8.333: Statistical Mechanics I Final Exam & Solutions 12/16/03 (1:30–4:30pm)

Answer all problems, but note that the first parts of each problem are easier than its last parts. Therefore, make sure to proceed to the next problem when you get stuck.

You may find the following information helpful:

Physical Constants

Electron mass	$m_e\approx 9.1\times 10^{-31}{\rm kg}$	Proton mass	$m_p pprox 1.7 imes 10^{-27} { m kg}$
Electron Charge	$e\approx 1.6\times 10^{-19}{\rm C}$	Planck's constant/ 2π	$\hbar\approx 1.1\times 10^{-34} \rm Js$
Speed of light	$c\approx 3.0\times 10^8 \rm ms^{-1}$	Stefan's constant	$\sigma\approx 5.7\times 10^{-8} \rm Wm^{-2}^{\circ} K^{-4}$
Boltzmann's constant	$k_B \approx 1.4 \times 10^{-23} J K^{-1}$	¹ Avogadro's number	$N_0 \approx 6.0 \times 10^{23} \mathrm{mol}^{-1}$
Gravitational constant	$G \approx 6.7 \times 10^{-11} \mathrm{Nm^2 kg}$	<u>r</u> -2	

Conversion Factors

$$1atm \equiv 1.0 \times 10^5 Nm^{-2}$$
 $1\mathring{A} \equiv 10^{-10}m$ $1eV \equiv 1.1 \times 10^4 \, {}^{\circ}K$

Thermodynamics

dE = TdS + dW	For a gas: $dW = -PdV$	For a film: $dW = \sigma dA$
	0	

Mathematical Formulas

1. Helium 4: ⁴He at low temperatures can be converted from liquid to solid by application of pressure. An interesting feature of the phase boundary is that the melting pressure is reduced slightly from its $T = 0^{\circ}K$ value, by approximately 20Nm^{-2} at its minimum at $T = 0.8^{\circ}K$. We will use a simple model of liquid and solid phases of ⁴He to account for this feature.

(a) By equating chemical potentials, or by any other technique, prove the Clausius– Clapeyron equation $(dP/dT)_{\text{melting}} = (s_{\ell} - s_s)/(v_{\ell} - v_s)$, where (v_{ℓ}, s_{ℓ}) and (v_s, s_s) are the volumes and entropies per atom in the liquid and solid phases respectively.

• *Clausius-Clapeyron equation* can be obtained by equating the chemical potentials at the phase boundary,

$$\mu_{\ell}(T, P) = \mu_s(T, P), \text{ and } \mu_{\ell}(T + \Delta T, P + \Delta P) = \mu_s(T + \Delta T, P + \Delta P).$$

Expanding the second equation, and using the thermodynamic identities

$$\left(\frac{\partial\mu}{\partial T}\right)_P = S$$
, and $\left(\frac{\partial\mu}{\partial P}\right)_T = -V$,

results in

$$\left(\frac{\partial P}{\partial T}\right)_{melting} = \frac{s_{\ell} - s_s}{v_{\ell} - v_s}$$

(b) The important excitations in liquid ⁴He at $T < 1^{\circ}K$ are phonons of velocity c. Calculate the contribution of these modes to the heat capacity per particle C_V^{ℓ}/N , of the liquid.

• The important excitations in liquid ⁴He at $T < 1^{\circ}K$ are phonons of velocity c. The corresponding dispersion relation is $\varepsilon(k) = \hbar ck$. From the average number of phonons in mode \vec{k} , given by $\langle n(\vec{k}) \rangle = [\exp(\beta \hbar ck) - 1]^{-1}$, we obtain the net excitation energy as

$$E_{phonons} = \sum_{\vec{k}} \frac{\hbar ck}{\exp(\beta\hbar ck) - 1}$$

= $V \times \int \frac{4\pi k^2 dk}{(2\pi)^3} \frac{\hbar ck}{\exp(\beta\hbar ck) - 1}$ (change variables to $x = \beta\hbar ck$)
= $\frac{V}{2\pi^2} \hbar c \left(\frac{k_B T}{\hbar c}\right)^4 \frac{6}{3!} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^2}{30} V \hbar c \left(\frac{k_B T}{\hbar c}\right)^4$,

where we have used

$$\zeta_4 \equiv \frac{1}{3!} \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{90}.$$

