

# Thermal Physics Notes

Refined Landau Style ( $k_B = 1$ )

April 4, 2025

## Part 1: Foundations and Thermodynamics

### 1 Foundations: Probability and Statistics

#### 1.1 The Random Walk and Binomial Distribution

Consider a 1D random walk of  $N$  steps, length  $l$ .  $P(\text{Right}) = p$ ,  $P(\text{Left}) = q = 1 - p$ . Let  $n_R$  be steps right,  $n_L$  steps left ( $N = n_R + n_L$ ). Position  $x = (n_R - n_L)l$ . Let  $m = x/l$ . Then  $n_R = (N + m)/2$ ,  $n_L = (N - m)/2$ . The probability of position  $x = ml$  follows the Binomial Distribution:

$$P_N(m) = \binom{N}{n_R} p^{n_R} q^{n_L} = \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!} p^{(N+m)/2} (1-p)^{(N-m)/2} \quad (1)$$

#### 1.2 Moments of a Distribution

Mean:  $\bar{x} = \sum_i P(x_i) x_i$ . Variance:  $\text{var}(x) = \sigma^2 = \overline{(x - \bar{x})^2} = \overline{x^2} - (\bar{x})^2$ . Standard Deviation (RMS):  $\Delta x_{\text{rms}} = \sqrt{\text{var}(x)}$ .

For Binomial  $n_R$ :  $\overline{n_R} = Np$ ,  $\text{var}(n_R) = Npq$ ,  $\Delta n_{R,\text{rms}} = \sqrt{Npq}$ . Relative Width:

$$\frac{\Delta n_{R,\text{rms}}}{\overline{n_R}} = \frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{p}} \frac{1}{\sqrt{N}} \xrightarrow{N \rightarrow \infty} 0 \quad (2)$$

#### 1.3 Gaussian Approximation (Large N Limit)

Stirling's formula:  $\ln N! \approx N \ln N - N + \frac{1}{2} \ln(2\pi N)$ . For large  $N$ , the Binomial distribution approaches a Gaussian (Normal) distribution:

$$P_N(n_R) \approx \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left[ -\frac{(n_R - \mu)^2}{2\sigma^2} \right] \quad (3)$$

with mean  $\mu = Np$  and variance  $\sigma^2 = Npq$ . Valid for  $N \gg 1, Npq \gg 1$ .

#### 1.4 Multivariable Probability and Change of Variables

Marginal Probability:  $P_u(u_i) = \sum_j P(u_i, v_j)$ . Uncorrelated Variables:  $P(u_i, v_j) = P_u(u_i)P_v(v_j)$ . Change of Variables: For  $y = f(x)$ , density  $\tilde{p}(y) = \sum_i p(x_i) \left| \frac{dx}{dy} \right|_{x=x_i}$  over roots  $x_i$ .

#### Example: Component of a Random 2D Vector

Vector  $\vec{B}$  fixed length  $B$ , random angle  $\theta \in [0, 2\pi)$ ,  $p(\theta) = 1/(2\pi)$ . Find  $\tilde{p}(B_x)$  for  $B_x = B \cos \theta$ . For  $|B_x| < B$ , two angles  $\theta_1, \theta_2$ .  $\left| \frac{d\theta}{dB_x} \right| = 1/\sqrt{B^2 - B_x^2}$ .

$$\tilde{p}(B_x) = p(\theta_1) \left| \frac{d\theta}{dB_x} \right|_{\theta_1} + p(\theta_2) \left| \frac{d\theta}{dB_x} \right|_{\theta_2} = 2 \cdot \frac{1}{2\pi} \frac{1}{\sqrt{B^2 - B_x^2}} \quad (4)$$

$$\tilde{p}(B_x) = \begin{cases} \frac{1}{\pi\sqrt{B^2-B_x^2}} & \text{if } |B_x| < B \\ 0 & \text{otherwise} \end{cases} \quad (5)$$

## 2 The Statistical Basis of Thermodynamics

### 2.1 Microstates and Macrostates

Microstate: Specific configuration (positions, momenta; quantum state). Macrostate: Defined by macroscopic parameters (E, V, N).

### 2.2 The Fundamental Postulate

For an isolated system in equilibrium (fixed E, V, N), let  $\Omega(E, V, N)$  be the number of accessible microstates. *All accessible microstates are equally probable.* Probability of microstate  $\mu_i$ :  $P(\mu_i) = 1/\Omega$  if accessible, 0 otherwise.

### 2.3 Statistical Definition of Macroscopic Parameters

Probability of observing macro-parameter value  $y_k$ :  $P(y_k) = \Omega(E; y_k)/\Omega(E)$ . Average value:  $\bar{y} = \sum_k y_k P(y_k) = \frac{\sum_k y_k \Omega(E; y_k)}{\Omega(E)}$ .

#### Example: Three Spin-1/2 Particles

Energy  $E_i = \mp \mu H$  for  $m_s = \pm 1/2$ . Total  $E = \sum E_i$ . If  $E = -\mu H$ , accessible states are  $(+, +, -)$ ,  $(+, -, +)$ ,  $(-, +, +)$ .  $\Omega(E) = 3$ . States with  $m_1 = +1/2$ :  $(+, +, -)$ ,  $(+, -, +)$ .  $\Omega(E; m_1 = +1/2) = 2$ . Probability  $P(m_1 = +1/2) = 2/3$ .

### 2.4 Density of States

For continuous energy, density of states  $\omega(E)$  gives number of states in  $[E, E + \delta E]$  as  $\Omega(E) \equiv \omega(E)\delta E$ .

#### Example: Classical Monatomic Ideal Gas

$N$  particles, volume  $V$ .  $H = \sum \tilde{p}_i^2/(2m)$ . Phase space volume for  $E \leq \sum \tilde{p}_i^2/(2m) \leq E + \delta E$ . Position integral:  $V^N$ . Momentum integral: volume of hyperspherical shell radius  $\sqrt{2mE}$ , dimension  $3N$ . Volume  $\propto R^{3N} \propto E^{3N/2}$ . Shell volume  $\propto E^{3N/2-1}\delta E$ .  $\omega(E) \propto V^N E^{3N/2-1}$ . Often simplified for large  $N$ :  $\Omega(E) \propto V^N E^{3N/2}$ .

## 3 Interaction Between Systems and Laws of Thermodynamics

### 3.1 Types of Interaction

Heat  $Q$ : Energy transfer due to temperature difference (fixed external parameters).  $Q = \overline{\Delta E}$ . Work  $W$ : Energy transfer due to change in external parameters. Work *by* system:  $W = -\Delta_x E$ . General Interaction:  $Q = \Delta \bar{E} + W$ .

### 3.2 The First Law of Thermodynamics

Conservation of energy. For an infinitesimal process:

$$dE = \delta Q - \delta W \quad (6)$$

$E$  is state function (exact differential),  $Q, W$  are path-dependent (inexact).

