

Notes on Physics 415:
Statistical and Thermal Physics
Harry Luo

Contents

1	Basic Statistical Methods	2
1.1	Random walk: Binomial distribution and the Emergence of Gaussian	2
1.2	Probability Distribution with Multivariables	3
1.3	Continuous probability distribution	3
2	Stat. Mech setup	3
3	Density of states	4
4	Interaction between Macro bodies	4
5	Quasistatic process	5
6	Thermal int. btwn sys: Entropy	5
7	The 2nd law	6
8	Reversible and Irreversible process	6
9	Fundamental relation	6
10	Laws of Thermodynamics	7
11	Response function	7
12	Ideal Gas	7
13	Summary of Thermal laws	8
14	Response function	8
15	Thermodynamic Potentials	9
16	Maxwell Relations	9
17	Entropy and Internal Energy : Take (T, V) as indep. var.	9
18	Free Expansion: Start from T_1, V_1 and $V_1 \rightarrow V_2$:	10
19	Joule-Thomson Process: start p_1, T_1 ; $p_1 \rightarrow p_2$ and so $T_1 = T_2$	10
20	Heat Engines and Refrigerators	11
20.1	Heat engine	11
20.2	fridge	11
21	Cononical Ensemble: fix T, N, V	11
21.1	Ex: spin in H-field	11
21.2	Properties of Z , and thermo potential	12
22	Fundamental Relation:	12
23	Grand Canonical Ensemble	12
24	Classical Ideal gas	12
25	Thermal Classical Limit	12
26	Equipartition theroem	13
27	Solid Lattice	13
28	Paramagnetism	13
29	Kinetic Theory	14
29.1	Examples:	14

1 Basic Statistical Methods

1.1 Random walk: Binomial distribution and the Emergence of Gaussian

- **Example:** We introduce important ideas from Probability via an example of **1D random walk**:

Consider a drunkard walking along a straight line, starting from Origin $x = 0$, and taking random steps of length l at regular intervals. Each step is independent of the last. He takes a probability p of stepping to the left, and $1 - p$ to step to the right. After taking N steps, what is the probability that the walker is at position $x = ml$?

Let $P_N(m)$ be the position $x = ml$ of the drunkard after N steps; denote n_1 = number of steps to the left, $n_2 = N - n_1$ number of steps to the right. Notice that $-N \leq m \leq N$, $N = n_1 + n_2$, $m = n_1 - n_2$. Then the number of walking combinations, indexed with either direction left (n_1) or right (n_2), is given by the binomial coefficient:

$$\binom{N}{n_1} = \frac{N!}{n_1!(N - n_1)!} = \frac{N!}{n_1! n_2!} = \binom{N}{n_2}. \quad (1)$$

Then the probability of the walker taking n_1 steps to the left and n_2 steps to the right is given by the **binomial distribution**:

$$P_N(n_1) = \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2}. \quad (2)$$

Noticing $n_1 = \left(\frac{N+m}{2}\right)$ and $n_2 = \left(\frac{N-m}{2}\right)$:

$$P_N(m) = \frac{N!}{\left[\frac{N+m}{2}\right]! \left[\frac{N-m}{2}\right]!} p^{\frac{N+m}{2}} (1-p)^{\frac{N-m}{2}}. \quad (3)$$

■

1.1.1 General Notions from probability:

Let X be a random variable, taking N possible values x_1, x_2, \dots, x_N with associated probabilities $P(x_1), P(x_2), \dots, P(x_N)$. Note that $0 \leq P(x_i) \leq 1$, $\sum_{i=1}^N P(x_i) = 1$

- Mean: $\bar{x} := \sum_{i=1}^N P(x_i) x_i$ Var: $\text{var}(x) := \overline{(x - \bar{x})^2} = \sum_{i=1}^N P(x_i) (x_i - \bar{x})^2 = \overline{x^2} - \bar{x}^2$
 - RMS: $\Delta x_{\text{rms}} = \sqrt{\overline{x^2} - \bar{x}^2}$
 - For Binomial Distribution: $\bar{x} = Np$, Dispersion : $\text{var}(x) = Npq$, $\Delta x_{\text{rms}} = \sqrt{Npq}$
- Relative Width: $\frac{\Delta x_{\text{rms}}}{\bar{x}} = \frac{q}{p} \frac{1}{\sqrt{N}} \rightarrow 0 \quad (n \gg 1)$

