# MAU34405 - Statistical Physics I Brief Notes

### Liam Kavanagh B.A. Theoretical Physics

## Thermodynamics

#### **First Law of Thermodynamics**

The heat flux to a system in any process is the difference in internal energy between the states minus the work done to the environment in the process.

$$\mathrm{d}Q = dE + \mathrm{d}W$$

e.g. A system in chemical isolation (dN = 0) has dW = PdV (mechanical work), so dQ = dE + PdV. More generally, for a quasistatic/reversible process, the work increment  $dW = dW_M + dW_{CH}$ , consisting of  $dW_M = PdV$  (mechanical work) and  $dW_{CH} = \mu dN$  (chemical work).

In a reversible process, the incremental heat transfer dQ is the product of the temperature T and the incremental change in entropy dS. i.e.

$$dQ = TdS \implies dE = TdS - PdV + \sum_{i} \mu_i dN_i.$$

This can be rearranged to

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_{i} \frac{\mu_{i}}{T}dN_{i}.$$

The coefficients on each term give the intensive variables  $T, P, \mu_i$  in terms of partial derivatives of the extensive variables  $S, E, V, N_i$ . e.g.  $T = \left(\frac{\partial E}{\partial S}\right)_{V,N_i}, P = T\left(\frac{\partial S}{\partial V}\right)_{E,N_i}$ .

#### Second Law of Thermodynamics

The change in entropy  $\Delta S$  of a system is non-negative, and  $\Delta S = 0$  for reversible processes. The entropy S of a system takes its maximum value at equilibrium.

#### Third Law of Thermodynamics

The entropy S of a system vanishes when

$$\left(\frac{\partial E}{\partial S}\right)_{V,N_i} = T = 0.$$

#### **Thermodynamic Potentials**

The thermodynamic potentials are given by the Legendre transforms of the internal energy  $E(S, V, N_i)$ .

$$\mathcal{F} = E - \left(\frac{\partial E}{\partial S}\right)_{V,N_i} S = E - TS \quad \text{(Free Energy / Helmholtz Free Energy)}$$
$$\mathcal{G} = \mathcal{F} - \left(\frac{\partial F}{\partial V}\right)_{S,N_i} V = \mathcal{F} + PV \quad \text{(Gibbs Free Energy)}$$
$$\mathcal{H} = E - \left(\frac{\partial E}{\partial V}\right)_{S,N_i} V = E + PV \quad \text{(Enthalpy)}$$
$$\mathcal{J} = \mathcal{F} - \left(\frac{\partial E}{\partial N_i}\right)_{S,V} N_i = \mathcal{F} - \mu_i N_i \quad \text{(Grand Canonical Potential)}$$

#### Maxwell Relations and the Thermodynamic Square

The Maxwell relations are equivalences between derivatives of different thermodynamic quantities. They, as well as the thermodynamic potentials, can be remembered using the Thermodynamic Square.

-S	E	V
Η		F
-P	G	Т

The clockwise layout of the square can be remembered using the mnemonic "Every Very Fine Teacher Gives Physics Homework Solutions" and the locations of the negative signs correspond to the words "Statistical Physics".

The Maxwell relations can be reclaimed from this square by drawing a  $\sqcup$ -shape (or any 90° rotation, eg.  $\Box$ ) and creating partial derivatives from the components. For example,  $\sqcup$  gives the relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

where the derivative takes the sign of the quantity being held constant in the square (in this case, P is negative in the square, so there is a - sign). In the case of  $\Box$ , we have

$$-\left(\frac{\partial V}{\partial S}\right)_P = -\left(\frac{\partial T}{\partial P}\right)_S \implies \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S.$$

We can also write the differential forms of the thermodynamic potentials. For example, if we want the Gibbs Free Energy  $\mathcal{G}$ , then we take the two opposite corners -S and V. These are the coefficients of the differentials in  $\mathcal{G}$ . The differentials themselves are in the opposite corner to the coefficient, so the coefficient -S is multiplied by dT and the coefficient V is multiplied by dP (ignoring sign) to give

$$d\mathcal{G} = VdP - SdT + \mu dN$$

(we always add on  $\mu dN$ ). Notice also, that the quantities to either side of each potential are its natural dependent variables, not including N. e.g. E = E(S, V, N).

### **Ideal Gas**

The ideal gas equations are

$$PV = NkT, \quad E = \frac{3}{2}NkT.$$

The heat capacity at constant volume for an ideal gas is

$$C_V := \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{3}{2}kN$$

and at constant pressure

$$C_P := \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = C_V + Nk = \frac{5}{2}Nk.$$

#### **Clausius-Clapeyron Equation**

For a first order phase transition of liquid to gas (or similar),

$$\left. \frac{\partial P}{\partial T} \right|_{\text{near boundary}} = \frac{\Delta s}{\Delta v} = \frac{L}{T \left( v_{\text{gas}} - v_{\text{liquid}} \right)}$$

where  $v_{\text{gas/liquid}} = \frac{V_{\text{gas/liquid}}}{N_{\text{gas/liquid}}}$ , and similarly for  $s_{\text{gas/liquid}}$ .  $\Delta s = s_{\text{gas}} - s_{\text{liquid}}$  and similarly for  $\Delta v$ , and  $L = T\Delta s$  is the Latent Heat.