The corresponding heat capacity is now obtained as

$$C_V = \frac{dE}{dT} = \frac{2\pi^2}{15} V k_B \left(\frac{k_B T}{\hbar c}\right)^3,$$

resulting in a heat capacity per particle for the liquid of

$$\frac{C_V^\ell}{N} = \frac{2\pi^2}{15} k_B v_\ell \left(\frac{k_B T}{\hbar c}\right)^3.$$

(c) Calculate the low temperature heat capacity per particle C_V^s/N , of solid ⁴He in terms of longitudinal and transverse sound velocities c_L , and c_T .

• The elementary excitations of the solid are also phonons, but there are now two transverse sound modes of velocity c_T , and one longitudinal sound mode of velocity c_L . The contributions of these modes are additive, each similar inform to the liquid result calculated above, resulting in the final expression for solid heat capacity of

$$\frac{C_V^s}{N} = \frac{2\pi^2}{15} k_B v_s \left(\frac{k_B T}{\hbar}\right)^3 \times \left(\frac{2}{c_T^3} + \frac{1}{c_L^3}\right).$$

(d) Using the above results calculate the entropy difference $(s_{\ell} - s_s)$, assuming a single sound velocity $c \approx c_L \approx c_T$, and approximately equal volumes per particle $v_{\ell} \approx v_s \approx v$. Which phase (solid or liquid) has the higher entropy?

• The entropies can be calculated from the heat capacities as

$$s_{\ell}(T) = \int_{0}^{T} \frac{C_{V}^{\ell}(T')dT'}{T'} = \frac{2\pi^{2}}{45}k_{B}v_{\ell}\left(\frac{k_{B}T}{\hbar c}\right)^{3},$$

$$s_{s}(T) = \int_{0}^{T} \frac{C_{V}^{s}(T')dT'}{T'} = \frac{2\pi^{2}}{45}k_{B}v_{s}\left(\frac{k_{B}T}{\hbar}\right)^{3} \times \left(\frac{2}{c_{T}^{3}} + \frac{1}{c_{L}^{3}}\right)$$

Assuming approximately equal sound speeds $c \approx c_L \approx c_T \approx 300 \text{ms}^{-1}$, and specific volumes $v_\ell \approx v_s \approx v = 46 \text{\AA}^3$, we obtain the entropy difference

$$s_{\ell} - s_s \approx -\frac{4\pi^2}{45} k_B v \left(\frac{k_B T}{\hbar c}\right)^3.$$

The solid phase has more entropy than the liquid because it has two more phonon excitation bands.

(e) Assuming a small (temperature independent) volume difference $\delta v = v_{\ell} - v_s$, calculate the form of the melting curve. To explain the anomaly described at the beginning, which phase (solid or liquid) must have the higher density?

• Using the Clausius-Clapeyron equation, and the above calculation of the entropy difference, we get

$$\left(\frac{\partial P}{\partial T}\right)_{melting} = \frac{s_{\ell} - s_s}{v_{\ell} - v_s} = -\frac{4\pi^2}{45} k_B \frac{v}{\delta v} \left(\frac{k_B T}{\hbar c}\right)^3.$$

Integrating the above equation gives the melting curve

$$P_{melt}(T) = P(0) - \frac{\pi^2}{45} k_B \frac{v}{\delta v} \left(\frac{k_B T}{\hbar c}\right)^3 T.$$

To explain the reduction in pressure, we need $\delta v = v_{\ell} - v_s > 0$, i.e. the solid phase has the higher density, which is expected.