### 3.3 Quasistatic Processes and Generalized Forces

Quasistatic: Slow process, system near equilibrium always. Hamiltonian  $H(q, p; x)$ , external parameter  $x$ .  $dE = (\partial H / \partial x) dx$ . Average change:  $dE = \overline{\partial H / \partial x} dx$ . Generalized Force  $\chi$ :  $\chi \equiv -\overline{\partial H / \partial x}$ . Work done by system:  $\delta W = -dE = \chi dx$ .

#### Example: Piston

External parameter  $V$ . Generalized force is pressure  $P$ .  $P = -\frac{\partial E}{\partial V}$  (at constant S). Work:  $\delta W = PdV$ . Finite work:  $W = \int_{V_i}^{V_f} P(V) dV$ .

### 3.4 Thermal Equilibrium, Entropy, and Temperature

Two systems in thermal contact, isolated total system.  $E = E_1 + E_2$ . Most probable state maximizes  $\Omega_{total} = \Omega_1(E_1)\Omega_2(E - E_1)$ . Condition:  $\frac{\partial \ln \Omega_1}{\partial E_1} = \frac{\partial \ln \Omega_2}{\partial E_2}$ . Define Entropy  $S$ : (Dimensionless)

$$S(E, V, N) \equiv \ln \Omega(E, V, N) \quad (7)$$

Entropy is additive  $S_{total} = S_1 + S_2$ . Equilibrium maximizes  $S_{total}$ . Define Temperature  $T$ : (Units of Energy)

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E}_{V, N} \quad (8)$$

Thermal equilibrium condition:  $T_1 = T_2$ . Stability requires  $\frac{\partial^2 S}{\partial E^2}_V \leq 0$ . Fluctuations  $\Delta E / \overline{E} \sim 1/\sqrt{N}$ .

### 3.5 The Second Law of Thermodynamics

Spontaneous energy flow from high T to low T increases total entropy.  $dS_{total} = dS_1 + dS_2 = (\frac{1}{T_1} - \frac{1}{T_2})dE_1$ . If  $T_2 > T_1$ ,  $dE_1 > 0$ ,  $dS_{total} > 0$ . If  $T_1 > T_2$ ,  $dE_1 < 0$ ,  $dS_{total} > 0$ . *For any process in an isolated system, the total entropy never decreases:*

$$\Delta S_{total} \geq 0 \quad (9)$$

Equality holds for reversible processes, inequality for irreversible processes.

### 3.6 The Fundamental Thermodynamic Relation

Consider infinitesimal quasistatic change in  $E(S, V)$ .  $dE = \frac{\partial E}{\partial S}_V dS + \frac{\partial E}{\partial V}_S dV$ . Identify partial derivatives:  $T = \frac{\partial E}{\partial S}_V$  and  $P = -\frac{\partial E}{\partial V}_S$ .

$$\boxed{dE = TdS - PdV} \quad (10)$$

Combines 1st and 2nd Laws for quasistatic processes. Comparing with  $dE = \delta Q - PdV$ :

$$\delta Q_{rev} = TdS \implies dS = \frac{\delta Q_{rev}}{T} \quad (11)$$

Also, from  $S(E, V)$ :  $dS = \frac{1}{T}dE + \frac{P}{T}dV$ , yielding  $\frac{P}{T} = \frac{\partial S}{\partial V}_E$ . Full equilibrium (thermal and mechanical):  $T_1 = T_2$  and  $P_1 = P_2$ .

### 3.7 Summary of Thermodynamic Laws

0. Zeroth Law: Thermal equilibrium is transitive. (Defines T empirically).
1. First Law:  $dE = \delta Q - \delta W$ . (Energy conservation).
2. Second Law:  $\Delta S \geq 0$  (isolated);  $dS \geq \delta Q/T$ . (Direction of time, limits efficiency).
3. Third Law:  $\lim_{T \rightarrow 0} S(T, X) = S_0$  (constant, usually  $S_0 = \ln(\text{ground state degeneracy}) = 0$ ). (Absolute zero unattainable).

## 4 Thermodynamic Response Functions

(Using  $k_B = 1$ , so  $T$  is energy,  $S$  is dimensionless,  $R = N_A$ )

### 4.1 Heat Capacities

$\delta Q = C_x dT$  for quasistatic process at constant  $x$ .

$$C_V = \left( \frac{\delta Q}{dT} \right)_V = T \frac{\partial S}{\partial T}_V = \frac{\partial E}{\partial T}_V \quad (12)$$

$$C_P = \left( \frac{\delta Q}{dT} \right)_P = T \frac{\partial S}{\partial T}_P = \frac{\partial H}{\partial T}_P \quad (\text{where } H = E + PV) \quad (13)$$

Entropy change:  $S(T_2, x) - S(T_1, x) = \int_{T_1}^{T_2} \frac{C_x(T)}{T} dT$ .

### 4.2 Compressibility and Expansivity

Isothermal Compressibility:  $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P}_T$ . Isobaric Expansion Coefficient:  $\alpha_P = \frac{1}{V} \frac{\partial V}{\partial T}_P$ .

## 5 Application: The Ideal Gas

### 5.1 Statistical Derivation (Monatomic)

Using  $\Omega(E) \propto V^N E^{3N/2}$ ,  $S = \ln \Omega \approx N \ln V + \frac{3N}{2} \ln E + \text{const.}$

$$\frac{1}{T} = \frac{\partial S}{\partial E}_{V,N} = \frac{3N}{2E} \implies E = \frac{3}{2} NT \quad (14)$$

$$\frac{P}{T} = \frac{\partial S}{\partial V}_{E,N} = \frac{N}{V} \implies PV = NT \quad (15)$$

Energy depends only on  $T$ .

### 5.2 Ideal Gas Law and Molar Quantities

$N = \nu N_A$ . Gas constant  $R = N_A$ .  $PV = \nu N_A T$ . Energy  $E = \frac{3}{2} \nu N_A T$ .

### 5.3 Specific Heats (Monatomic)

Molar specific heat  $c_x = C_x/\nu$ .

$$c_v = \frac{1}{\nu} \frac{\partial E}{\partial T}_V = \frac{1}{\nu} \frac{d}{dT} = \frac{3}{2} N_A \quad (16)$$

$$c_p = c_v + N_A = \frac{5}{2} N_A \quad (\text{Using } H = E + PV = E + \nu N_A T) \quad (17)$$

Generally for ideal gas:  $dE = \nu c_v dT$ .  $c_p - c_v = N_A$ .

### 5.4 Adiabatic Index

$\gamma = c_p/c_v$ . For monatomic ideal gas:  $\gamma = (5/2 N_A)/(3/2 N_A) = 5/3$ .

## 5.5 Ideal Gas Processes

Isothermal ( $T=\text{const}$ ):  $PV = \text{const.}$ . Adiabatic ( $Q=0$ ,  $S=\text{const}$ ):  $dE = -PdV \implies \nu c_v dT + PdV = 0$ . Substituting  $P = \nu N_A T/V$  and  $N_A = c_p - c_v$ :  $\nu c_v dT + \frac{\nu(c_p - c_v)T}{V} dV = 0 \implies \frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0$ . Integrating gives:

$$TV^{\gamma-1} = \text{const.} \quad \text{or} \quad PV^\gamma = \text{const.} \quad (18)$$

# Part 2: Thermodynamic Potentials, Ensembles, and Applications

## 6 Thermodynamic Potentials

Choosing different independent variables leads to different potentials, useful under different experimental conditions.