1.1.2 Central Limit Theorem: Appox. of Binom.

Recall Equation 2, taking logarithm on both sides:

$$\ln(P_N(m)) = \ln(N!) - \ln(n_1!) - \ln(N - n_1)! + n_1 \ln(p) + (N - n_1) \ln(q). \quad (4)$$

For $N \gg 1$, we can approximate using Stirling's formula:

$$N! \approx \sqrt{2\pi N} N^N e^{-N}, \quad (5)$$

and further algebra gives

$$P_N(m) \approx \sqrt{\frac{N}{2\pi n(N-n)}} \exp\left[-N f\left(\frac{n}{N}\right)\right], \quad (N \gg 1) \quad (6)$$

where

$$f(x) = [x \ln x + (1-x) \ln(1-x)] - [x \ln p + (1-x) \ln q]. \quad (7)$$

For N large, P_N peaks sharply near $\max \tilde{n} = Np$, which is found by maximizing $f(x)$. Expanding $f(x)$ about \tilde{n} , and taking $n \approx \tilde{n}$ in P_N we have :

$$\boxed{P_N(m) \approx \frac{1}{\sqrt{2\pi Npq}} \exp\left[-\frac{(n - Np)^2}{2Npq}\right]}, \quad (8)$$

which is a Gaussian distribution with mean $\mu = \bar{x} = Np$, $\sigma^2 = Npq$, $\Delta x_{\text{rms}} = \sqrt{Npq}$.

1.2 Probability Distribution with Multivariables

Consider two r.v. u, v , which can assume possible values u_i, v_j for $i = 1, 2, \dots, M; j = 1, 2, \dots, N$.

- Normalization condition

$$\sum_{i=1}^M \sum_{j=1}^N P(u_i, v_j) = 1. \quad (9)$$

- Unconditioned prob. distribution:

$$P(u_i) = \sum_{j=1}^N P(u_i, v_j), \quad P(v_j) = \sum_{i=1}^M P(u_i, v_j). \quad (10)$$

- Statistical independence:

$$P(u_i, v_j) = P(u_i)P(v_j), \quad (11)$$

in which case the mean of the product is the product of the means:

$$\overline{uv} = \bar{u} \bar{v}. \quad (12)$$

1.3 Continuous probability distribution

For continuous r.v. $x \in (a_1, a_2)$, assign value of r.v. to $f(x)$.

The probability density function $p(x)$ is normalized:

$$\int_{a_1}^{a_2} p(x) dx = 1. \quad (13)$$

The mean and variance are defined as:

$$\bar{x} = \int_{a_1}^{a_2} x p(x) dx, \quad \text{var}(x) = \int_{a_1}^{a_2} (x - \bar{x})^2 p(x) dx. \quad (14)$$

- Especially, $p(x) dx$ represents prob. to find x in $[x, x + dx]$.

•

2 Stat. Mech setup

- $\Omega(E, V)$: # of accessible states in range $(E, E + dE)$
 - More genrally: number of all possible states.

- Fundamental Postulate: All accessible states are equally likely.

$$p(\mu_i) = \frac{1}{\Omega(E, V)}, \text{ if } \mu_i = \text{acc.} \quad (15)$$

- Probability and average of states: prob of system havin gsome value of macro. param. $y = y_k$ is given by

$$p(y_k) = \frac{\Omega(E; y_k)}{\Omega(E)} \quad (16)$$

- Average value of the parameter y :

$$\bar{y} = \sum_k p(y_k) y_k = \sum_k \frac{\Omega(E; y_k)}{\Omega(E)} y_k \quad (17)$$

Example: 1D harmonic Oscillator. $H(q, p) = \frac{p^2}{2m} + \frac{1}{2}kq^2$, $H = E_n = (n + \frac{1}{2})\hbar\omega$ const. $n = 0, 1, 2, \dots$; $\omega = \sqrt{k/m}$ Defines an ellipse in phase space. Consider energy variation δE , phase space cell resides on a ring.

$$\Omega(E) = \frac{\text{area of ring}}{\text{area of phase space cell}} \quad (18)$$

Example: 1D particle in a box :

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}, n = 1, 2, 3, \dots \quad (19)$$

