a) What is the probability $p(N_A, N)$ that N_A out of the N particles are of type A?

• The answer is the binomial probability distribution

$$p(N_A, N) = \frac{N!}{N_A!(N-N_A)!}p_A^{N_A}p_B^{N-N_B}.$$

(b) Calculate the mean and the variance of N_A.

• We can write

$$n_A = \sum_{i=1}^{N} t_i,$$

where $t_i = 1$ if the i-th particle is A, and 0 if it is B. The mean value is then equal to

$$\langle N_A \rangle = \sum_{i=1}^{N} \langle t_i \rangle = \sum_{i=1}^{N} (p_A \times 1 + p_B \times 0) = N p_A.$$

Similarly, since the $\{t_i\}$ are independent variables,

$$\left\langle N_A^2 \right\rangle_c = \sum_{i=1}^{N} \left(\langle t_i^2 \rangle - \langle t_i \rangle^2 \right) = \sum_{i=1}^{N} \left(p_A - p_A^2 \right) = N p_A p_B.$$

(c) Use the central limit theorem to obtain the probability $p(N_A, N)$ for large N.

• According to the *central limit theorem* the PDF of the sum of independent variables for large N approaches a Gaussian of the right mean and variance. Using the mean and variance calculated in the previous part, we get

$$\lim_{N \gg 1} p(N_A, N) \approx \exp\left[-\frac{(N_A - N p_A)^2}{2 N p_A p_B} \right] \frac{1}{\sqrt{2\pi N p_A p_B}}.$$

(d) Apply Stirling's approximation ($\ln N! \approx N \ln N - N$) to $\ln p(N_A, N)$ [using the probability calculated in part (a), **not** part (c)] to find the most likely value, $\overline{N_A}$, for $N \gg 1$.

• Applying Stirling's approximation to the logarithm of the binomial distribution gives

$$\begin{aligned} \ln p(N_A, N) &= \ln N! - \ln N_A! - \ln(N - N_A)! + N_A \ln p_A + (N - N_A) \ln p_B \\ &\approx -N_A \ln\left(\frac{N_A}{N} \right) - (N - N_A) \ln\left(1 - \frac{N_A}{N} \right) + N_A \ln p_A + (N - N_A) \ln p_B. \end{aligned}$$

The most likely value, $\overline{N_A}$, is obtained by setting the derivative of the above expression with respect to N_A to zero, i.e.

$$\frac{d \ln p}{d N_A} = -\ln\left[\frac{\overline{N_A}}{N} \frac{N}{N - \overline{N_A}} \right] + \ln \frac{p_A}{p_B} = 0, \quad \Longrightarrow \quad \overline{N_A} = p_A N.$$

Thus the most likely value is the same as the mean in this limit.

(e) Expand $\ln p(N_A, N)$ calculated in (d) around its maximum to second order in $\left(N_A - \overline{N_A}\right)$, and check for consistency with the result from the central limit theorem.

• Taking a second derivative of $\ln p$ gives

$$\frac{d^2 \ln p}{d N_A^2} = -\frac{1}{\overline{N_A}} - \frac{1}{N - \overline{N_A}} = -\frac{N}{\overline{N_A}\left(N - \overline{N_A}\right)} = -\frac{1}{N p_A p_B}.$$

The expansion of $\ln p$ around its maximum thus gives

$$\ln p \approx -\frac{\left(N_A - p_A N\right)^2}{2Np_A p_B},$$

which is consistent with the result from the central limit theorem. The correct normalization is also obtained if the next term in the Stirling approximation is included.

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3. *Thermal Conductivity:* Consider a classical gas between two plates separated by a distance w. One plate at $y = 0$ is maintained at a temperature T_1, while the other plate at $y = w$ is at a different temperature T_2. The gas velocity is zero, so that the initial zeroth order approximation to the one particle density is,

$$f_1^0(\vec{p}, x, y, z) = \frac{n(y)}{\left[2\pi m k_B T(y)\right]^{3/2}} \exp\left[-\frac{\vec{p}\cdot\vec{p}}{2mk_B T(y)}\right].$$

(a) What is the necessary relation between $n(y)$ and $T(y)$, to ensure that the gas velocity $\vec{u}$ remains zero? (Use this relation between $n(y)$ and $T(y)$ in the remainder of this problem.)

• Since there is no external force acting on the gas between plates, the gas can only flow locally if there are variations in pressure. Since the local pressure is $P(y) = n(y)k_B T(y)$, the condition for the fluid to be stationary is

$$n(y)T(y) = \text{constant}.$$

(b) Using Wick's theorem, or otherwise, show that

$$\left\langle p^2 \right\rangle^0 \equiv \left\langle p_\alpha p_\alpha \right\rangle^0 = 3\left(mk_B T\right), \quad \text{and} \quad \left\langle p^4 \right\rangle^0 \equiv \left\langle p_\alpha p_\alpha p_\beta p_\beta \right\rangle^0 = 15\left(mk_B T\right)^2,$$

where $\langle \mathcal{O} \rangle^0$ indicates local averages with the Gaussian weight f_1^0. Use the result $\left\langle p^6 \right\rangle^0 = 105(mk_B T)^3$ (*you don't have to derive this*) in conjunction with symmetry arguments to conclude

$$\left\langle p_y^2 p^4 \right\rangle^0 = 35\left(mk_B T\right)^3.$$

• The Gaussian weight has a covariance $\langle p_\alpha p_\beta \rangle^0 = \delta_{\alpha\beta}(mk_B T)$. Using Wick's theorem gives

$$\left\langle p^2 \right\rangle^0 = \left\langle p_\alpha p_\alpha \right\rangle^0 = \left(mk_B T\right)\delta_{\alpha\alpha} = 3\left(mk_B T\right).$$

