

**PHYSICS 140A : STATISTICAL PHYSICS
FINAL EXAMINATION SOLUTIONS**

(1) Provide clear, accurate, and brief answers for each of the following:0

(a) What is the Gibbs-Duhem for a single-component system and how is it derived from homogeneity of the energy function $E(S, V, N)$? [5 points]

(b) What are the separate conditions guaranteeing thermal, mechanical, and chemical (or particle) equilibrium between two single-component systems, and what equalities do they entail? [5 points]

(c) What is a virial equation of state? What are the dimensions of the k^{th} virial coefficient B_k , and on what intensive quantity or quantities does B_k depend? [5 points]

(d) Consider a noninteracting classical system consisting of distinguishable particles situated on each of N_s sites. The available energy states for each particle are $\varepsilon_1 = 0$, $\varepsilon_2 = 0$, $\varepsilon_3 = \Delta$, and $\varepsilon_4 = \Omega$. What is the free energy $F(T, N_s)$? What is the entropy at $T = 0$? [5 points]

(e) For a noninteracting Bose gas with density of states $g(\varepsilon) = A \varepsilon^5$, find the condensation temperature $T_c(n)$. You may find the following helpful:

$$\int_0^{\infty} dt \frac{t^{r-1}}{\exp(t) - 1} = \Gamma(r) \zeta(r) \quad .$$

[5 points]

Solution :

(a) The Gibbs-Duhem relation for single-component systems relates and three independent intensive quantities (typically T , p , and n). It follows from the fact that $E(S, V, N)$ is homogeneous of degree 1 in its arguments. Euler's theorem therefore says

$$E = S \left(\frac{\partial E}{\partial S} \right)_{V,N} + V \left(\frac{\partial E}{\partial V} \right)_{S,N} + N \left(\frac{\partial E}{\partial N} \right)_{S,V} = TS - pV + \mu N \quad .$$

Taking the differential,

$$dE = T dS + S dT - p dV - V dp + \mu dN + N d\mu \quad \Rightarrow \quad S dT - V dp + N d\mu = 0 \quad ,$$

since $dE = T dS - p dV + \mu dN$.

(b) In thermal equilibrium, two systems are free to exchange energy, and $T_1 = T_2$. In mechanical equilibrium, to systems are free to exchange volume, and $p_1/T_1 = p_2/T_2$. In chemical (particle) equilibrium, two systems are free to exchange particle number, and $\mu_1/T_1 = \mu_2/T_2$. This is because entropy must be maximized with respect to exchanges of energy, volume, and particle number, respectively, and

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN \quad .$$

(c) A virial equation of state is an expansion in powers of the density. Typically the lowest order form is the ideal gas law $p = nk_B T$. To higher order,

$$p = nk_B T (1 + B_2(T) n + B_3(T) n^2 + \dots) \quad .$$

Since $[n] = V^{-1}$, we must have $[B_k(T)] = V^{k-1}$. Each virial coefficient is a function of temperature alone.

(d) We have $Z(T, N_s) = (2 + e^{-\beta\Delta} + e^{-\beta\Omega})^{N_s}$ and thus

$$F(T, N_s) = -k_B T \log Z(T, N_s) = -N_s k_B T \log (2 + e^{-\Delta/k_B T} + e^{-\Omega/k_B T}) \quad .$$

Since the lowest energy state is doubly degenerate, $S(T = 0, N_s) = N_s k_B \log 2$.

(e) The implicit relation for $T_c(n)$ in a noninteracting Bose gas is

$$n = \int_0^\infty d\varepsilon \frac{g(\varepsilon)}{\exp(\varepsilon/k_B T_c) - 1} \quad .$$

For $g(\varepsilon) = A \varepsilon^{r-1}$, we have, after substituting $t \equiv \varepsilon/k_B T$,

$$n = A \Gamma(r) \zeta(r) (k_B T_c)^r \quad \Rightarrow \quad k_B T_c(n) = \left(\frac{n}{\Gamma(r) \zeta(r) A} \right)^{1/r} \quad .$$

For our case, $r = 6$.