**Internal Energy**  $E(S, V, N)$ :  $dE = TdS - PdV + \mu dN$  (Fundamental)

**Enthalpy**  $H = E + PV$ .  $H(S, P, N)$ :  $dH = TdS + VdP + \mu dN$  (Useful for constant  $P$ )

**Helmholtz Free Energy**  $F = E - TS$ .  $F(T, V, N)$ :  $dF = -SdT - PdV + \mu dN$  (Useful for constant  $T$ ,  $V$ ; connection to partition function)

**Gibbs Free Energy**  $G = F + PV = E - TS + PV$ .  $G(T, P, N)$ :  $dG = -SdT + VdP + \mu dN$  (Useful for constant  $T$ ,  $P$ ; chemical reactions)

**Grand Potential**  $\Phi = F - \mu N = E - TS - \mu N$ .  $\Phi(T, V, \mu)$ :  $d\Phi = -SdT - PdV - Nd\mu$  (Useful for constant  $T$ ,  $V$ ,  $\mu$ ; grand canonical ensemble)

Here  $\mu = \frac{\partial E}{\partial N}_{S,V} = \frac{\partial F}{\partial N}_{T,V} = \frac{\partial G}{\partial N}_{T,P}$  is the chemical potential.

## 7 Maxwell Relations

Derived from the equality of mixed second partial derivatives of the potentials (exact differentials). E.g., from  $dF = -SdT - PdV$ :  $\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \implies -\frac{\partial S}{\partial V}_T = -\frac{\partial P}{\partial T}_V$ . The four main relations:

$$\frac{\partial T}{\partial V}_S = -\frac{\partial P}{\partial S}_V \quad (\text{from } dE) \quad (19)$$

$$\frac{\partial T}{\partial P}_S = \frac{\partial V}{\partial S}_P \quad (\text{from } dH) \quad (20)$$

$$\frac{\partial S}{\partial V}_T = \frac{\partial P}{\partial T}_V \quad (\text{from } dF) \quad (21)$$

$$\frac{\partial S}{\partial P}_T = -\frac{\partial V}{\partial T}_P \quad (\text{from } dG) \quad (22)$$

### 7.1 Relation between Heat Capacities

We can derive  $C_P - C_V$  using Maxwell relations. Consider  $S(T, V)$ .  $dS = \frac{\partial S}{\partial T}_V dT + \frac{\partial S}{\partial V}_T dV$ . Multiply by  $T$ :  $TdS = T \frac{\partial S}{\partial T}_V dT + T \frac{\partial S}{\partial V}_T dV = C_V dT + T \frac{\partial P}{\partial T}_V dV$  (using (21)). Now consider  $S(T, P)$ .  $dS = \frac{\partial S}{\partial T}_P dT + \frac{\partial S}{\partial P}_T dP$ .  $TdS = C_P dT + T \frac{\partial S}{\partial P}_T dP = C_P dT - T \frac{\partial V}{\partial T}_P dP$  (using (22)). Express  $dV = \frac{\partial V}{\partial T}_P dT + \frac{\partial V}{\partial P}_T dP$ . Substitute into the first  $TdS$  equation:  $TdS = C_V dT + T \frac{\partial P}{\partial T}_V (\frac{\partial V}{\partial T}_P dT + \frac{\partial V}{\partial P}_T dP)$ . Equating coefficients of  $dT$  in

the two  $TdS$  expressions:  $C_P = C_V + T \frac{\partial P}{\partial T} \frac{\partial V}{\partial T} \frac{\partial V}{\partial P}$ . Using the cyclic relation  $\frac{\partial P}{\partial T} \frac{\partial T}{\partial V} \frac{\partial V}{\partial P} = -1$ , we have  $\frac{\partial P}{\partial T} \frac{\partial V}{\partial P} = -\frac{\partial V}{\partial T}$ .  $C_P - C_V = -T \left( \frac{\partial V}{\partial T} \right)^2 / \frac{\partial V}{\partial P}$ . Using  $\alpha_P = \frac{1}{V} \frac{\partial V}{\partial T}$  and  $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P}$ :

$$C_P - C_V = \frac{VT\alpha_P^2}{\kappa_T} \quad (23)$$

Since  $V, T, \kappa_T > 0$  and  $\alpha_P^2 \geq 0$ , we have  $C_P \geq C_V$ .

## 7.2 Implications of the Third Law ( $S \rightarrow S_0$ as $T \rightarrow 0$ )

As  $T \rightarrow 0$ :

- $C_V = T \frac{\partial S}{\partial T} \rightarrow 0$ .
- $C_P = T \frac{\partial S}{\partial T} \rightarrow 0$ .
- $\frac{\partial S}{\partial P} = -\frac{\partial V}{\partial T} = -V\alpha_P$ . Since  $\frac{\partial S}{\partial P}$  must be finite or zero as  $T \rightarrow 0$ ,  $\alpha_P \rightarrow 0$ .
- $\frac{\partial S}{\partial V} = \frac{\partial P}{\partial T}$ . Since  $\frac{\partial S}{\partial V}$  must be finite or zero as  $T \rightarrow 0$ ,  $\frac{\partial P}{\partial T} \rightarrow 0$ .
- $\frac{C_P - C_V}{C_V} = \frac{VT\alpha_P^2}{\kappa_T C_V}$ . Since  $\alpha_P \rightarrow 0$  and  $C_V \rightarrow 0$ , the limit depends on how fast they approach zero. Often  $C_P/C_V \rightarrow 1$ .

## 8 Calculating Entropy and Energy

Let's find  $S(T, V)$  and  $E(T, V)$  given an equation of state  $P(T, V)$  and  $C_V(T, V_0)$  at some reference volume  $V_0$ .

### 8.1 Entropy $S(T, V)$

Use  $(T, V)$  as independent variables.  $dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial V} dV$ . Using  $C_V = T \frac{\partial S}{\partial T}$  and the Maxwell relation  $\frac{\partial S}{\partial V} = \frac{\partial P}{\partial T}$ :

$$dS = \frac{C_V(T, V)}{T} dT + \frac{\partial P}{\partial T} dV \quad (24)$$

Integrating from a reference state  $(T_0, V_0)$  to  $(T, V)$  along a path, e.g.,  $(T_0, V_0) \rightarrow (T_0, V) \rightarrow (T, V)$ :

$$S(T, V) - S(T_0, V_0) = \int_{V_0}^V \frac{\partial P(T_0, V')}{\partial T} dV' + \int_{T_0}^T \frac{C_V(T', V)}{T'} dT' \quad (25)$$

Note that  $C_V(T, V)$  might depend on  $V$ . From  $dS$  being exact,  $\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$ :  $\frac{\partial}{\partial V} \left( \frac{C_V}{T} \right) = \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial T} \right) \implies \frac{1}{T} \frac{\partial C_V}{\partial V} = \frac{\partial^2 P}{\partial T^2 \partial V}$ . So,  $\frac{\partial C_V}{\partial V} = T \frac{\partial^2 P}{\partial T^2 \partial V}$ . This allows finding  $C_V(T, V)$  from  $C_V(T, V_0)$ :  $C_V(T, V) = C_V(T, V_0) + \int_{V_0}^V T \frac{\partial^2 P(T, V')}{\partial T^2 \partial V} dV'$ .