Example: Three spin $-1/2$ particles in equil, in ext. H field. The energy of each spin is $-\mu H$ (if $m = \frac{1}{2}$); $+\mu H$ (if $m = -\frac{1}{2}$) There are $2^3 = 8$ possible combinations of states. Microstate is specified by m_1, m_2, m_3 . Suppose the total energy is known to be $-\mu H$, then the accessible states are

$$\left\{ +\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2} \right\}, \left\{ +\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2} \right\}, \left\{ -\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2} \right\} \quad (20)$$

The prob. that first spin has $m_1 = +\frac{1}{2}$ is given by

$$\begin{aligned} \Omega\left(E; m_1 = +\frac{1}{2}\right) &= 2; \Omega(E) = 3 \\ \Rightarrow p\left(m_1 = +\frac{1}{2}\right) &= \frac{2}{3}. \end{aligned} \quad (21)$$

3 Density of states

Define $\omega(E)$ to be density of states, s.t. $\Omega(E) = \omega(E) dE$

- TO find relation Ω with (E, N) s.t. $\Omega = \Omega(N, E)$, consider **Classical Monatomic ideal gas**, enclosed in vol. V :

$H = \sum_i^N \frac{\vec{p}_i^2}{2m}$, energy range $(E, E + \delta E)$.

$$\begin{aligned} \Omega(E) &\propto V^N \int_E^{E+\delta E} \prod_i d^3 \vec{p}_i \\ &\propto V^N E^{3N/2} \delta E \\ \omega(E) &\propto V^N E^{3N/2} \end{aligned} \quad (22)$$

4 Interaction between Macro bodies

- Thermal Interaction: External param. fixed.

- $Q \equiv \overline{\Delta E}$. heat absorbed (+) or released (-) by system.
- Mech. Interaction: External param. can change.
 - $W \equiv -\overline{\Delta_x E}$. macro work done by system with variation in ext. param. x
- **General int.:** $Q \equiv \Delta \overline{E} - \Delta_x \overline{E} = \Delta \overline{E} + W$, ttl change in energy in exclusion of that due to mech. interaction (change in ext. param. x).

From genreal interaction we arrive at the first law:

$$\delta Q \equiv d\overline{E} + \delta W \quad (23)$$

5 Quasistatic process

- Slow int. s.t. system remains in equil. at all times, so that intensive params. are uniform throughout the system.
- Generalized force: consider sys. with ext. param x and $H(q, p; x)$:

$$\frac{dH}{dt} = \frac{\partial H}{\partial x} \frac{dx}{dt} \Rightarrow dE = \frac{\partial H}{\partial x} \frac{dx}{dt} dt. \quad (24)$$

Quasistatic so we can avg this over equil. ensemble with value of x at time t . Noticing $dE = -\delta W$:

$$\delta W = -\frac{\partial \overline{H}}{\partial x} \frac{dx}{dt} dt \equiv X dx, \quad (25)$$

where $X \equiv -\frac{\partial \overline{H}}{\partial x}$:generalized force

Example: Piston (ext. param. $x = V$)

$$\delta W = \overline{p} dV. \quad (26)$$

For vol. change $V_i \rightarrow V_f$:

$$W = \int_{V_i}^{V_f} \delta W = \int_{V_i}^{V_f} \overline{p}(V) dV. \quad (27)$$

6 Thermal int. btwn sys: Entropy

- Consider adiabatic system with two partitions, $\{E_1, \Omega_1(E_1)\}, \{E_2, \Omega_2(E_2)\}$. $E_1 + E_2 = E$ const.
 - $\Omega(E) = \sum_{E_1} \Omega_1(E_1) \Omega_2(E - E_1)$, and prob. of sys 1 has energy = E_1 is

$$P_1(E_1) = \frac{\Omega_1(E_1) \times \Omega_2(E - E_1)}{\Omega(E)}, \quad (28)$$

with $\Omega(E) \approx E^{aN}$.

