

Phys 210A — Spring 2024
Solution to Mock Final Exam

1. Short questions

(a) Explain the two key ingredients that underly van der Waals model of a “real” gas.

The van der Waals equation of state reads

$$(P + av^2)(v - v_0) = k_B T. \quad (1)$$

The pressure is modified relative to the ideal gas law by the term av^2 , which arises from the attraction between pairs of gas molecules. The molecules are also assumed to interact through the excluded-volume interaction, each molecule having a specific volume v_0 .

(b) Explain why $\frac{dP}{dV} > 0$ implies an instability.

The statement $\frac{dP}{dV} > 0$ is a condition for mechanical stability of the system. Supposing that decreasing pressure also decreases volume, the system will continue to decrease its volume until $\frac{dP}{dV} < 0$ and volume decrease is no longer favorable.

(c) Explain the difference in the physical origin of the thermodynamic singularity associated with first-order and second-order phase transitions.

For a first-order phase transition, the first thermodynamic derivative, such as the volume, experiences a discontinuity at the critical point. As a result, the quantity $\frac{\partial V}{\partial P}$ diverges at the critical point, since $\delta V \neq 0$ for small changes in P near the critical point. For second-order phase transition, there is no discontinuity in the first derivatives of the potential, such as V .

(d) Explain why the mean-field theory describes the Ising model exactly as the spatial dimension d approaches infinity.

The validity of the mean-field approach requires $\delta m^2 \equiv (m - \langle m \rangle)^2 \ll \langle m \rangle^2$, since we neglect terms of order δm^2 in the mean-field approach. The magnitude of these terms can be estimated by using the Ginzburg criterion $\delta m^2 \sim \xi^{4-d} \ll \frac{K^2}{a^d}$. For the Ising model, $\xi \sim |t|^{-1/2}$, so as $d \rightarrow \infty$, fluctuations can be neglected.

(e) Explain why there cannot be long-range order for the one-dimensional Ising model at any finite temperature.

Consider a system of spins with $M = xN$ spins pointed along one direction. The entropy associated with this ordering of spins is

$$S = k_B \ln \binom{N}{M}. \quad (2)$$

The free energy of this configuration is obtained in the $N \gg 1$ limit:

$$F = E - TS = N\{2Jx + k_B T [x \ln x + (1 - x) \ln(1 - x)]\}. \quad (3)$$

Minimizing with respect to x gives

$$x_0 = \frac{1}{e^{\frac{2J}{k_B T}} + 1}, \quad (4)$$

which is nonzero for $T > 0$. Therefore, there is always a macroscopic number of domain walls in the system and there is no ordering.

(f) What is the temperature dependence of the specific heat of an ideal Fermi gas at very low temperatures (i.e., where $k_B T$ is much smaller than the Fermi energy ε_F). Explain qualitatively how this temperature dependence arises.

The temperature dependence of the energy of a Fermi gas is as

$$\varepsilon - \varepsilon(T = 0) = C\varepsilon(T = 0)\frac{T^2}{\varepsilon_F}, \quad (5)$$

where C is a dimensionless constant. This dependence can be obtained on very general grounds: an excitation happens with probability proportional to $\frac{T}{\varepsilon_F}$ to excite. After this process, a region of phase space is freed with probability $\frac{T}{\varepsilon_F}$ for the excitation. Therefore, the probability of such an excitation goes as $P \sim \frac{T^2}{\varepsilon_F^2}$. The heat capacity of a degenerate Fermi gas is therefore $C \propto T$.

2. Confinement cost of a polymer

(a) Explain the physical origin of this confinement cost.

As explained in class, the origin of a finite confinement cost is tied to the number of distinct configurations of the polymer in a d -dimensional box of volume W^d . Provided that the polymer is tangled, that is, its length $R_0 \gg W$, then its typical size R_0 in the absence of confinement is given by

$$R_0 = a_0 L^{1/2}, \quad (6)$$

where a_0 is the usual spacing between monomers, and L is the number of links. For a Gaussian chain, that is, if the orientation of each link are random and independent, with the length scaling as the square root of the number of links. One expects that reducing the system size to a box of size W^d as opposed to R_0^d will restrict the number of microstates and, thus, the entropy.