### 8.2 Internal Energy $E(T, V)$

Use  $dE = TdS - PdV$ . Substitute  $dS$ :  $dE = T \left( \frac{C_V}{T} dT + \frac{\partial P}{\partial T} dV \right) - PdV$

$$dE = C_V(T, V) dT + \left[ T \frac{\partial P}{\partial T} - P \right] dV \quad (26)$$

This implies  $\frac{\partial E}{\partial T} = C_V$  and  $\frac{\partial E}{\partial V} = T \frac{\partial P}{\partial T} - P$ . Integrating from  $(T_0, V_0)$  to  $(T, V)$  along path  $(T_0, V_0) \rightarrow (T_0, V) \rightarrow (T, V)$ :

$$E(T, V) - E(T_0, V_0) = \int_{V_0}^V \left[ T_0 \frac{\partial P(T_0, V')}{\partial T} - P(T_0, V') \right] dV' + \int_{T_0}^T C_V(T', V) dT' \quad (27)$$

## 9 Thermodynamic Processes

### 9.1 Free Expansion (Joule Expansion)

Gas expands into vacuum, isolated system.  $V_1 \rightarrow V_2$ .  $Q = 0, W = 0$ . First Law:  $\Delta E = Q - W = 0$ . Internal energy is constant. Temperature change is given by the Joule coefficient:  $\mu_J = \frac{\partial T}{\partial V}_E = \frac{1}{C_V} [P - T \frac{\partial P}{\partial T}_V] = -\frac{1}{C_V} \frac{\partial E}{\partial V}_T$ .  $T_2 - T_1 = \int_{V_1}^{V_2} \mu_J(E, V) dV$ . (Integration at constant E). Entropy change: Since  $E$  is constant,  $dS = \frac{P}{T} dV$ .  $\frac{\partial S}{\partial V}_E = \frac{P}{T} > 0$ . Expansion always increases entropy.  $S_2 - S_1 = \int_{V_1}^{V_2} \frac{P(E, V)}{T(E, V)} dV$ .

#### Ideal Gas

$E = E(T)$ . Since  $\Delta E = 0$ , then  $\Delta T = 0$ .  $\mu_J = 0$ .  $\Delta S = \int_{V_1}^{V_2} \frac{P}{T} dV = \int_{V_1}^{V_2} \frac{N}{V} dV = N \ln(V_2/V_1)$ .

#### Van der Waals Gas

Eq. of State:  $(P + a/v^2)(v - b) = N_A T$  where  $v = V/\nu$ .  $P = \frac{N_A T}{v-b} - \frac{a}{v^2}$ .  $\frac{\partial P}{\partial T}_V = \frac{N_A}{v-b}$ .  $\frac{\partial E}{\partial V}_T = T \frac{\partial P}{\partial T}_V - P = T \frac{N_A}{v-b} - \left( \frac{N_A T}{v-b} - \frac{a}{v^2} \right) = \frac{a}{v^2} = \frac{aN^2}{V^2}$  (using  $N = \nu N_A$ ).  $\mu_J = -\frac{1}{C_V} \frac{aN^2}{V^2}$ .  $\Delta T = T_2 - T_1 = -\int_{V_1}^{V_2} \frac{aN^2}{C_V V^2} dV = -\frac{aN^2}{C_V} \left( \frac{1}{V_1} - \frac{1}{V_2} \right)$ . (Assuming  $C_V$  constant). Since  $V_2 > V_1$ ,  $\Delta T < 0$ . VdW gas cools upon free expansion.

### 9.2 Joule-Thomson Process (Throttling)

Gas flows through porous plug/valve from constant  $P_1$  to constant  $P_2$ . Insulated system. Work done on gas entering:  $W_{in} = P_1 V_1$ . Work done by gas leaving:  $W_{out} = P_2 V_2$ . Net work by gas:  $W = P_2 V_2 - P_1 V_1$ . First Law:  $\Delta E = E_2 - E_1 = Q - W = 0 - (P_2 V_2 - P_1 V_1)$ .  $E_2 - E_1 = P_1 V_1 - P_2 V_2 \implies E_1 + P_1 V_1 = E_2 + P_2 V_2$ . Process occurs at constant enthalpy:  $H_1 = H_2$ . Temperature change given by Joule-Thomson coefficient:  $\mu_{JT} = \frac{\partial T}{\partial P}_H = \frac{1}{C_P} [T \frac{\partial V}{\partial T}_P - V] = \frac{V}{C_P} (T \alpha_P - 1)$ .  $T_2 - T_1 = \int_{P_1}^{P_2} \mu_{JT}(H, P) dP$ . (Integration at constant H). If  $\mu_{JT} > 0$ , gas cools on expansion ( $dP < 0$ ). If  $\mu_{JT} < 0$ , gas heats. Entropy change:  $dH = T dS + V dP = 0 \implies dS = -(V/T) dP$ .  $\frac{\partial S}{\partial P}_H = -V/T < 0$ . Expansion ( $dP < 0$ ) always increases entropy.  $\Delta S = -\int_{P_1}^{P_2} \frac{V(H, P)}{T(H, P)} dP$ .

#### Ideal Gas

$H = E + PV = E(T) + NT = H(T)$ . Since  $\Delta H = 0$ , then  $\Delta T = 0$ .  $\mu_{JT} = 0$ .

## 10 Heat Engines and Refrigerators

Based on the Second Law:  $\Delta S_{total} \geq 0$ . Consider cycles interacting with hot reservoir ( $T_1$ ) and cold reservoir ( $T_2 < T_1$ ).

### 10.1 Heat Engine

Absorbs heat  $Q_1$  from  $T_1$ , rejects heat  $Q_2$  to  $T_2$ , produces work  $W = Q_1 - Q_2$ . Cycle:  $\Delta S_{engine} = 0$ . Reservoirs:  $\Delta S_{res} = -Q_1/T_1 + Q_2/T_2$ . Second Law:  $\Delta S_{total} = \Delta S_{engine} + \Delta S_{res} = -Q_1/T_1 + Q_2/T_2 \geq 0 \implies Q_2/T_2 \geq Q_1/T_1 \implies Q_2/Q_1 \geq T_2/T_1$ . Efficiency  $\eta = W/Q_1 = (Q_1 - Q_2)/Q_1 = 1 - Q_2/Q_1$ .

$$\eta \leq 1 - T_2/T_1 \quad (28)$$

Maximum efficiency  $\eta_{max} = 1 - T_2/T_1$  is achieved by a reversible engine (e.g., Carnot cycle), where  $\Delta S_{total} = 0$ . Kelvin statement of 2nd Law: Cannot have  $\eta = 1$  ( $Q_2 = 0$ ) unless  $T_2 = 0$ .

