1. Show that the Meissner effect causes momentarily $\boldsymbol{E} \neq 0$ in superconductors.

   Solution: Meissner effect: the exclusion of magnetic field in the superconducting phase transition. See the Figure at page 2 of the lecture notes.

   Let us assume that $\mathbf{E}(t) = 0$ for all times t and apply Maxwell equation:

   $$\boldsymbol{\nabla} \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad \Rightarrow \qquad \mathbf{B}(t) = \mathbf{C}$$

   But $\mathbf{B}(t) = \mathbf{C}$ is in conflict with the Meissner effect: B is not constant in time. It must hold: $\mathbf{E} \neq$ momentarily during the superconducting phase transition.

2. Consider a two-state system, in which the Hamiltonian has only two eigenstates with an energy difference Δ. By first calculating the free energy F, show that the specific heat of the system is

   $$C = \frac{\Delta^2 e^{\frac{\Delta}{k_B T}}}{k_B T^2 \left(1 + e^{\frac{\Delta}{k_B T}}\right)^2}.$$

   Show that at low temperatures this behaves as

   $$C \propto e^{-\frac{\Delta}{k_B T}}.$$

   (Hint: you can use Mathematica for derivations.)

   Solution: Let us choose the energy levels without loss of generality: $E_0 = 0$ and $E_1 = \Delta$. The definition of free energy in the case of two-level system stands

   $$F = -k_B T \ln(\sum_{i=0}^{1} \mathrm{e}^{-\beta E_i}) = -k_B T \ln(1 + \mathrm{e}^{-\frac{\Delta}{k_B T}}).$$

   The specific heat of the system at constant volume is calculated from equation

   $$C_V = -T \left(\frac{\partial^2 F}{\partial T^2}\right)_V.$$

   The assumption of constant volume implies that the energy levels remain unchanged during the change of temperature. Let us, for simplicity, set $k_B = 1$ in the following. The final result must then be divided by k_B to reinstate the correct units. (In other words, we change the variable temporarily from T to $k_B T$ and rename it as T.) The first derivative

   $$\frac{\partial F}{\partial T} = -\ln(1 + \mathrm{e}^{-\frac{\Delta}{T}}) - \frac{\Delta}{T} \frac{1}{1 + \mathrm{e}^{\frac{\Delta}{T}}}$$

and the second derivative

$$\frac{\partial^2 F}{\partial T^2} = -\frac{\Delta}{T^2}\frac{\mathrm{e}^{-\frac{\Delta}{T}}}{1+\mathrm{e}^{-\frac{\Delta}{T}}} + \frac{\Delta}{T^2}\frac{1}{1+\mathrm{e}^{\frac{\Delta}{T}}} - \frac{\Delta^2}{T^3}\frac{\mathrm{e}^{\frac{\Delta}{T}}}{(1+\mathrm{e}^{\frac{\Delta}{T}})^2}$$

are calculated by brute force. In the second derivative the first two terms cancel each other. Finally, the specific heat has the right form

$$C = \frac{\Delta^2}{T^2}\frac{\mathrm{e}^{\frac{\Delta}{T}}}{(1+\mathrm{e}^{\frac{\Delta}{T}})^2}$$

or, putting the the k_Bs back

$$C = \frac{\Delta^2}{k_B T^2}\frac{\mathrm{e}^{\frac{\Delta}{k_B T}}}{(1+\mathrm{e}^{\frac{\Delta}{k_B T}})^2}.$$

At low temperatures ($k_B T \ll \Delta$ and so also $\mathrm{e}^{\frac{\Delta}{k_B T}} \gg 1$) the result simplifies to

$$C \approx \frac{\Delta^2}{k_B T^2}\frac{\mathrm{e}^{\frac{\Delta}{k_B T}}}{(\mathrm{e}^{\frac{\Delta}{k_B T}})^2} = \frac{\Delta^2}{k_B T^2}\mathrm{e}^{-\frac{\Delta}{k_B T}} \propto \mathrm{e}^{-\frac{\Delta}{k_B T}},$$

where the last step just means that e^x overwhelms all powers of x as $x \to \infty$, so that C is exponentially suppressed at low temperature despite the factor $1/T^2$. Such exponential behavior is typical of systems with discrete energy levels or otherwise a gap in the excitation spectrum.

3.

(a) At low temperatures, the specific heat of a normal state metal is linear in temperature $C_\mathrm{n}(T) = \gamma T$. Using the third law of thermodynamics (i. e. the entropy has to vanish at $T = 0$) calculate the entropy of the normal state.

(b) A phase transition is said to be of order n if the n:th derivative of $F(T)$ is discontinuous at T_C but lower derivatives as well of $F(T)$ are continuous.

(i) Show that there is a latent heat associated with a first order transition (such as melting), but a second order transition has discontinuity of specific heat $C(T)$ but no latent heat.

(ii) Thus deduce that the superconducting transition is of second order.

(c) Show that the specific heat in the superconducting state $C_\mathrm{s}(T)$ has to satisfy

$$\int_0^{T_\mathrm{c}} \frac{C_\mathrm{s}(T)}{T}\,\mathrm{d}T = \gamma T_\mathrm{c}.$$

Solution:

(a) The entropy S and specific heat are related through: $C_n(T) = T\frac{\mathrm{d}S}{\mathrm{d}T}$. Now

$$\mathrm{d}S = \frac{C_n \mathrm{d}T}{T} \quad \Rightarrow \quad \int_{S(0)}^{S(T)} \mathrm{d}S = \int_0^T \frac{C_n \mathrm{d}T}{T} \quad \Rightarrow \quad S_n(T) = \gamma T$$

where the given facts $S(0) = 0$ and $C_n(T) = \gamma T$ are applied .