2. Surfactant Condensation: N surfactant molecules are added to the surface of water over an area A. They are subject to a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p_i}^2}{2m} + \frac{1}{2} \sum_{i,j} \mathcal{V}(\vec{r_i} - \vec{r_j}),$$

where \vec{r}_i and \vec{p}_i are two dimensional vectors indicating the position and momentum of particle *i*.

(a) Write down the expression for the partition function Z(N, T, A) in terms of integrals over $\vec{r_i}$ and $\vec{p_i}$, and perform the integrals over the momenta.

• The partition function is obtained by integrating the Boltzmann weight over phase space, as

$$Z(N,T,A) = \int \frac{\prod_{i=1}^{N} d^2 \vec{p}_i d^2 \vec{q}_i}{N! h^{2N}} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta \sum_{i$$

with $\beta = 1/(k_B T)$. The integrals over momenta are simple Gaussians, yielding

$$Z(N,T,A) = \frac{1}{N!} \frac{1}{\lambda^{2N}} \int \prod_{i=1}^{N} d^2 \vec{q}_i \exp\left[-\beta \sum_{i < j} \mathcal{V}(\vec{q}_i - \vec{q}_j)\right],$$

where as usual $\lambda = h/\sqrt{2\pi m k_B T}$ denotes the thermal wavelength.

The inter-particle potential $\mathcal{V}(\vec{r})$ is infinite for separations $|\vec{r}| < a$, and attractive for $|\vec{r}| > a$ such that $\int_{a}^{\infty} 2\pi r dr \mathcal{V}(r) = -u_0$.

(b) Estimate the total non–excluded area available in the positional phase space of the system of N particles.

• To estimate the joint phase space of particles with excluded areas, add them to the system one by one. The first one can occupy the whole area A, while the second can explore only $A - 2\Omega$, where $\Omega = \pi a^2$. Neglecting three body effects (i.e. in the dilute limit), the area available to the third particle is $(A - 2\Omega)$, and similarly $(A - n\Omega)$ for the *n*-th particle. Hence the joint excluded volume in this dilute limit is

$$A(A - \Omega)(A - 2\Omega) \cdots (A - (N - 1)\Omega) \approx (A - N\Omega/2)^N,$$

where the last approximation is obtained by pairing terms m and (N - m), and ignoring order of Ω^2 contributions to their product.

(c) Estimate the total *potential* energy of the system, assuming a constant density n = N/A. Assuming this potential energy for all configurations allowed in the previous part, write down an approximation for Z.

• Assuming a uniform density n = N/A, an average attractive potential energy, \overline{U} , is estimated as

$$\begin{split} \bar{U} &= \frac{1}{2} \sum_{i,j} \mathcal{V}_{\text{attr.}}(\vec{q_i} - \vec{q_j}) = \frac{1}{2} \int d^2 \vec{r_1} d^2 \vec{r_2} n(\vec{r_1}) n(\vec{r_2}) \mathcal{V}_{\text{attr.}}(\vec{r_1} - \vec{r_2}) \\ &\approx \frac{n^2}{2} A \int d^2 \vec{r} \, \mathcal{V}_{\text{attr.}}(\vec{r}) \equiv -\frac{N^2}{2A} \, u_0. \end{split}$$

Combining the previous results gives

$$Z(N,T,A) \approx \frac{1}{N!} \frac{1}{\lambda^{2N}} \left(A - N\Omega/2\right)^N \exp\left[\frac{\beta u_0 N^2}{2A}\right].$$

(d) The surface tension of water without surfactants is σ_0 , approximately independent of temperature. Calculate the surface tension $\sigma(n, T)$ in the presence of surfactants.

