

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:

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

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

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 $dF = -SdT - pdV + \mu dN$
- 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 $pV = Nk_B T$