(2) A surface consists of a collection of N_s sites, each of which hosts an electric dipole $\mathbf{p}_j = \mu_0 \hat{\mathbf{n}}_j$. In an electric field \mathbf{E} , the energy of the j^{th} dipole is $-\mathbf{E} \cdot \mathbf{p}_j$. Each $\hat{\mathbf{n}}_j$ is a unit vector in $d = 3$ dimensions and can be expressed in terms of Cartesian components as $\hat{\mathbf{n}}_j = (\sin \theta_j \cos \phi_j, \sin \theta_j \sin \phi_j, \cos \theta_j)$ with polar angle $\theta_j \in [0, \pi]$ and azimuthal angle $\phi_j \in [0, 2\pi)$. The dipoles are situated at unique locations in the crystal, and are thus distinguishable.

(a) What is the partition function $Z(T, N_s, E)$? You may assume \mathbf{E} is parallel to $\hat{\mathbf{z}}$. *Hint: First find the single site partition function $\zeta(T, E)$.* [5 points]

(b) Find the average dipole moment $\langle \mathbf{p} \rangle$. [5 points]

(c) Now suppose that each site is either empty, with energy zero, or contains a dipole with energy $-\mathbf{E} \cdot \mathbf{p}$. The chemical potential for dipoles is μ . Find the grand potential $\Omega(T, N_s, \mu, \mathbf{E})$. [10 points]

(d) Next, let the surface be in equilibrium with a nonrelativistic monatomic ideal gas of number density n . Gas atoms can be adsorbed on the surface, in which case they acquire a dipole moment and are bound to a surface adsorption site with energy $-\Delta < 0$. They can also desorb and join the gas as mass m atoms with zero dipole moment $\mathbf{p} = 0$ (not to be confused with momentum!). Find the surface site occupation fraction $f = N_{\text{surface}}/N_s$ in terms of T, E, Δ , the gas number density n , and other constants. [5 points]

Solution :

(a) The single site partition function is

$$\begin{aligned}\zeta(T, E) &= \int \frac{d\hat{\mathbf{n}}}{4\pi} e^{-\beta h(\hat{\mathbf{n}})} = \frac{1}{4\pi} \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi e^{\mu_0 E \cos \theta / k_B T} \\ &= \frac{1}{2} \int_{-1}^1 dx e^{\mu_0 E x / k_B T} = \frac{k_B T}{\mu_0 E} \sinh\left(\frac{\mu_0 E}{k_B T}\right) ,\end{aligned}$$

with $h(\hat{\mathbf{n}}) = -\mu_0 \mathbf{E} \cdot \hat{\mathbf{n}}$. For N_s independent and distinguishable sites, the partition function is $Z(T, N_s, E) = \zeta(T, E)^{N_s}$.

(b) The Helmholtz free energy is

$$F(T, N_s, E) = -N_s k_B T \log \zeta(T, E) = -N_s k_B T \log\left(\frac{\sinh u}{u}\right)$$

where $u \equiv \mu_0 E / k_B T$. The average moment is

$$\begin{aligned}\langle \mathbf{p} \rangle &= \mu_0 \langle \hat{\mathbf{n}} \rangle = -\frac{1}{N_s} \left(\frac{\partial F}{\partial \mathbf{E}} \right)_{T, N_s} = -\frac{\hat{\mathbf{E}}}{N_s} \left(\frac{\partial F}{\partial E} \right)_{T, N_s} \\ &= \mu_0 \left\{ \operatorname{ctnh}\left(\frac{\mu_0 E}{k_B T}\right) - \frac{k_B T}{\mu_0 E} \right\} \hat{\mathbf{E}} .\end{aligned}$$

(c) The grand canonical partition function is

$$\Xi(T, N_s, E, \mu) = \left(1 + e^{\mu/k_B T} \zeta(T, E) \right)^{N_s}$$

and therefore

$$\Omega(T, N_s, E, \mu) = -N_s k_B T \log\left(1 + e^{\mu/k_B T} \zeta(T, E) \right) .$$