• Since the work done is changing the surface area is $dW = \sigma dA$, we have $dF = -TdS + \sigma dA + \mu dN$, where $F = -k_BT \ln Z$ is the free energy. Hence, the contribution of the surface tension of the film is

$$\sigma_s = -\left. \frac{\partial \ln Z}{\partial A} \right|_{T,N} = -\frac{Nk_BT}{A - N\Omega/2} + \frac{u_0 N^2}{2A^2},$$

which is a two-dimensional variant of the familiar van der Waals equation. Adding the (constant) contribution in the absence of surfactants gives

$$\sigma(n,T) = \sigma_0 - \left. \frac{\partial \ln Z}{\partial A} \right|_{T,N} = -\frac{Nk_BT}{A - N\Omega/2} + \frac{u_0N^2}{2A^2}.$$

(e) Show that below a certain temperature, T_c , the expression for σ is manifestly incorrect. What do you think happens at low temperatures?

• Thermodynamic stability requires $\delta\sigma\delta A \ge 0$, i.e. σ must be a monotonically increasing function of A at any temperature. This is the case at high temperatures where the first

term in the equation for σ_s dominates, but breaks down at low temperatures when the term from the attractive interactions becomes significant. The critical temperature is obtained by the usual conditions of $\partial \sigma_s / \partial A = \partial^2 \sigma_s / \partial A^2 = 0$, i.e. from

$$\left(\begin{array}{c} \left. \frac{\partial \sigma_s}{\partial A} \right|_T = \frac{Nk_BT}{(A - N\Omega/2)^2} - \frac{u_0N^2}{A^3} = 0 \\ \left. \left(\left. \frac{\partial^2 \sigma_s}{\partial A^2} \right|_T = -\frac{2Nk_BT}{(A - N\Omega/2)^3} + \frac{3u_0N^2}{A^4} = 0 \right. \right)$$

The two equations are simultaneously satisfied for $A_c = 3N\Omega/2$, at a temperature

$$T_c = \frac{8u_0}{27k_B\Omega}.$$

As in the van der Waals gas, at temperatures below T_c , the surfactants separate into a high density (liquid) and a low density (gas) phase.

(f) Compute the heat capacities, C_A and write down an expression for C_{σ} without explicit evaluation, due to the surfactants.

• The contribution of the surfactants to the energy of the film is given by

$$E_s = -\frac{\partial \ln Z}{\partial \beta} = 2N \times \frac{k_B T}{2} - \frac{u_0 N^2}{2A}.$$

The first term is due to the kinetic energy of the surfactants, while the second arises from their (mean-field) attraction. The heat capacities are then calculated as

$$C_A = \left. \frac{dQ}{dT} \right|_A = \left. \frac{\partial E}{\partial T} \right|_A = Nk_B,$$

and

$$C_{\sigma} = \left. \frac{dQ}{dT} \right|_{\sigma} = \left. \frac{\partial E}{\partial T} \right|_{\sigma} - \sigma \left. \frac{\partial A}{\partial T} \right|_{\sigma}.$$

3. Dirac Fermions are non-interacting particles of spin 1/2. The one-particle states come in pairs of positive and negative energies,

$$\mathcal{E}_{\pm}(\vec{k}) = \pm \sqrt{m^2 c^4 + \hbar^2 k^2 c^2}$$

,

independent of spin.

(a) For any fermionic system of chemical potential μ , show that the probability of finding an occupied state of energy $\mu + \delta$ is the same as that of finding an unoccupied state of energy $\mu - \delta$. (δ is any constant energy.)

• According to Fermi statistics, the probability of occupation of a state of of energy \mathcal{E} is

$$p[n(\mathcal{E})] = \frac{e^{\beta(\mu-\mathcal{E})n}}{1+e^{\beta(\mu-\mathcal{E})}}, \quad \text{for} \quad n=0,1$$

For a state of energy $\mu + \delta$,

$$p\left[n(\mu+\delta)\right] = \frac{e^{\beta\delta n}}{1+e^{\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu+\delta)=1\right] = \frac{e^{\beta\delta}}{1+e^{\beta\delta}} = \frac{1}{1+e^{-\beta\delta}}.$$

Similarly, for a state of energy $\mu - \delta$,

$$p\left[n(\mu-\delta)\right] = \frac{e^{-\beta\delta n}}{1+e^{-\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu-\delta)=0\right] = \frac{1}{1+e^{-\beta\delta}} = p\left[n(\mu+\delta)=1\right],$$

i.e. the probability of finding an occupied state of energy $\mu + \delta$ is the same as that of finding an unoccupied state of energy $\mu - \delta$.