## 10.2 Refrigerator

Uses work  $W$  to extract heat  $Q_2$  from  $T_2$  and reject heat  $Q_1 = Q_2 + W$  to  $T_1$ .  $\Delta S_{total} = -Q_2/T_2 + Q_1/T_1 \geq 0$ .  
 $\implies Q_1/T_1 \geq Q_2/T_2 \implies (Q_2 + W)/T_1 \geq Q_2/T_2 \implies W/T_1 \geq Q_2(1/T_2 - 1/T_1) = Q_2(T_1 - T_2)/(T_1 T_2)$ .  
 $\implies W \geq Q_2(T_1 - T_2)/T_2$ . Coefficient of Performance (COP)  $\text{COP}_{ref} = Q_2/W$ .

$$\text{COP}_{ref} \leq \frac{T_2}{T_1 - T_2} \quad (29)$$

Maximum COP achieved by reversible refrigerator. Clausius statement of 2nd Law: Cannot have  $W = 0$  (transfer heat from cold to hot spontaneously) unless  $T_1 = T_2$ .

## 11 Canonical Ensemble (Constant T, V, N)

System in thermal contact with a large heat reservoir at temperature  $T$ . Probability of the system being in a specific microstate  $r$  with energy  $E_r$ :

$$P_r = \frac{e^{-E_r/T}}{Z} \quad (30)$$

where  $Z$  is the Partition Function:

$$Z(T, V, N) = \sum_r e^{-E_r/T} \quad (31)$$

The sum is over all possible microstates  $r$  of the system.  $E_r = E_r(V, N)$ . Average value of an observable  $O$  (whose value in state  $r$  is  $O_r$ ):

$$\bar{O} = \sum_r O_r P_r = \frac{1}{Z} \sum_r O_r e^{-E_r/T} \quad (32)$$

Classical case: Replace sum over states  $\sum_r$  with integral over phase space  $\int \frac{d^{3N}q d^{3N}p}{N! h^{3N}}$ .  $Z_{cl} = \frac{1}{N! h^{3N}} \int e^{-H(q,p)/T} d^{3N}q d^{3N}p$ . (Factor  $1/N!$  for identical particles).

### 11.1 Connection to Thermodynamics: Helmholtz Free Energy

The central connection is through the Helmholtz free energy  $F$ :

$$F(T, V, N) = -T \ln Z(T, V, N) \quad (33)$$

Derivation: Average energy  $\bar{E} = \sum_r E_r P_r = \frac{1}{Z} \sum_r E_r e^{-E_r/T} = -\frac{\partial(\ln Z)}{\partial(1/T)}_V = T^2 \frac{\partial(\ln Z)}{\partial T}_V$ .  $\implies \bar{E} = T^2 \frac{\partial}{\partial T} \left(-\frac{F}{T}\right)_V = -T^2 \left(\frac{1}{T} \frac{\partial F}{\partial T}_V - \frac{F}{T^2}\right) = F - T \frac{\partial F}{\partial T}_V$ . From thermodynamics,  $F = E - TS$ , so  $E = F + TS = F - T \frac{\partial F}{\partial T}_V$ . This matches. Other thermodynamic quantities from  $F = -T \ln Z$ :

$$S = -\frac{\partial F}{\partial T}_{V,N} = \frac{\partial}{\partial T}_{V,N} \ln Z + T \frac{\partial(\ln Z)}{\partial T}_{V,N} \quad (34)$$

$$P = -\frac{\partial F}{\partial V}_{T,N} = T \frac{\partial(\ln Z)}{\partial V}_{T,N} \quad (35)$$

$$\mu = \frac{\partial F}{\partial N}_{T,V} = -T \frac{\partial(\ln Z)}{\partial N}_{T,V} \quad (36)$$

$$E = F + TS = -T \ln Z + T(\ln Z + T \frac{\partial(\ln Z)}{\partial T}_{V,N}) = T^2 \frac{\partial(\ln Z)}{\partial T}_{V,N} = -\frac{\partial \ln Z}{\partial \beta}_{V,N} \quad (\text{where } \beta = 1/T) \quad (37)$$

Energy fluctuations:  $\overline{(\Delta E)^2} = \overline{E^2} - \bar{E}^2$ .  $\overline{E^2} = \frac{1}{Z} \sum_r E_r^2 e^{-E_r/T} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial^2(\ln Z)}{\partial \beta^2} + \left(\frac{\partial \ln Z}{\partial \beta}\right)^2$ .  $\overline{(\Delta E)^2} = \frac{\partial^2(\ln Z)}{\partial \beta^2} = -\frac{\partial \bar{E}}{\partial \beta} = -\frac{\partial \bar{E}}{\partial T} \frac{\partial T}{\partial \beta} = -\frac{\partial \bar{E}}{\partial T} (-T^2) = T^2 C_V$ .

$$\overline{(\Delta E)^2} = T^2 C_V \quad (38)$$

Relative fluctuation  $\frac{\sqrt{\overline{(\Delta E)^2}}}{\bar{E}} = \frac{\sqrt{T^2 C_V}}{\bar{E}}$ . Since  $E, C_V \propto N$ , this is  $\propto 1/\sqrt{N}$ .



## 11.2 First and Second Laws in Canonical Ensemble

Second Law: System at const  $T$ ,  $V$  tends to minimize Helmholtz free energy  $F$ . First Law: Consider quasistatic change.  $d\bar{E} = \sum_r E_r dP_r + \sum_r P_r dE_r$ . Identify heat  $\delta Q = \sum_r E_r dP_r = T dS$ . Identify work  $\delta W = -\sum_r P_r dE_r$ . If  $dE_r = \frac{\partial E_r}{\partial V} dV$ , then  $\delta W = -(\sum_r P_r \frac{\partial E_r}{\partial V}) dV = P dV$ .