(d) The surface coverage fraction is

$$f = \frac{\langle \hat{N}_{\text{surface}} \rangle}{N_s} = -\frac{1}{N_s} \left(\frac{\partial \Omega}{\partial \mu} \right)_{T, N_s, E}$$

where $z = \exp(\mu/k_B T)$ is the surface fugacity, and where

$$\Omega(T, N_s, E, \Delta, \mu) = -N_s k_B T \log\left(1 + e^{(\mu+\Delta)/k_B T} \zeta(T, E) \right) .$$

to account for the binding energy of the adsorbates. Since the surface adsorbate is in thermal and particle equilibrium with a monatomic ideal gas the temperatures and chemical

potentials are the same for both systems, hence the fugacities are the same as well. The ideal gas fugacity is $z = n\lambda_T^3$, hence

$$f(T, E, \Delta, n) = \frac{z \zeta e^{\Delta/k_B T}}{1 + z \zeta e^{\Delta/k_B T}} = \frac{n\lambda_T^3 \zeta(T, E) e^{\Delta/k_B T}}{1 + n\lambda_T^3 \zeta(T, E) e^{\Delta/k_B T}} .$$

(3) Consider an ultrarelativistic gas of N identical and indistinguishable particles in three space dimensions. The Hamiltonian of each particle is $\hat{h} = c|\mathbf{p}|$.

(a) What is the single particle partition function ζ . Assume the system is confined to a box of volume V . [5 points]

(b) What is the Helmholtz free energy $F(T, V, N)$? [5 points]

(c) What is the entropy $S(T, V, N)$? [5 points]

(d) What is the chemical potential $\mu(T, V, N)$? [5 points]

(e) What is the heat capacity at constant volume $C_{V,N}(T, V, N)$? [5 points]

Solution :

(a) Integrating over momentum and summing over electronic states,

$$\zeta(T, V) = V \int \frac{d^3 p}{h^3} e^{-c|\mathbf{p}|/k_B T} = \frac{V}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 .$$

(b) We have $F = -k_B T \ln Z(T, V, N)$ where $Z = \zeta^N / N!$. Thus,

$$F(T, V, N) = -Nk_B T \log \left[\frac{V}{N\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 \right] - Nk_B T ,$$

where we have used Stirling's rule $\ln K! = K \ln K - K + \mathcal{O}(\ln K)$ for K large.

(c) The entropy is

$$S(T, V, N) = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = Nk_B \log \left[\frac{V}{N\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 \right] + 4Nk_B .$$

(d) The chemical potential is

$$\mu(T, V, N) = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \log \left[\frac{V}{N\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 \right] .$$

(e) The heat capacity is

$$C_{V,N} = T \left(\frac{\partial S}{\partial T} \right)_{V,N} = 3Nk_B .$$

(4) Consider a three-dimensional Bose gas of particles which have two internal polarization states, labeled by $\sigma = \pm 1$. The single particle energies are given by (with $\Delta > 0$)

$$\varepsilon(\mathbf{p}, \sigma) = \frac{\mathbf{p}^2}{2m} + \sigma\Delta \quad ,$$

(a) Find the density of states per unit volume $g(\varepsilon)$. Recall that the DOS for nonrelativistic particles in three dimensions is given by

$$g_0(\varepsilon) = \frac{\sqrt{2m^3}}{2\pi^2\hbar^3} \varepsilon^{1/2} \Theta(\varepsilon) \quad .$$

Hint: The answer can be expressed as a sum of the DOS for $\sigma = \pm 1$ polarization states.
[10 points]

(b) Into what single particle state does the gas condense? What is the value of the chemical potential μ in the condensed phase? [5 points]

(c) Find an implicit expression for the condensation temperature $T_c(n, \Delta)$, and from it obtain an analytical expression for $T_c(n, \Delta = \infty)$. You may find the following useful:

$$\int_{-\infty}^{\infty} d\varepsilon \frac{g_0(\varepsilon)}{e^{(\varepsilon-\mu)/k_B T} - 1} = \lambda_T^{-3} \text{Li}_{3/2}(e^{\mu/k_B T})$$

as well as $\text{Li}_s(1) = \zeta(s)$. *Hint: This obviates the need for you to do any actual integrals!*
[10 points]