(b) At zero temperature all negative energy Dirac states are occupied and all positive energy ones are empty, i.e. $\mu(T = 0) = 0$. Using the result in (a) find the chemical potential at finite temperatures T.

• The above result implies that for $\mu = 0$, $\langle n(\mathcal{E}) \rangle + \langle n - \mathcal{E} \rangle \rangle$ is unchanged for an temperature; any particle leaving an occupied negative energy state goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if μ stays at zero. Thus, the particle-hole symmetry enfrces $\mu(T) = 0$.

(c) Show that the mean excitation energy of this system at finite temperature satisfies

$$E(T) - E(0) = 4V \int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{\mathcal{E}_+(\vec{k})}{\exp(\beta \mathcal{E}_+(\vec{k})) + 1}$$

• Using the label +(-) for the positive (energy) states, the excitation energy is calculated as

$$E(T) - E(0) = \sum_{k,s_z} \left[\langle n_+(k) \rangle \mathcal{E}_+(k) + (1 - \langle n_-(k) \rangle) \mathcal{E}_-(k) \right]$$
$$= 2 \sum_k 2 \langle n_+(k) \rangle \mathcal{E}_+(k) = 4V \int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta \mathcal{E}_+(\vec{k})\right) + 1}.$$

- (d) Evaluate the integral in part (c) for massless Dirac particles (i.e. for m = 0).
- For m = 0, $\mathcal{E}_+(k) = \hbar c |k|$, and

$$E(T) - E(0) = 4V \int_0^\infty \frac{4\pi k^2 dk}{8\pi^3} \frac{\hbar ck}{e^{\beta\hbar ck} + 1} = \qquad (\text{set } \beta\hbar ck = x)$$
$$= \frac{2V}{\pi^2} k_B T \left(\frac{k_B T}{\hbar c}\right)^3 \int_0^\infty dx \frac{x^3}{e^x + 1}$$
$$= \frac{7\pi^2}{60} V k_B T \left(\frac{k_B T}{\hbar c}\right)^3.$$

For the final expression, we have noted that the needed integral is $3!f_4^-(1)$, and used the given value of $f_4^-(1) = 7\pi^4/720$.

- (e) Calculate the heat capacity, C_V , of such massless Dirac particles.
- The heat capacity can now be evaluated as

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{7\pi^2}{15} V k_B \left(\frac{k_B T}{\hbar c} \right)^3.$$

(f) Describe the qualitative dependence of the heat capacity at low temperature if the particles are massive.

• When $m \neq 0$, there is an energy gap between occupied and empty states, and we thus expect an exponentially activated energy, and hence heat capacity. For the low energy excitations,

$$\mathcal{E}_+(k) \approx mc^2 + \frac{\hbar^2 k^2}{2m} + \cdots,$$

and thus

$$\begin{split} E(T) - E(0) &\approx \frac{2V}{\pi^2} mc^2 e^{-\beta mc^2} \frac{4\pi\sqrt{\pi}}{\lambda^3} \int_0^\infty dx x^2 e^{-x} \\ &= \frac{48}{\sqrt{\pi}} \frac{V}{\lambda^3} mc^2 e^{-\beta mc^2}. \end{split}$$

The corresponding heat capacity, to leading order thus behaves as

$$C(T) \propto k_B \frac{V}{\lambda^3} \left(\beta mc^2\right)^2 e^{-\beta mc^2}.$$