(b): A self-avoiding polymer is larger than the non-interacting Gaussian chain in the long length ($L \gg 1$) limit, with the expected end-to-end distance being $R = aL^\nu$, where a is a microscopic size and the exponent ν is between 1/2 and 1. Find how the confinement cost scales with W in term of the exponent ν for the self-avoiding polymer.

The energy cost of this confinement can be estimate from counting the number of states as follows. Consider diving the polymer into “blobs” of length L_b . In the absence of the box, the size of the polymer is

$$R = aL^\nu. \quad (7)$$

In the presence of the box, it is given by the same expression as with the characteristic length scale now being given by the size of the box W :

$$W = aL_b^\nu. \quad (8)$$

Note that the inequality $R \gg W$ implies $L \gg L_b$. We expect that the reduction in the number of states because of this loss of phase space is exponentially small in system size:

$$\Delta\Omega = e^{-A\frac{L}{L_b}}, \Delta S = k_B \frac{L}{L_b} - k_B \ln A. \quad (9)$$

Aside from the numerical constant A which cannot be determined from scaling analysis, we estimate the free energy cost (note the sign!) from our expression for W :

$$F_{\text{confine}} \propto T\Delta S = \frac{k_B T L}{(W/a)^{1/\nu}}. \quad (10)$$

For the Gaussian case, we recover the formula derived in class; if we place additional constraints on the polymer, ν may be greater than 1/2, and the confinement energy may be smaller.

3. Quantum ideal gas

Show that in d spatial dimensions, the average energy $E \equiv \langle \mathcal{H} \rangle$ of a quantum ideal gas with the Hamiltonian $\mathcal{H} = \frac{p^2}{2m}$ is given by $E = cPV$. Find how the constant c depends on d for bosons and fermions. Based on your solution, what can you say about the classical gas obeying Boltzmann statistics?

The grand potential of an ideal gas is given by

$$\Omega = -PV = -T \int_0^\infty d\varepsilon D(\varepsilon) \ln \mathcal{Z}(\varepsilon), \quad (11)$$

with density of states $D(\varepsilon)$ and grand partition function $\ln \mathcal{Z}(\varepsilon)$. The latter is given by

$$\ln \mathcal{Z}_{\text{FD/BE}}(\varepsilon) = \pm \ln \left[1 \pm e^{\beta(\mu-\varepsilon)} \right]. \quad (12)$$

The density of states in d dimensions for fermions with degeneracy g_s per momentum state was found in previous homeworks:

$$D(\varepsilon) = \frac{g_s V}{\Gamma(d/2)} \left(\frac{2\pi m}{h} \right)^{d/2} \varepsilon^{d/2-1}. \quad (13)$$

The average energy is also found through the density of states:

$$E = \int_0^\infty d\varepsilon D(\varepsilon) n(\varepsilon) \varepsilon, \quad (14)$$

where $n(\varepsilon)$ is the appropriate weight assigned to the single particle state. For fermions/bosons, the weight is

$$n_{\text{FD/BE}} = \frac{1}{e^{\beta(\varepsilon-\mu)} \pm 1}. \quad (15)$$

To compare energy to the grand potential, we can integrate Eq. (11) by parts:

$$\Omega = -\frac{2}{d} \int_0^\infty d\varepsilon D(\varepsilon) n(\varepsilon) \varepsilon. \quad (16)$$

Therefore, $E = \frac{\alpha}{d} PV$, with α being the power of momentum in the dispersion and d being the dimensionality.

5. Vibrational Specific Heat of Solids

In this problem, we will analyze the contribution to the specific heat of a crystalline solid due to its quantized lattice vibrations, the *phonons*. In the Einstein model of lattice vibration, one approximates a lattice of N atoms by noninteracting (quantum) harmonic oscillators, each with frequency ω . Three oscillators per atom are used to describe motion in the x , y , z directions.