(d) When $\Delta = \infty$, the condensation temperature should agree with the familiar result for three-dimensional Bose condensation. Assuming $\Delta \gg k_B T_c(n, \Delta = \infty)$, find analytically the leading order difference $T_c(n, \Delta) - T_c(n, \Delta = \infty)$. [100 quatlouos extra credit]

Solution :

(a) Let $g_0(\varepsilon)$ be the DOS per unit volume for the case $\Delta = 0$. Then

$$g_0(\varepsilon) d\varepsilon = \frac{d^3k}{(2\pi)^3} = \frac{k^2 dk}{2\pi^2} \quad \Rightarrow \quad g_0(\varepsilon) = \frac{\sqrt{2m^3}}{2\pi^2\hbar^3} \varepsilon^{1/2} \Theta(\varepsilon) \quad .$$

For finite Δ , the single particle energies are shifted uniformly by $\pm\Delta$ for the $\sigma = \pm 1$ states, hence

$$g(\varepsilon) = g_0(\varepsilon + \Delta) + g_0(\varepsilon - \Delta) \quad .$$

(b) In the condensed phase, μ is the minimum value for the single particle energy, which occurs for $\mathbf{k} = 0$ and $\sigma = -1$. Thus, the system condenses into the state $|\mathbf{k} = 0, \sigma = -1\rangle$, and the chemical potential in the condensed phase is $\mu = -\Delta$.

(c) For Bose statistics, we have in the uncondensed phase,

$$n = \int_{-\infty}^{\infty} d\varepsilon \frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/k_B T} - 1} = \text{Li}_{3/2}(e^{(\mu+\Delta)/k_B T}) \lambda_T^{-3} + \text{Li}_{3/2}(e^{(\mu-\Delta)/k_B T}) \lambda_T^{-3} .$$

In the condensed phase, $\mu = -\Delta - \mathcal{O}(N^{-1})$ is pinned just below the lowest single particle energy, which occurs for $\mathbf{k} = \mathbf{p}/\hbar = 0$ and $\sigma = -1$. We then have

$$n = n_0 + \zeta(3/2) \lambda_T^{-3} + \text{Li}_{3/2}(e^{-2\Delta/k_B T}) \lambda_T^{-3} .$$

To find the critical temperature, set $n_0 = 0$ and $\mu = -\Delta$:

$$n = \zeta(3/2) \lambda_{T_c}^{-3} + \text{Li}_{3/2}(e^{-2\Delta/k_B T_c}) \lambda_{T_c}^{-3} .$$

This is a nonlinear and implicit equation for $T_c(n, \Delta)$. When $\Delta = \infty$, we have

$$k_B T_c^\infty(n) = \frac{2\pi\hbar^2}{m} \left(\frac{n}{\zeta(3/2)} \right)^{2/3} .$$

(d) For finite Δ , we still have the implicit nonlinear equation to solve, but in the limit $\Delta \gg k_B T_c$, we can expand $T_c(\Delta) = T_c^\infty + \Delta T_c(\Delta)$. We may then set $T_c(n, \Delta)$ to $T_c^\infty(n)$ in the second term of our nonlinear implicit equation, move this term to the LHS, whence

$$\zeta(3/2) \lambda_{T_c}^{-3} \approx n - \text{Li}_{3/2}(e^{-2\Delta/k_B T_c^\infty}) \lambda_{T_c^\infty}^{-3} .$$

which is a simple algebraic equation for $T_c(n, \Delta)$. The second term on the RHS is tiny since $\Delta \gg k_B T_c^\infty$. We then find

$$T_c(n, \Delta) = T_c^\infty(n) \left\{ 1 - \frac{3}{2} e^{-2\Delta/k_B T_c^\infty(n)} + \mathcal{O}(e^{-4\Delta/k_B T_c^\infty(n)}) \right\} .$$