## 11.3 Example: Maxwell Velocity Distribution

Consider classical monatomic ideal gas. Treat one particle (A) as the system, rest (A') as reservoir at  $T$ . Energy  $E = m\vec{v}^2/2$ . Probability density for velocity  $\vec{v}$ :  $P(\vec{v}) \propto e^{-E/T} = e^{-m\vec{v}^2/(2T)}$ . Normalization constant:  $\int P(\vec{v}) d^3v = 1$ .  $\int C e^{-m(v_x^2+v_y^2+v_z^2)/(2T)} dv_x dv_y dv_z = C \left( \int_{-\infty}^{\infty} e^{-mv_x^2/(2T)} dv_x \right)^3 = C (\sqrt{2\pi T/m})^3 = 1$ .  $C = (m/(2\pi T))^{3/2}$ .

$$f(\vec{v}) d^3v = \left( \frac{m}{2\pi T} \right)^{3/2} e^{-m\vec{v}^2/(2T)} d^3v \quad (39)$$

## 12 Grand Canonical Ensemble (Constant $T$ , $V$ , $\mu$ )

System can exchange energy and particles with a large reservoir at temperature  $T$  and chemical potential  $\mu$ . Probability of system being in state  $r$  with energy  $E_r$  and particle number  $N_r$ :

$$P_r = \frac{e^{-(E_r - \mu N_r)/T}}{\mathcal{Z}} \quad (40)$$

where  $\mathcal{Z}$  is the Grand Partition Function:

$$\mathcal{Z}(T, V, \mu) = \sum_r e^{-(E_r - \mu N_r)/T} = \sum_{N=0}^{\infty} \sum_{r(N)} e^{-(E_r(N) - \mu N)/T} \quad (41)$$

Sum over all possible states (including different particle numbers). Can be written using canonical partition function  $Z(T, V, N)$ :

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} e^{\mu N/T} Z(T, V, N) = \sum_{N=0}^{\infty} z^N Z(T, V, N) \quad (42)$$

where  $z = e^{\mu/T}$  is the fugacity.

### 12.1 Connection to Thermodynamics: Grand Potential

The relevant potential is the Grand Potential  $\Phi = E - TS - \mu N$ :

$$\Phi(T, V, \mu) = -T \ln \mathcal{Z}(T, V, \mu) \quad (43)$$

From  $d\Phi = -SdT - PdV - Nd\mu$ :

$$S = -\frac{\partial \Phi}{\partial T}_{V, \mu} = \frac{\partial}{\partial T}_{V, \mu} \quad (44)$$

$$P = -\frac{\partial \Phi}{\partial V}_{T, \mu} = T \frac{\partial (\ln \mathcal{Z})}{\partial V}_{T, \mu} \quad (45)$$

$$\bar{N} = -\frac{\partial \Phi}{\partial \mu}_{T, V} = T \frac{\partial (\ln \mathcal{Z})}{\partial \mu}_{T, V} = z \frac{\partial (\ln \mathcal{Z})}{\partial z}_{T, V} \quad (46)$$

Average energy  $\bar{E} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}_{V, \mu} + \mu \bar{N}$ . Particle number fluctuations:  $\overline{(\Delta N)^2} = \overline{N^2} - \bar{N}^2 = T \frac{\partial \bar{N}}{\partial \mu}_{T, V} = T^2 \frac{\partial^2 (\ln \mathcal{Z})}{\partial \mu^2}_{T, V}$ .

## 13 Classical Ideal Gas Revisited

### 13.1 Partition Function

Single particle (monatomic) in volume  $V$ .  $H = p^2/(2m)$ . Canonical partition function for one particle ( $N = 1$ , ignore  $N!$ ):  $\zeta = Z(T, V, N = 1)_{distinguishable} = \frac{1}{h^3} \int d^3q d^3p e^{-p^2/(2mT)}$   $\zeta = \frac{V}{h^3} \left( \int_{-\infty}^{\infty} e^{-p_x^2/(2mT)} dp_x \right)^3 = \frac{V}{h^3} (\sqrt{2\pi mT})^3 = V \left( \frac{2\pi mT}{h^2} \right)^{3/2}$ . Define the thermal de Broglie wavelength:  $\lambda_{th} = h/\sqrt{2\pi mT}$ .

$$\zeta = \frac{V}{\lambda_{th}^3} \quad (47)$$

For  $N$  non-interacting, distinguishable particles:  $Z_{dist} = \zeta^N$ . For  $N$  non-interacting, indistinguishable particles (dilute limit, avoid multiple occupancy): Correct by Gibbs factor  $N!$ .

$$Z(T, V, N) = \frac{\zeta^N}{N!} = \frac{1}{N!} \left( \frac{V}{\lambda_{th}^3} \right)^N \quad (48)$$

Helmholtz Free Energy:  $F = -T \ln Z = -T (N \ln \zeta - \ln N!)$ . Using Stirling approx  $\ln N! \approx N \ln N - N$ :  $F \approx -T (N \ln(V/\lambda_{th}^3) - N \ln N + N) = -NT \left( \ln \left[ \frac{V}{N\lambda_{th}^3} \right] + 1 \right)$ . This is the Sackur-Tetrode equation (up to constants). Check thermodynamics:  $P = -\frac{\partial F}{\partial V}_{T,N} = -(-NT) \frac{\partial}{\partial V} = NT/V \implies PV = NT$ .  $E = F + TS$ .  $S = -\frac{\partial F}{\partial T}_{V,N}$ .  $S = N(\ln[\frac{V}{N\lambda_{th}^3}] + 1) + NT \frac{\partial}{\partial T}_{V,N} S = N(\ln[\frac{V}{N\lambda_{th}^3}] + 1) + NT \frac{\partial}{\partial T} = N(\ln[\frac{V}{N\lambda_{th}^3}] + 1) + NT(\frac{3}{2T})$ .  $S = N \left( \ln \left[ \frac{V}{N\lambda_{th}^3} \right] + \frac{5}{2} \right)$ .  $E = F + TS = -NT(\ln[\dots] + 1) + NT(\ln[\dots] + 5/2) = \frac{3}{2}NT$ . Correct.

## 14 Equipartition Theorem

For a classical system in thermal equilibrium at temperature  $T$ , each quadratic degree of freedom in the Hamiltonian contributes  $\frac{1}{2}T$  to the average internal energy. Let  $H = \sum_i A_i p_i^2 + \sum_j B_j q_j^2 + H_{other}$ .  $\overline{A_i p_i^2} = \frac{\int (A_i p_i^2) e^{-H/T} d\Gamma}{\int e^{-H/T} d\Gamma}$ . Integrate over  $p_i$  first:  $\overline{A_i p_i^2} = \frac{\int A_i p_i^2 e^{-A_i p_i^2/T} dp_i}{\int e^{-A_i p_i^2/T} dp_i}$ . Let  $x = \sqrt{A_i/T} p_i$ .  $\overline{A_i p_i^2} = T \frac{\int x^2 e^{-x^2} dx}{\int e^{-x^2} dx} = T \frac{\sqrt{\pi}/2}{\sqrt{\pi}} = \frac{1}{2}T$ . Similarly  $\overline{B_j q_j^2} = \frac{1}{2}T$ .