## Background Knowledge

**Gaussian Integrals** 

$$\int_{-\infty}^{\infty} e^{-ax^{2}} dx = \sqrt{\frac{\pi}{a}}, \quad a > 0$$

$$I_{2n} = \int_{-\infty}^{\infty} x^{2n} e^{-ax^{2}} dx = (-1)^{n} \frac{d^{n}}{da^{n}} \int_{-\infty}^{\infty} e^{-ax^{2}} dx = (-1)^{n} \frac{d^{n}}{da^{n}} \sqrt{\frac{\pi}{a}}$$

$$\int_{-\infty}^{\infty} e^{-(ax^{2}+bx)} dx = e^{b^{2}/4a} \sqrt{\frac{\pi}{a}}$$

Gamma Function

$$\Gamma(n) = (n-1)!, \quad n \in \mathbb{N}$$
  
$$\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt, \quad z \in \mathbb{C} \setminus \mathbb{Z}_{\le 0}$$
  
$$\Gamma(z+1) = z \Gamma(z)$$
  
$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

## **Stirling Approximation**

$$\ln(\Gamma(n+1)) = \ln(n!) \simeq n(\ln(n) - 1), \quad n >> 1$$

#### Volume of Hyperballs

The volume of an n-dimensional hyperball of radius R has volume

$$V_n(R) = \frac{\pi^{n/2}}{\Gamma(\frac{n}{2}+1)}R^n$$

#### Probability

The expectation value/average/mean of a discrete random variable X is

$$\langle X \rangle = \sum_{i=1}^{n} P_i X_i$$

and for a continuous random variable X, is

$$\langle X \rangle = \int_{a}^{b} X P(X) dX.$$

The variance of a random variable X is

$$\sigma^{2} = \left\langle (X - \langle X \rangle)^{2} \right\rangle = \left\langle X^{2} \right\rangle - \left\langle X \right\rangle^{2}.$$

The Binomial Distribution for n trials with m successes with probability of success p is

$$P(n,m,p) = \binom{n}{m} p^m (1-p)^{n-m}$$

The number of ways to place m distinct objects in m boxes is m!.

The number of ways to place m distinct objects in n > m boxes is  $\frac{n!}{(n-m)!}$ . The number of ways to place m identical objects in n > m boxes is  $\binom{n}{m} = \frac{n!}{m!(n-m)!}$ . For k outcomes with probabilities  $p_1, p_2, ..., p_k$ , the Multinomial Distribution is

$$P = \frac{n!}{m_1!m_2!...m_k!} p_1^{m_1} p_2^{m_2} ... p_k^{m_k}$$

The Poisson Distribution for a discrete random variable X is

$$P(X) = \frac{\langle X \rangle^X}{X!} e^{-\langle X \rangle}.$$

For the Poisson Distribution, the variance  $\sigma^2 = \langle X \rangle$ .

The Gaussian Distribution for a continuous random variable X with mean value  $\mu$  and variance  $\sigma^2$  is

$$P(X) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(X-\mu)^2/2\sigma^2}$$

## **Statistical Ensembles**

## Microcanonical Ensemble

For an isolated system with f degrees of freedom,

$$\Omega(E, V, N) = \int_{\mathcal{H} \le E} \frac{dqdp}{h^f}$$

which yields

$$\mathcal{W}(E, V, N) = \frac{\partial \Omega}{\partial E}, \quad S = k \ln \Omega.$$

Note that the f-dimensional hyperball volume is

$$V_f(R) = \int_{\sum_{i=1}^{f} p_i^2 \le R^2} dp_1 dp_2 ... dp_f$$

and for an ideal gas of N free particles in 3D space (f = 3N d.o.f)

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

So,

$$\Omega(E,V,N) = \frac{1}{h^{3N}} \int_{\sum_{i=1}^{3N} p_i^2 \le 2mE} \prod_{i=1}^{3N} dq_i dp_i = \frac{V^N}{h^{3N}} \frac{\pi^{3N/2} (2mE)^{3N/2}}{\Gamma(\frac{3N}{2}+1)}$$

If the particles are identical, we also divide by N!.

The probability of finding n < N particles in a volume v < V in an isolated system is

$$P(E, v, n) = \frac{\mathcal{W}(E, v, n)\mathcal{W}(E, V - v, N - n)}{\mathcal{W}(E, V, N)}$$

The probability distribution of finding a particle with particular energy  $\varepsilon$  is

$$P(\varepsilon)d\varepsilon = \frac{\mathcal{W}(\varepsilon, V, 1)\mathcal{W}(E - \varepsilon, V, N - 1)}{\mathcal{W}(E, V, N)}d\varepsilon.$$

#### **Canonical Ensemble**

Suitable for systems at equilibrium with a heat reservoir (constant temperature T).

The Canonical Partition Function Z is given by

$$Z(T, V, N) = \int_{\text{all energies}} \mathcal{W}(E) e^{-\beta E} dE = \int_{\text{all phase space}} \frac{dqdp}{h^f} e^{-\beta \mathcal{H}(q, p)}$$

where  $\beta = \frac{1}{kT}$ .

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \left[ \ln Z \right], \quad \sigma^2 = \frac{\partial^2}{\partial \beta^2} \left[ \ln Z \right]$$

The Free Energy can be recovered from

$$\mathcal{F}(T, V, N) = -kT \ln Z$$

## Grand Canonical Ensemble

Suitable for systems at equilibrium with a heat bath and particle reservoir (constant temperature T and constant chemical potential  $\mu$ ).

The Grand Canonical Partition Function  ${\mathcal Z}$  is given by

$$\begin{split} \mathcal{Z}(T,V,\mu) &= \sum_{N_i} e^{\beta \mu N_i} Z(T,V,N_i) \\ \langle N \rangle &= h \frac{\partial}{\partial h} \left[ \ln \mathcal{Z} \right] \end{split}$$

where  $h = e^{\beta \mu}$  is the fugacity.

The Grand Canonical Potential is recovered from  $\mathcal{Z}$  by

$$\mathcal{J}(T, V, \mu) = -kT\ln \mathcal{Z}$$