(a) Compute the partition function of this system, and hence obtain the mean energy $\bar{\varepsilon}(T; \omega)$ per atom.

Since we are interested in the low- T as well as the high- T regime, we must work with the quantum harmonic oscillator. In the limit of high temperature, we expect to recover the classical result from a previous homework. The energies of a quantum harmonic oscillator are given by

$$\varepsilon_n = \hbar\omega \left(n_x + n_y + n_z + \frac{3}{2} \right). \quad (17)$$

The partition function is found by summing over all quantum numbers n_i :

$$Z = \left(\sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} e^{-\beta\hbar\omega(n_x+n_y+n_z+\frac{3}{2})} \right)^N = \left(\frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \right)^{3N} \quad (18)$$

The total energy is found from Z as

$$\bar{\varepsilon}(T; \omega) = -\frac{\partial \ln Z}{\partial \beta} = 3N\hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right), \quad (19)$$

and the energy per atom is $\bar{\varepsilon}(\omega, T) = \frac{E}{N}$.

(b) Find the specific heat $C_V(T)$. Show that in the limit $T \rightarrow \infty$, the *Dulong-Petit law* of classical physics is recovered. Show also that $C_V(T) \rightarrow 0$ as $T \rightarrow 0$.

The heat capacity C_V is found from the total energy:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3Nk_B \frac{(\beta\hbar\omega)^2 e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}. \quad (20)$$

For high temperature $\beta\hbar\omega \ll 1$, we can see $\exp(-\beta\hbar\omega) \simeq 1 - \beta\hbar\omega$, giving $C_V \simeq 3Nk_B$. In the low temperature limit $\beta\hbar\omega \gg 1$, the exponential in the denominator dominates and $C_V \simeq 3Nk_B(\beta\hbar\omega)^2 \exp(-\beta\hbar\omega)$. This exponential decay is not consistent with experiment.

The explanation of vanishing specific heat at low T , as a result of quantum mechanics, was a great triumph of the Einstein theory. A more quantitatively accurate theory was due to Debye, who assumed that each oscillator can take on a range of frequencies ω_i , corresponding to the different normal mode \mathbf{k} of lattice vibration. Alternatively, one can view the quantized lattice vibrations (phonons) as an ideal Bose gas, with energies $\varepsilon(\mathbf{k}) = \hbar\omega(\mathbf{k})$. It is useful to introduce the frequency distribution function $\mathcal{D}(\omega)$, where $\mathcal{D}(\omega)d\omega$ describes the number of modes having frequency between ω and $\omega + d\omega$.

(c) What is the mean energy per atom $\bar{\varepsilon}(T)$ in terms of $\mathcal{D}(\omega)$? Find $\bar{\varepsilon}(T)$ in the limit of high temperature, thereby showing that the high temperature behavior is independent of the choice $\mathcal{D}(\omega)$.

Given the phonon density of states $\mathcal{D}(\omega)$, we can find the mean energy just as we do for any Bose or Fermi gas:

$$\bar{\varepsilon}(T) = \frac{V}{N} \int_{-\infty}^{\infty} d\omega \mathcal{D}(\omega) \hbar\omega n_B(\omega), \quad n_B(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}, \quad 3N = \int_{-\infty}^{\infty} d\omega \mathcal{D}(\omega). \quad (21)$$

As seen in part (b), we expect that the total number of independent modes is equal to $3N$, which fixes the total number of modes. At high temperature, we expand $\exp(\beta\hbar\omega) - 1 \simeq \beta\hbar\omega$, removing the frequency-dependence. Using Eq. (21), we recover

$$\bar{\varepsilon}(T) = \frac{3}{\beta}, C_V = 3Nk_B, \quad (22)$$

as in the classical case.

(d) Low temperature behavior does depend on the form of $\mathcal{D}(\omega)$, which can be obtained from the knowledge of the phonon dispersion relation $\omega(\mathbf{k})$. Assuming that $\omega(\mathbf{k}) = v|\mathbf{k}|$, where v is the sound speed, show that $\mathcal{D}(\omega) = \alpha V\omega^2$, with V being the volume of the solid and α being a proportionality constant.