### 14.1 Examples

- Monatomic ideal gas:  $H = \sum_{i=1}^N (p_{ix}^2 + p_{iy}^2 + p_{iz}^2)/(2m)$ .  $3N$  quadratic terms.  $\overline{E} = 3N \times (\frac{1}{2}T) = \frac{3}{2}NT$ .  $C_V = \frac{\partial E}{\partial T}_V = \frac{3}{2}N$ .
- Diatomic ideal gas (rigid rotor): Add rotational kinetic energy  $H_{rot} = (L_x^2 + L_y^2)/(2I)$  (rotation about axes perp. to bond). 2 quadratic terms.  $E = \frac{3}{2}NT + 2 \times \frac{1}{2}NT = \frac{5}{2}NT$ .  $C_V = \frac{5}{2}N$ .
- Diatomic ideal gas (with vibration): Add  $H_{vib} = p_{\xi}^2/(2\mu) + \frac{1}{2}k\xi^2$  (relative motion along bond). 2 quadratic terms.  $E = \frac{5}{2}NT + 2 \times \frac{1}{2}NT = \frac{7}{2}NT$ .  $C_V = \frac{7}{2}N$ . (Only at high  $T$  where vibration is classical).
- Solid (Dulong-Petit): Model as  $N$  atoms in 3D harmonic potential.  $H = \sum_{i=1}^{3N} (p_i^2/(2m) + \frac{1}{2}m\omega_i^2 q_i^2)$ .  $6N$  quadratic terms.  $\overline{E} = 6N \times (\frac{1}{2}T) = 3NT$ .  $C_V = 3N$ . (Classical limit).

## 15 Quantum Statistics Examples

### 15.1 Harmonic Oscillator (Quantum)

Energy levels  $E_n = \hbar\omega(n+1/2)$ ,  $n = 0, 1, 2, \dots$ . Partition function  $Z = \sum_{n=0}^{\infty} e^{-E_n/T} = \sum_{n=0}^{\infty} e^{-\hbar\omega(n+1/2)/T}$ .  $Z = e^{-\hbar\omega/(2T)} \sum_{n=0}^{\infty} (e^{-\hbar\omega/T})^n$ . Geometric series sum  $1/(1-x)$ .

$$Z = \frac{e^{-\hbar\omega/(2T)}}{1 - e^{-\hbar\omega/T}} = \frac{1}{2 \sinh(\hbar\omega/(2T))} \quad (49)$$

Average energy  $\bar{E} = T^2 \frac{\partial(\ln Z)}{\partial T}$ .  $\ln Z = -\frac{\hbar\omega}{2T} - \ln(1 - e^{-\hbar\omega/T})$ .  $\frac{\partial(\ln Z)}{\partial T} = \frac{\hbar\omega}{2T^2} - \frac{-e^{-\hbar\omega/T}(\hbar\omega/T^2)}{1 - e^{-\hbar\omega/T}} = \frac{\hbar\omega}{T^2} \left[ \frac{1}{2} + \frac{e^{-\hbar\omega/T}}{1 - e^{-\hbar\omega/T}} \right]$ .  $\bar{E} = \hbar\omega \left[ \frac{1}{2} + \frac{e^{-\hbar\omega/T}}{1 - e^{-\hbar\omega/T}} \right] = \hbar\omega \left[ \frac{1}{2} + \frac{1}{e^{\hbar\omega/T} - 1} \right]$ . This is the Planck distribution plus zero-point energy. Heat capacity  $C = \frac{\partial \bar{E}}{\partial T}$ .  $C = \hbar\omega \frac{d}{dT} (e^{\hbar\omega/T} - 1)^{-1} = \hbar\omega(-1)(\dots)^{-2} e^{\hbar\omega/T} (-\hbar\omega/T^2)$ .

$$C = \left( \frac{\hbar\omega}{T} \right)^2 \frac{e^{\hbar\omega/T}}{(e^{\hbar\omega/T} - 1)^2} \quad (50)$$

Limits:

- High T ( $T \gg \hbar\omega$ ):  $e^{\hbar\omega/T} \approx 1 + \hbar\omega/T + \dots$ .  $\bar{E} \approx \hbar\omega(\frac{1}{2} + \frac{1}{\hbar\omega/T}) \approx T$ .  $C \rightarrow 1$ . (Equipartition recovered,  $k_B = 1$ ).
- Low T ( $T \ll \hbar\omega$ ):  $e^{\hbar\omega/T} \gg 1$ .  $\bar{E} \approx \hbar\omega(\frac{1}{2} + e^{-\hbar\omega/T}) \rightarrow \frac{1}{2}\hbar\omega$  (Zero-point energy).  $C \approx (\frac{\hbar\omega}{T})^2 e^{-\hbar\omega/T} \rightarrow 0$ .

### 15.2 Einstein Solid

Model solid as  $N$  independent 3D harmonic oscillators, all with same frequency  $\omega$ . Total energy  $\bar{E}_{total} = 3N\bar{E}_{1DHO} = 3N\hbar\omega \left[ \frac{1}{2} + \frac{1}{e^{\hbar\omega/T} - 1} \right]$ . Heat capacity  $C_V = \frac{\partial \bar{E}_{total}}{\partial T}$ . Define Einstein Temperature  $\Theta_E = \hbar\omega$ .

$$C_V = 3N \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \quad (51)$$

Limits:

- High T ( $T \gg \Theta_E$ ):  $C_V \rightarrow 3N$ . (Dulong-Petit recovered).
- Low T ( $T \ll \Theta_E$ ):  $C_V \approx 3N(\Theta_E/T)^2 e^{-\Theta_E/T} \rightarrow 0$ . (Matches experiment qualitatively, but exponential decay is too fast. Debye model gives  $T^3$ ).

### 15.3 Paramagnetism (Spin J)

$N$  non-interacting magnetic moments  $\vec{\mu}$  in external field  $\vec{H} = H\hat{z}$ . Energy levels  $E_m = -\vec{\mu} \cdot \vec{H}$ . For spin  $J$ ,  $\mu_z = g\mu_B m_J$ ,  $m_J = -J, -J+1, \dots, J$ . (Assume simple case  $E_m = -\mu_0 H m$ , where  $m$  is quantum number). Energy  $E_m = -\gamma m H$ ,  $m = -J, \dots, +J$ . ( $\gamma$  is gyromagnetic ratio). Let's use your notation  $E_m = -g\mu_B H m$ . Single particle partition function  $Z_1$ :  $Z_1 = \sum_{m=-J}^J e^{-E_m/T} = \sum_{m=-J}^J e^{g\mu_B H m/T}$ . Let  $\eta = g\mu_B H/T$ .  $Z_1 = \sum_{m=-J}^J (e^\eta)^m = e^{-J\eta} \sum_{k=0}^{2J} (e^\eta)^k$ . Geometric series  $\frac{1-x^{N+1}}{1-x}$ . Here  $N = 2J$ .  $Z_1 = e^{-J\eta} \frac{1 - e^{(2J+1)\eta}}{1 - e^\eta} = \frac{e^{-J\eta} - e^{-(J+1)\eta}}{1 - e^\eta} = \frac{e^{(J+1/2)\eta} - e^{-(J+1/2)\eta}}{e^{\eta/2} - e^{-\eta/2}} \frac{e^{-\eta/2}}{e^{-\eta/2}}$