(b)

(i) The latent heat is defined as the finite heat release/absorption occurring at a phase transition, during which the temperature remains constant. Thus it is $\Delta Q = T\Delta S$, where

$$\Delta S = S_2 - S_1 = -\left[\left(\frac{\partial F}{\partial T}\right)_2 - \left(\frac{\partial F}{\partial T}\right)_1\right].$$

The relation $S = -\partial F/\partial T$ between free energy F and entropy S is seen from the relation: $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$. In the case of first order phase transition it holds $\left[\left(\frac{\partial F}{\partial T}\right)_2 - \left(\frac{\partial F}{\partial T}\right)_1\right] \neq 0$ and thus $\Delta S \neq 0$ and $\Delta Q \neq 0$. In the second order transition $\left[\left(\frac{\partial F}{\partial T}\right)_2 - \left(\frac{\partial F}{\partial T}\right)_1\right] = 0$ and so $\Delta S = 0$ and $\Delta Q = 0$. The specific heat is defined through

$$C = -T\left(\frac{\partial^2 F}{\partial T^2}\right).$$

The discontinuity stands as

$$C_2 - C_1 = -T\left[\left(\frac{\partial^2 F}{\partial T^2}\right)_2 - \left(\frac{\partial^2 F}{\partial T^2}\right)_1\right].$$

In the case of second-order phase transition, the second T derivative of free energy F is discontinous, the specific heat C is also discontinous.

(ii) In the lecture notes (at the page 2) it is shown in the figure that the specific heat of superconducting phase transition is discontinous at $T = T_c$. It is also mentioned that no latent heat is associated with the transition. The superconducting phase transition is therefore of second order.

(c) The superconducting phase transition is of second order $\Rightarrow$ the first derivative of $\frac{\mathrm{d}F}{\mathrm{d}T}$ is continous $\Rightarrow$ Entropy S is continous, $S_s(T_c) = S_n(T_c) = \gamma T_C$.

$$\mathrm{d}S_s = \frac{C_s \mathrm{d}T}{T} \quad \Rightarrow \quad \int_{S_s(0)}^{S_s(T_c)} \mathrm{d}S = \int_0^{T_c} \frac{C_s \mathrm{d}T}{T} \quad \Rightarrow \quad \int_0^{T_c} \frac{C_s \mathrm{d}T}{T} = \gamma T_c$$

4. In the lecture notes it is explained how the thermodynamic relations

$$F = E - ST, \qquad dF = -SdT - PdV, \qquad dE = TdS - PdV$$

follow from the Gibbs distribution for a system in equilibrium with a heat bath at temperature T. Show this in detail.

Solution:
The first formula:

$$\hat{\rho} = \mathrm{e}^{\beta(F-\hat{H})} \quad \Rightarrow \quad \ln\hat{\rho} = \beta(F-\hat{H}) \quad \Rightarrow \quad \langle \ln\hat{\rho}\rangle = \beta(F-\langle\hat{H}\rangle)$$

The operation $\langle\cdot\rangle$ is linear and $\langle F\rangle = F$ as F is constant or number, not operator as $\hat{\rho}$ or $\hat{H}$.

$$F = \langle\hat{H}\rangle - T(-k_b\langle\ln\hat{\rho}\rangle) = E - TS$$

The second formula:

$$\mathrm{Tr}\,(\hat{\rho}) = 1 \quad \Rightarrow \quad \mathrm{d}\mathrm{Tr}\,(\hat{\rho}) = 0 \quad \Rightarrow \quad \mathrm{Tr}\,(\,\mathrm{d}\hat{\rho}\,) = 0$$

The operation Tr is linear and in addition, commutative with the differential operator.

$$\begin{aligned}
0 = \mathrm{Tr}\left(\,\mathrm{d}\mathrm{e}^{\beta(F-\hat{H})}\,\right) &= \mathrm{Tr}\left(\beta\,\mathrm{d}F\,\mathrm{e}^{\beta(F-\hat{H})} - \beta\frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda}\,\mathrm{d}\lambda\,\mathrm{e}^{\beta(F-\hat{H})} - \frac{\mathrm{d}T}{k_bT^2}(F-\hat{H})\mathrm{e}^{\beta(F-\hat{H})}\right)\\
&= \beta\,\mathrm{d}F\,\mathrm{Tr}\,(\hat{\rho}) - \beta\,\mathrm{d}\lambda\,\mathrm{Tr}\left(\frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda}\hat{\rho}\right) - \frac{\mathrm{d}T}{T}\mathrm{Tr}\,(\hat{\rho}\ln\hat{\rho})\\
&= \beta\,\mathrm{d}F + \beta P\,\mathrm{d}V + \beta\,\mathrm{d}T\,S\\
&\Rightarrow \qquad \mathrm{d}F = -P\,\mathrm{d}V - \mathrm{d}T\,S
\end{aligned}$$

The third formula:

$$\begin{aligned}
E &= F + ST\\
\mathrm{d}E &= -P\,\mathrm{d}V - \mathrm{d}T\,S + T\,\mathrm{d}S + S\,\mathrm{d}T\\
&= T\,\mathrm{d}S - P\,\mathrm{d}V
\end{aligned}$$