Similarly

$$\left\langle p^4\right\rangle^0 = \left\langle p_\alpha p_\alpha p_\beta p_\beta\right\rangle^0 = \left(mk_BT\right)^2\left(\delta_{\alpha\alpha} + 2\delta_{\alpha\beta}\delta_{\alpha\beta}\right) = 15\left(mk_BT\right)^2.$$

The symmetry along the three directions implies

$$\left\langle p_x^2 p^4\right\rangle^0 = \left\langle p_y^2 p^4\right\rangle^0 = \left\langle p_z^2 p^4\right\rangle^0 = \frac{1}{3}\left\langle p^2 p^4\right\rangle^0 = \frac{1}{3}\times 105\left(mk_BT\right)^3 = 35\left(mk_BT\right)^3.$$

(c) The zeroth order approximation does not lead to relaxation of temperature/density variations related as in part (a). Find a better (time independent) approximation $f_1^1(\vec{p}, y)$, by linearizing the Boltzmann equation in the single collision time approximation, to

$$\mathcal{L}\left[f_1^1\right] \approx \left[\frac{\partial}{\partial t} + \frac{p_y}{m}\frac{\partial}{\partial y}\right] f_1^0 \approx -\frac{f_1^1 - f_1^0}{\tau_K},$$

where τ_K is of the order of the mean time between collisions.

• Since there are only variations in y, we have

$$\begin{aligned}\left[\frac{\partial}{\partial t} + \frac{p_y}{m}\frac{\partial}{\partial y}\right] f_1^0 &= f_1^0\frac{p_y}{m}\partial_y \ln f_1^0 = f_1^0\frac{p_y}{m}\partial_y\left[\ln n - \frac{3}{2}\ln T - \frac{p^2}{2mk_BT} - \frac{3}{2}\ln\left(2\pi m k_B\right)\right]\\ &= f_1^0\frac{p_y}{m}\left[\frac{\partial_y n}{n} - \frac{3}{2}\frac{\partial_y T}{T} + \frac{p^2}{2mk_BT}\frac{\partial T}{T}\right] = f_1^0\frac{p_y}{m}\left[-\frac{5}{2} + \frac{p^2}{2mk_BT}\right]\frac{\partial_y T}{T},\end{aligned}$$

where in the last equality we have used $nT =$ constant to get $\partial_y n/n = -\partial_y T/T$. Hence the first order result is

$$f_1^1(\vec{p}, y) = f_1^0(\vec{p}, y)\left[1 - \tau_K\frac{p_y}{m}\left(\frac{p^2}{2mk_BT} - \frac{5}{2}\right)\frac{\partial_y T}{T}\right].$$

(d) Use f_1^1, along with the averages obtained in part (b), to calculate h_y, the y component of the heat transfer vector, and hence find K, the coefficient of thermal conductivity.

• Since the velocity $\vec{u}$ is zero, the heat transfer vector is

$$h_y = n\left\langle c_y\frac{mc^2}{2}\right\rangle^1 = \frac{n}{2m^2}\left\langle p_y p^2\right\rangle^1.$$

In the zeroth order Gaussian weight all odd moments of p have zero average. The corrections in f_1^1, however, give a non-zero heat transfer

$$h_y = -\tau_K\frac{n}{2m^2}\frac{\partial_y T}{T}\left\langle\frac{p_y}{m}\left(\frac{p^2}{2mk_BT} - \frac{5}{2}\right)p_y p^2\right\rangle^0.$$

Note that we need the Gaussian averages of $\left\langle p_y^2 p^4 \right\rangle^0$ and $\left\langle p_y^2 p^2 \right\rangle^0$. From the results of part (b), these averages are equal to $35(mk_BT)^3$ and $5(mk_BT)^2$, respectively. Hence

$$h_y = -\tau_K \frac{n}{2m^3} \frac{\partial_y T}{T} (mk_BT)^2 \left(\frac{35}{2} - \frac{5 \times 5}{2} \right) = -\frac{5}{2} \frac{n\tau_K k_B^2 T}{m} \partial_y T.$$

The coefficient of thermal conductivity relates the heat transferred to the temperature gradient by $\vec{h} = -K\nabla T$, and hence we can identify

$$K = \frac{5}{2} \frac{n\tau_K k_B^2 T}{m}.$$

(e) What is the temperature profile, $T(y)$, of the gas in steady state?

• Since $\partial_t T$ is proportional to $-\partial_y h_y$, there will be no time variation if h_y is a constant. But $h_y = -K\partial_y T$, where K, which is proportional to the product nT, is a constant in the situation under investigation. Hence $\partial_y T$ must be constant, and $T(y)$ varies linearly between the two plates. Subject to the boundary conditions of $T(0) = T_1$, and $T(w) = T_2$, this gives

$$T(y) = T_1 + \frac{T_2 - T_1}{w} y.$$

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