$$Z_1 = \frac{\sinh((J+1/2)\eta)}{\sinh(\eta/2)} \quad (52)$$

Total partition function  $Z = (Z_1)^N$  (distinguishable sites). Average magnetic moment  $\bar{\mu}_z = T \frac{\partial(\ln Z_1)}{\partial H}$ .  $\ln Z_1 = \ln \sinh((J+1/2)\eta) - \ln \sinh(\eta/2)$ .  $\frac{\partial(\ln Z_1)}{\partial H} = \frac{\cosh((J+1/2)\eta)}{\sinh((J+1/2)\eta)} (J+1/2) \frac{\partial \eta}{\partial H} - \frac{\cosh(\eta/2)}{\sinh(\eta/2)} (1/2) \frac{\partial \eta}{\partial H}$ .  $\frac{\partial \eta}{\partial H} = g\mu_B/T$ .  $\bar{\mu}_z = T[\coth((J+1/2)\eta)(J+1/2) - \coth(\eta/2)(1/2)](g\mu_B/T)$

$$\bar{\mu}_z = g\mu_B [(J+1/2) \coth((J+1/2)\eta) - (1/2) \coth(\eta/2)] \equiv g\mu_B J B_J(\eta) \quad (53)$$

where  $B_J(x) = \frac{1}{J}[(J+1/2) \coth((J+1/2)x) - (1/2) \coth(x/2)]$  is the Brillouin function. Total Magnetization  $M = N\bar{\mu}_z = Ng\mu_B JB_J(\eta)$ . Limits:

- High T / Low H ( $\eta \ll 1$ ):  $\coth(x) \approx 1/x + x/3$ .  $B_J(\eta) \approx \frac{1}{J}[(J+1/2)(\frac{1}{(J+1/2)\eta} + \frac{(J+1/2)\eta}{3}) - (1/2)(\frac{1}{\eta/2} + \frac{\eta/2}{3})]$   $B_J(\eta) \approx \frac{1}{J}[\frac{1}{\eta} + \frac{(J+1/2)^2\eta}{3} - \frac{1}{\eta} - \frac{\eta}{12}] = \frac{\eta}{3J}[(J^2 + J + 1/4) - 1/4] = \frac{\eta(J^2 + J)}{3J} = \frac{J+1}{3}\eta$ .  $M \approx Ng\mu_B J \frac{J+1}{3} \frac{g\mu_B H}{T} = \frac{N(g\mu_B)^2 J(J+1)}{3T} H$ . Curie Law:  $M = \chi H$  with  $\chi = C/T$ .  $C = \frac{N(g\mu_B)^2 J(J+1)}{3}$ .
- Low T / High H ( $\eta \gg 1$ ):  $\coth(x) \rightarrow 1$ .  $B_J(\eta) \rightarrow \frac{1}{J}[(J+1/2) - 1/2] = 1$ .  $M \rightarrow Ng\mu_B J$ . (Saturation).

## 16 Elements of Kinetic Theory

Focuses on microscopic origins of macroscopic phenomena like pressure, transport.

### 16.1 Maxwell Velocity and Speed Distributions

Velocity distribution (derived earlier):  $f(\vec{v}) = (\frac{m}{2\pi T})^{3/2} e^{-mv^2/(2T)}$ . Speed distribution  $F(v)$ : Integrate  $f(\vec{v})$  over angles in velocity space.  $d^3v = v^2 \sin\theta dv d\theta d\phi$ . Angle integral gives  $4\pi$ .

$$F(v)dv = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} v^2 e^{-mv^2/(2T)} dv \quad (54)$$

Characteristic speeds:

- Most probable speed  $\tilde{v}$ : Max of  $F(v)$ .  $\frac{d(v^2 e^{-mv^2/(2T)})}{dv} = 0 \implies \tilde{v} = \sqrt{2T/m}$ .
- Mean speed  $\bar{v}$ :  $\int_0^\infty v F(v) dv = \sqrt{8T/(\pi m)}$ .
- RMS speed  $v_{rms}$ :  $\sqrt{\overline{v^2}}$ .  $\overline{v^2} = \int_0^\infty v^2 F(v) dv = 3T/m$ .  $v_{rms} = \sqrt{3T/m}$ .

Note  $\tilde{v} < \bar{v} < v_{rms}$ .

### 16.2 Particle Flux and Effusion

Flux  $\Phi(\vec{v})d^3v$ : Number of particles with velocity in  $d^3v$  crossing unit area perpendicular to  $\hat{z}$  per unit time. Volume is  $v_z dt dA$ . Number density is  $n f(\vec{v})$ .  $\Phi(\vec{v})d^3v = (n f(\vec{v}) d^3v) (v_z) / (dA dt) = n v_z f(\vec{v}) d^3v$ . Total particle flux  $\Phi_0$  (particles crossing in  $+z$  direction): Integrate for  $v_z > 0$ .  $\Phi_0 = \int_{v_x=-\infty}^\infty \int_{v_y=-\infty}^\infty \int_{v_z=0}^\infty n v_z f(\vec{v}) dv_x dv_y dv_z$ . The  $v_x, v_y$  integrals give  $(2\pi T/m)$ .  $\Phi_0 = n (\frac{m}{2\pi T})^{3/2} (2\pi T/m) \int_0^\infty v_z e^{-mv_z^2/(2T)} dv_z$ . Integral is  $T/m$ .  $\Phi_0 = n (\frac{m}{2\pi T})^{1/2} (T/m) = n \sqrt{T/(2\pi m)} = n \frac{\sqrt{8T/(\pi m)}}{4} = \frac{1}{4} n \bar{v}$ . Using ideal gas law  $P = nT$ :

$$\Phi_0 = \frac{1}{4} n \bar{v} = \frac{P}{\sqrt{2\pi m T}} \quad (55)$$

Effusion: Rate of particles leaking out of small hole (area A) if  $P_{in} \gg P_{out}$ .  $I = \Phi_0 A = \frac{PA}{\sqrt{2\pi m T}}$ .

### 16.3 Pressure of an Ideal Gas

Particles elastically colliding with wall (area A) perpendicular to z. Momentum change  $\Delta p_z = 2mv_z$ . Number colliding in  $dt$  with velocity  $\vec{v}$  (and  $v_z > 0$ ) is  $n f(\vec{v}) d^3v (Av_z dt)$ . Total force  $F_z = \frac{\text{Total momentum change}}{dt} = \int_{v_z>0} (2mv_z) (n f(\vec{v}) d^3v Av_z)$ .  $F_z = 2mnA \int_{v_z>0} v_z^2 f(\vec{v}) d^3v$ . Since  $f(\vec{v})$  is even in  $v_z$ ,  $\int_{v_z>0} v_z^2 f(\vec{v}) d^3v = \frac{1}{2} \int v_z^2 f(\vec{v}) d^3v = \frac{1}{2} \overline{v_z^2}$ .  $F_z = mnA \overline{v_z^2}$ . Pressure  $P = F_z/A = mn \overline{v_z^2}$ . By isotropy  $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$ . Since  $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_z^2}$ .  $\overline{v^2} = 3T/m$ . So  $\overline{v_z^2} = T/m$ .  $P = mn(T/m) = nT$ . Recovered ideal gas law.