The DOS for a three-dimensional system composed of linearly dispersing particles is found as

$$\mathcal{D}(\omega)d\omega = 4\pi g V k(\omega)^2 \frac{dk}{d\omega} d\omega = \alpha V \omega^2, \quad (23)$$

where we used the fact that the group velocity is a constant and $k \propto \omega$. The degeneracy g and the speed of sound are also included in α .

To satisfy the normalization condition on $\mathcal{D}(\omega)$, Debye Debye introduced an approximation in which he took the result of (d) up to some cutoff frequency ω_D , chosen to give a total of $3N$ modes. For $\omega > \omega_D$, Debye assumed $\mathcal{D}(\omega) = 0$.

(e) Using Debye's approximation, write down an expression for the mean energy per atom $\bar{\varepsilon}$ in terms of $\hbar\omega_D$ and a dimensionless parameter T/T_D , where the *Debye temperature* is defined by $k_B T_D = \hbar\omega_D$.

Taking the DOS cutoffs to be $\omega = 0$ below and ω_D above, we write the full energy as

$$\frac{\bar{\varepsilon}(T)}{V} = \frac{\hbar}{2v^3\pi^2} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1}. \quad (24)$$

To obtain the temperature dependence for small T , it is entirely unnecessary to perform the integral, since the upper limit becomes infinity, and the result will just be a constant. To obtain the temperature dependence, we can define $x = \beta\hbar\omega$ to rewrite the integral in a dimensionless form (defining $\hbar\omega_D = k_B T_D$):

$$\frac{\bar{\varepsilon}(T)}{V} = \frac{(k_B T)^4}{2v^3\hbar^3\pi^2} \int_0^{T_D/T} dx \frac{x^3}{e^x - 1}. \quad (25)$$

At low temperatures, the upper limit of integration can be taken to infinity, so the energy scales as T^4 . The energy at low temperature is therefore

$$\bar{\varepsilon}(T) = \frac{(k_B T)^4}{2v^3 \hbar^3 \pi^2} \int_0^\infty dx \frac{x^3}{e^x - 1}. \quad (26)$$

(f) Find the vibrational specific heat $C_V(T)$ for $T \ll T_D$. Show that the T -dependence follows generally from the $k \rightarrow 0$ limit of the dispersion relation and is insensitive to Debye's approximation.

From Eq.(26), it can be seen that the DOS does not play any role in the temperature scaling of the energy; all it will do is modify the power of x in the numerator of the integrand. Provided that power is one or greater, the integral converges and the result is a constant. In the particular case of Debye's approximation, it can be seen from the definition of DOS that there are d powers of ω in the numerator of the energy, meaning that $C_V \propto T^d$ in d spatial dimensions. Finally, let us actually calculate the value of $C_V(T)$ at low temperatures in the Debye approximation. We will first need the value of the Debye temperature in terms of the speed of sound v , found from the normalization condition:

$$\frac{3N}{V} = \frac{\omega_D^3}{6v^3 \pi^2}, \quad \hbar \omega_D = k_B T_D. \quad (27)$$

We will use the expression Eq. (24) and take a derivative with respect to temperature, obtaining

$$C_V = N k_B \frac{k_B^3 T^3}{2v^3 \pi^2} \int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2} \quad (28)$$

in the limit $T = 0$. Using our result for the Debye temperature, we finally obtain

$$C_V = 9N k_B \frac{T^3}{T_D^3} I, \quad I = \int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2}. \quad (29)$$

This integral can be evaluated in terms of special functions. After an integration by parts, the integral becomes

$$I = 4 \int_0^\infty dx \frac{x^3}{e^x - 1} \quad (30)$$

The denominator can be rewritten in terms of a geometric series and the result can be resummed, giving $I = 4\Gamma(4)\zeta(4) = \frac{4\pi^4}{15}$. The final answer is

$$C_V = N k_B \frac{12\pi^4}{5} \frac{T^3}{T_D^3}. \quad (31)$$