

Phys 7230

Final exam

May 5

Useful formulae

Thermodynamic potentials

- Energy $E(S, V, N)$: $dE = TdS - PdV + \mu dN$.
- Enthalpy $H(S, P, N)$: $H = E + PV$, $dH = TdS + VdP + \mu dN$.
- Helmholtz free energy $F(T, V, N)$: $F = E - TS$, $dF = -SdT - PdV + \mu dN$.
- Gibbs free energy $G(T, P, N)$: $G = E - TS + PV$, $dG = -SdT + VdP + \mu dN$.
 $G = N\mu$.
- Grand canonical potential $\Omega(T, V, \mu)$: $\Omega = E - TS - \mu N$, $d\Omega = -SdT - PdV - Nd\mu$.
 $\Omega = -PV$.

Canonical ensemble.

- Partition function $Z = \sum_n e^{-\frac{E_n}{T}}$, where E_n are the energy levels of the system.
- Free energy $F = -T \ln Z$. Energy of the system $E = F + TS$. $dF = -SdT - PdV + \mu dN$, $dE = TdS - PdV + \mu dN$.
- Probability that the system's energy is equal to E_n is $p_n = \frac{1}{Z} e^{-\frac{E_n}{T}}$.

Grand canonical ensemble.

- Partition function $Z = \sum_{N,n} e^{-\frac{E_{N,n}}{T} + \frac{\mu N}{T}}$, where $E_{N,n}$ are the energy levels of the system on the assumption that the system has exactly N particles.
- Grand canonical free energy $\Omega = -T \log Z$. $d\Omega = -SdT - PdV - Nd\mu$. $\Omega = F - \mu N$.
 $\Omega = -PV$.
- Probability that the system's energy is equal to $E_{N,n}$ if it has N particles (where n labels different energy levels of the system on a condition that it has N particles) is
 $p_{N,n} = \frac{1}{Z} e^{-\frac{E_{N,n}}{T} + \frac{\mu N}{T}}$.

Thermodynamic Fluctuations

- Probability of a fluctuation is proportional to $\sim \exp [(\Delta P \Delta V - \Delta T \Delta S)/(2T)]$.
- $\langle (\Delta T)^2 \rangle = \frac{T^2}{C_V}$, $\langle (\Delta V)^2 \rangle = -T \left(\frac{\partial V}{\partial P} \right)_T$, $\langle \Delta T \Delta V \rangle = 0$.
- $\langle (\Delta S)^2 \rangle = C_P$, $\langle (\Delta P)^2 \rangle = -T \left(\frac{\partial P}{\partial V} \right)_S$, $\langle \Delta P \Delta S \rangle = 0$.
- $\langle (\Delta N)^2 \rangle = T \left(\frac{\partial N}{\partial \mu} \right)_{T,V}$.

Other formulae

- Heat capacity is the amount of heat pumped into the system to increase its temperature by dT . At fixed volume it is given by $c_v = T \left(\frac{\partial S}{\partial T} \right)_V$. At fixed pressure it is given by $c_p = T \left(\frac{\partial S}{\partial T} \right)_P$. Specific heat is the heat capacity per particle.
- Maxwell relations are relations between derivatives which follow from the fact that partial second derivatives of thermodynamic potentials do not depend on the order of differentiation. For example,

$$dE = TdS - PdV \rightarrow \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V.$$

- Quasiclassical approximation to the partition function of a particle

$$Z = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} e^{-\frac{p^2}{2mT} - \frac{U(x)}{T}}$$

- Equipartition theorem: specific heat of a quasiclassical system is equal to 1/2 per degree of freedom which enters its energy quadratically.
- Fermi-Dirac and Bose-Einstein grand canonical free energy $\Omega = -Tsg \sum_n \ln \left(1 + s e^{-\frac{\epsilon_n}{T} + \frac{\mu}{T}} \right)$, where $s = 1$ for Fermi-Dirac and $s = -1$ for Bose-Einstein distributions and ϵ_n are energy levels of one particle. g is a degeneracy of each single particle level (due to spin, for example). The summation over n can be replaced by the integration over $d^3x d^3p/(2\pi\hbar)^3$.
- Bose-Einstein distribution $N = N_0 + \int \frac{d^3p d^3x}{(2\pi\hbar)^3} \frac{1}{e^{\frac{p^2}{2mT} - \frac{\mu}{T}} - 1}$, where N is the total number of particles, and N_0 are the particles in the condensate. $N_0 = 0$ at $T > T_c$, while $\mu = 0$ at $T < T_c$. It is assumed here that $g = 1$. Correspondingly,

$$E = \int \frac{d^3p d^3x}{(2\pi\hbar)^3} \frac{\frac{p^2}{2m}}{e^{\frac{p^2}{2mT} - \frac{\mu}{T}} - 1}, \quad (0.1)$$

- Fermi-Dirac distribution for a gas in a box

$$N = g \int \frac{d^3p d^3x}{(2\pi\hbar)^3} \frac{1}{e^{\frac{p^2}{2mT} - \frac{\mu}{T}} + 1}, \quad E = g \int \frac{d^3p d^3x}{(2\pi\hbar)^3} \frac{\frac{p^2}{2m}}{e^{\frac{p^2}{2mT} - \frac{\mu}{T}} + 1}$$

- Ideal gas

$$F = -TN \ln \left[\frac{e}{N} \int \frac{V d^3p}{(2\pi\hbar)^3} e^{-\frac{p^2}{2mT}} \right] = -TN \ln \left[\frac{eV}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right]. \quad (0.2)$$

Phase equilibrium and transitions

- For two phases to be in equilibrium, their chemical potentials must coincide $\mu_A(P, T) = \mu_B(P, T)$.
- The Clapeyron-Clausius equation for the phase equilibrium line follows from this (v is the volume per particle, s is the entropy per particle, $L = T(s_B - s_A)$ is the latent heat per particle)

$$\frac{\partial P}{\partial T} = \frac{L}{T(v_A - v_B)} = \frac{s_B - s_A}{v_B - v_A}. \quad (0.3)$$

- Three phases can only be in equilibrium at one specific value of T , as the equation $\mu_A(P, T) = \mu_B(P, T) = \mu_C(P, T)$ has only one solution (unless there are more parameters than just P and T).
- Landau's theory of second order phase transitions follows from the Landau free energy

$$F = \int d^d x \left[J(\nabla M)^2 + \alpha(T - T_c)M^2 + bM^4 \right]. \quad (0.4)$$

M is the order parameter, T_c is the critical temperature. Minimum of F with respect to M gives the observed value of M , zero at $T > T_c$ and nonzero at $T < T_c$.