

# Thermodynamics and Statistical Physics:

## A Summary of Lectures and Some Useful Formulae

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### USEFUL CONSTANTS

$k_B = 1.38 \times 10^{23} \text{ m}^2\text{kgs}^{-2}\text{K}^{-1}$	the Boltzmann constant
$N_A = 6.02 \times 10^{23}$	Avogadro's number
$R = N_A k_B = 8.31 \text{ JK}^{-1}\text{mol}^{-1}$	gas constant
$e = 1.60 \times 10^{-19} \text{ C}$	charge of the electron
$m_e = 9.11 \times 10^{-31} \text{ kg}$	mass of the electron
$c = 3.00 \times 10^8 \text{ ms}^{-1}$	speed of light in a vacuum

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## I. FUNDAMENTALS OF STATISTICAL PHYSICS

### A. The Microcanonical Ensemble

- Microcanonical ensemble distribution function:  $\rho = \delta(E - E')/\Omega(E)$ , where  $\Omega(E)$  is the number of microstates with energy  $E$
- Entropy for the Microcanonical ensemble  $S = k_B \ln \Omega(E)$

### B. The Canonical Ensemble

- Temperature  $\frac{1}{T} = \frac{\partial S}{\partial E}$
- Inverse temperature  $\beta = 1/k_B T$
- Canonical ensemble  $\rho(E_n) = e^{-\beta E_n}/Z$
- Partition function for the canonical ensemble  $Z = \sum_n e^{-\beta E_n}$
- Entropy for the canonical ensemble  $S = -k_B \sum_n \rho(E_n) \ln \rho(E_n)$
- Heat capacity  $C = \frac{\partial E}{\partial T}$ ,  $\frac{C}{T} = \frac{\partial S}{\partial T}$
- Pressure  $p = T \frac{\partial S}{\partial V}$
- Chemical potential  $\mu = -T \frac{\partial S}{\partial N}$
- (Helmholtz) Free energy  $F = -k_B T \ln Z$

We can write many useful quantities in terms of the partition function:

- $S = k_B \frac{\partial}{\partial T} (T \ln Z)$
- Average energy  $\equiv E \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$
- Energy fluctuations  $\Delta E^2 \equiv \langle (E - \bar{E})^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{\partial \bar{E}}{\partial \beta}$

We can also write many useful quantities in terms of the free energy:

- $S = -\left. \frac{\partial F}{\partial T} \right|_V$
- $p = -\left. \frac{\partial F}{\partial V} \right|_T$

- $\mu = \left. \frac{\partial F}{\partial N} \right|_{T,V}$
- $C_V = -T \left. \frac{\partial^2 F}{\partial T^2} \right|_V$

### C. The Grand Canonical Ensemble

- Grand Canonical ensemble  $\rho(E_n) = e^{-\beta E_n + \beta \mu N} / \mathcal{Z}$
- Partition function for the grand canonical ensemble  $\mathcal{Z} = \sum_n e^{-\beta E_n + \beta \mu N_n}$ .
- Partition function for the grand canonical ensemble in terms of the canonical ensemble partition function  $\mathcal{Z} = \sum_{N=0}^{\infty} Z(N, T, V) e^{\beta \mu N}$
- Entropy for the grand canonical ensemble:  $S = k_B \frac{\partial}{\partial T} (T \ln \mathcal{Z})$
- Grand canonical potential  $\Phi = -k_B T \ln \mathcal{Z}$

Some useful expressions:

- Average particle number  $\bar{N} \equiv \langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z}$
- Particle number fluctuations  $\Delta N^2 \equiv \langle (N - \bar{N})^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \ln \mathcal{Z} = \frac{1}{\beta} \frac{\partial \bar{N}}{\partial \mu}$

### D. Free Energies/Thermodynamic Potentials

- (Helmholtz) Free energy  $F = E - TS$  and  $dF = -SdT - pdV$
- Grand canonical potential  $\Phi = F - \mu N$  and  $d\Phi = -SdT = pdV - Nd\mu$
- Grand canonical potential can also be written as  $\Phi = -pV$

### E. Classical limit and gases

- Partition function for the canonical ensemble in d dimensions

$$Z = \frac{1}{h^d} \int \prod_i d^d \vec{p}_i d^d \vec{r}_i e^{-\beta H(\{\vec{r}_i, \vec{p}_i\})}.$$

$H(\{\vec{r}_i, \vec{p}_i\})$  for  $N$  particles labelled by momenta  $\vec{p}_i$  and positions  $\vec{r}_i$  for  $i = 1, 2, \dots, N$

- Ideal gas law  $pV = Nk_B T$

## II. CLASSICAL THERMODYNAMICS

### A. Definitions and the Laws of Thermodynamics

Preliminary definitions:

- A completely isolated system is referred to as *adiabatic*.
- A *diathermal* wall allows heat transfer.
- After a sufficiently long time an isolated system will relax to a state where no change is noticeable, this state is called *equilibrium*.
- A *quasi-static process* is one where at any time during the process the system is in equilibrium.

Laws:

- **Zeroth law:** If two systems,  $A$  and  $B$ , are each in thermal equilibrium with a third body  $C$ , then they are also in equilibrium with each other.
- **First law:** The amount of work required to change an isolated system from state 1 to state 2 is independent of how the work is performed.
- It follows for non-isolated systems we have  $\Delta E = Q + W$ , where the heat  $Q$  is the energy transferred other than by work.
- For quasi-static processes it is useful to use  $dE = dQ + dW$ .
- **Second law - Kelvin form:** No process is possible whose sole effect is to extract heat from a hot reservoir and convert this entirely into work.
- **Second law - Clausius form:** No process is possible whose sole effect is the transfer of heat from a colder to a hotter body.

### B. Thermodynamic Potentials

- Internal energy  $dE = TdS - pdV$
- Enthalpy  $H = E + pV$  and  $dH = TdS + Vdp$

- (Helmholtz) free energy  $F = E - TS$  and  $dF = -SdT - pdV$
- Gibbs free energy  $G = E + pV - TS$  and  $dG = -SdT + Vdp$

From these we can find Maxwell's relations:

### III. MATHEMATICAL PRELIMINARIES

- If three variables  $x, y, z$  have a single constraint then

$$\left. \frac{\partial x}{\partial y} \right|_z \left. \frac{\partial y}{\partial z} \right|_x \left. \frac{\partial z}{\partial x} \right|_y = -1$$

- Gaussian integral

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