Thermodynamics and Statistical Physics:
A Summary of Lectures and Some Useful Formulae

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CONTENTS

USEFUL CONSTANTS

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

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:

- Avergage 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 $i = 1, 2, \ldots N$

- Ideal gas law $pV = Nk_BT$

II.   CLASSICAL THEMODYNAMICS

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 $dE = đQ + đW$.

- **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.   Heat Engines and the Carnot Cycle

- Efficiency of a heat engine is the ratio of the work done to the heat absorbed from the reservoir:

$$\eta = \frac{W}{Q_H}$$

For the Carnot cycle (and by extension for any reversible cycle as we shall see):

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

- **Carnot's theorem:** Of all engines operating between two heat reservoirs, a reversible engine is the most efficient. Corollary: All reversible engines have the same efficiency which depends only in the temperature of the reservoirs.

$$\eta = 1 - \frac{T_C}{T_H}$$

This is the thermodynamic definition of temperature.

- We find from considering Carnot cycles that

$$\oint \frac{dQ}{T} = 0$$

which leads to the definition of entropy, a new function of state, for a state A as

$$S(A) = \int_0^A \frac{dQ}{T}$$

Typically then we have for a gas $S = S(p, V)$.

- It follows that $dS = dQ/T$ and using the first law we recover

$$dE = TdS - pdV$$

C.   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

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