

# Phys 7230

## Midterm

March 13

### 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  $\Omega = -T \log Z$ .  $d\Omega = -TdS - PdV - Nd\mu$ .  $\Omega = F - \mu N$ .  
 $\Omega = -PV$ .
- Probability that the system's energy is equal to  $E_{N,n}$  if it has  $N$  particles is  $p_n = \frac{1}{Z} e^{-\frac{E_{N,n}}{T} + \frac{\mu N}{T}}$ .

#### 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

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

- 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  $\epsilon_n$  are energy levels of one particle.  $g$  is a degeneracy of each single particle level (due to spin, for example).
- 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  $g = 1$ .