

Phys 210A — Spring 2024
Problem Set #3: Quantum Statistical Mechanics
Due date: Wednesday, May 22

1. **Weakly-interacting gas** — Consider a system of N molecules (with $N \rightarrow \infty$) contained in a box of volume V (with $V \rightarrow \infty$ but N/V finite). The Hamiltonian of the system is

$$\mathcal{H}_N = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i \neq j} u(|\vec{r}_i - \vec{r}_j|)$$

where \vec{p}_i and \vec{r}_i are, respectively, the moment and position of the i^{th} molecule, and $u(r)$ is an interaction potential which depends on the inter-particle distance r . In this problem, you will derive the equation of state of this system.

- (a) It will be convenient to work in the grand canonical ensemble. Write down the general expression for the Grand partition function $\mathcal{Z}(\beta, V, \mu)$ for this system at inverse temperature β and chemical potential μ . Write out explicitly the partition sum up to $N = 2$. Express your result in terms of a power series in

$$\zeta = \frac{e^{\beta\mu}}{h^3} \int d^3\vec{p} e^{-\beta p^2/(2m)},$$

i.e., $\mathcal{Z} = 1 + I_1\zeta + \frac{1}{2}I_2\zeta^2 + \dots$, with I_1, I_2 being integrals over the position vector(s). Use $\log \mathcal{Z} = \beta PV$ to express βPV as a power series in ζ to $O(\zeta^2)$.

- (b) Write down the average number \bar{N} in term of thermodynamic derivative of $\log \mathcal{Z}$; express the result as a power series in ζ to $O(\zeta^2)$. Invert the result by expressing ζ as a power series of the particle density $\rho \equiv \bar{N}/V$ to $O(\rho^2)$.
- (c) Combine this results in (a) and (b) to obtain βP as a power series in ρ to $O(\rho^2)$, i.e., $\beta P = \rho + B_2\rho^2$. Such an expansion is known as the virial expansion. Explain under what conditions is the virial expansion valid. Show that the second virial coefficient B_2 can be written as $B_2 = \int d^3\vec{r} f(r)$ where $f(r)$ is a function of $\beta u(r)$.
- (d) For repulsive potential, e.g., $u(r) = A/r$, plot $f(r)$ and indicate whether B_2 is positive or negative. How does the interaction modify the equation of state from that of the ideal gas?
- (e) Next, suppose the interaction has a repulsive hard core (of radius r_0) and an attractive tail, i.e., $u(r) = +\infty$ for $r < r_0$, and $u(r) = -u_0 e^{-(r-r_0)/\ell}$ for $r \geq r_0$, where $u_0 > 0$ is the magnitude of the attractive interaction and ℓ is the length scale of attraction. Find an explicit expression for B_2 if $\beta u_0 \ll 1$, i.e., if the strength of attraction is weak compared to thermal energy. Based on the temperature dependence of B_2 you have derived, what do you think happens to this system as the temperature is reduced?

2. **Fluctuation in occupation number** — For system of non-interacting, indistinguishable particles obeying Bose-Einstein, Fermi-Dirac, and Maxwell-Boltzmann statistics, write down the probability distribution function $\mathcal{P}_\alpha(n_\alpha; T, \mu)$ of finding n_α particles in a single-particle state α of energy ε_α if the system is in equilibrium with a reservoir kept at temperature T and chemical potential μ . Express \mathcal{P} in terms of n_α and the average $\langle n_\alpha \rangle$. Compute the relative fluctuation in the occupation number, $\Delta n_\alpha / \langle n_\alpha \rangle$, where $\Delta n_\alpha \equiv \sqrt{\langle n_\alpha^2 \rangle - \langle n_\alpha \rangle^2}$. What do your results tell you about the condition when the classical result is significantly affected by quantum fluctuation?
3. **Compressibility of a free electron gas** — Consider a gas of free electrons of density ρ placed in a d -dimensional box of volume V . In this problem, you will find the isothermal compressibility κ_T in the limit $T \rightarrow 0$.
- (a) Write down the grand potential $\log \mathcal{Z}(\beta, V, \mu)$ for the free electrons as a sum over the allowed state α involving the kinetic energy of that state ε_α . [Note that an electron has two allowed spin values which does not affect the energy.] Work out the single-particle density of state $\mathcal{D}(\varepsilon)$ in d -dimension and express $\log \mathcal{Z}$ and hence the pressure P in term of an integral over $\mathcal{D}(\varepsilon)$. Also express the density ρ in term of an integral of $\mathcal{D}(\varepsilon)$.
- (b) In the limit $T \rightarrow 0$, perform the above integral for ρ and express your result in term of the Fermi energy $\varepsilon_F \equiv \mu(T = 0)$. Show that the integral for P can also be performed exactly; thus express the pressure P in term of ε_F .
- (c) Find the isothermal compressibility $\kappa_T \equiv -V^{-1} \left(\frac{\partial V}{\partial P} \right)_{N,T}$ as a function of the density ρ . [Hint: Express κ_T in term of $\partial P / \partial \rho$ and note that ε_F depends on ρ .]
4. **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, *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.
- (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 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 $\mathcal{D}(\omega)$. [Note the normalization condition on $\mathcal{D}(\omega)$ is $\int_0^\infty d\omega \mathcal{D}(\omega) = 3N$.]
- (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 $\omega(\mathbf{k}) = v \cdot |\mathbf{k}|$, 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.

To satisfy the normalization condition on $\mathcal{D}(\omega)$, 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 that $\mathcal{D}(\omega) = 0$.

- (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_D/T , where the *Debye temperature* T_D is defined by $k_B T_D = \hbar\omega_D$.
- (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. What is the T -dependence for a d -dimensional solid?

5. Ideal Bose Gas in Two Dimensions — Consider an ideal gas consisting of N spin-0 particles of mass m in a two-dimensional periodic box of size $L \times L$, kept at a constant temperature T . In studying this problem, it will be convenient to introduce the grand canonical ensemble as a mathematical device.

- (a) Find the density of states, $\mathcal{D}(\varepsilon)$.
- (b) Write down the pressure P in terms of the fugacity f ; write down also the auxiliary condition which determines $f(N)$.
- (c) In the limit of low density and high temperature, find the equation of state $P(N)$ to leading nonlinear order.
- (d) Show that in the thermodynamic limit, no Bose-Einstein condensation occurs at any finite temperature. More specifically, show that $T_{BE} \propto 1/\log(N)$.