- Finding \tilde{E}_1 s.t. $P_1(E_1) = \max : \frac{\partial P_1(E_1)}{\partial E_1} = 0$

$$\Rightarrow \left. \frac{\partial \ln \Omega_1}{\partial E_1} \right|_{E_1=\tilde{E}_1} = \left. \frac{\partial \ln \Omega_2}{\partial E_2} \right|_{E_2=E-\tilde{E}_1} \quad (29)$$

- We are motivated to define entropy:

$$S(E, x) \equiv \ln \Omega(E, x) \quad (30)$$

so that P_1 peaks when

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \Leftrightarrow S = S_1 + S_2 = \max \quad (31)$$

- Further define temperature:

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} \quad (32)$$

So that P_1 peaks when $T_1 = T_2$

- Sharpness of $P_1(E_1)$:
 - Rel. width = $\frac{\Delta^* E}{\bar{E}_1} \approx \frac{1}{\sqrt{N}}$
 - $\frac{\partial T}{\partial E} \geq 0$

7 The 2nd law

For two systems in thermal contact

$$\begin{aligned} \frac{dS(E)}{dt} &= \frac{dS_1}{dt} + \frac{dS_2}{dt} = \left[\left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) \frac{dE_1}{dt} \right] \\ &= \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \frac{dE_1}{dt} \geq 0 \end{aligned} \quad (33)$$

8 Reversible and Irreversible process

- Reversible: total entropy of isolated sys. constant $\frac{dS}{dt} = 0$
 - Irreversible: total entropy of isolated sys increases $\frac{dS}{dt} > 0$
-

9 Fundamental relation

- For general interaction between macro bodies, equilibrium relation:

$$\begin{cases} T_1 = T_2 \\ \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1} = \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2} \end{cases} \quad (34)$$

where

$$\left(\frac{\partial S}{\partial V} \right)_{E_1} = \frac{p}{T} \quad (35)$$

Applied to the total differential of entropy, we have

$$\boxed{dE = T dS - p dV.} \quad (36)$$

- Further, for quasistatic process, we have $dE = \delta Q - p dV$. Comparing terms gives

$$dS = \frac{\delta Q}{T} \quad (37)$$

- Particularly, for adiabatic process, $\delta Q = 0$ so $dS = 0$, so adiabatic \Rightarrow reversible.
- Revisiting equil. condition:

$$\left(\frac{\partial S_1}{\partial V_1} \right)_{E_1} = \left(\frac{\partial S_2}{\partial V_2} \right)_{E_2} \Rightarrow p_1 = p_2 \quad (38)$$

10 Laws of Thermodynamics

- 0th law: thermal transitivity. If A, C in equil; B,C in equil; then A,B in equil.
- 1st Law:

$$dE = \delta Q - \delta W \quad (39)$$

- 2nd Law:

$$dS \geq \frac{\delta Q}{T} \quad (40)$$

- 3rd Law:

$$\lim_{T \rightarrow 0} S = 0 \quad (41)$$

11 Response function

- Heat Capacities: $\delta Q|_x = C_x dT$
 - for $\delta Q|_V = (dE + \delta W)|_V \Rightarrow C_V = \left(\frac{\partial E}{\partial T}\right)_V$.
 - for $\delta Q|_p = (dE + \delta W)|_p \Rightarrow C_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$.

Useful so that combined with $dS = \frac{\delta Q}{T} = \frac{C_V}{T} dT$:

$$S(x, T_2) = S(x, T_1) + \int_{T_1}^{T_2} \frac{C_x}{T} dT \quad (42)$$

- Compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (43)$$

- Expansivity:

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (44)$$

12 Ideal Gas

- For ideal Monatomic gas, recall $\Omega(E) = BV^N E^{3N/2}$

$$S = \ln \Omega = N \ln V + \frac{3N}{2} \ln E + C. \quad (45)$$

Combined with $p = T \left(\frac{\partial S}{\partial V} \right)_E, \frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V$ we have

$$pV = NT; \quad E = \frac{3}{2}NT = \frac{3}{2}\nu RT \quad (46)$$

- Ideal Gas Law Writing $N = \nu N_A$, we have

$$pV = \nu RT, \quad R \equiv N_A k_B \quad (47)$$

- It is proved that $E = E(T)$, independent of V .

- Specific Heat:

- Define $c_x \equiv \frac{C_x}{\nu}$, “heat capacity per mole”.
- Const. V: $\delta Q|_V = C_V dT = \nu c_v dT$. A general relation is

$$c_v = \frac{1}{\nu} \left(\frac{\partial E}{\partial T} \right)_V > 0. \quad (48)$$

for ideal gas: $dE = \nu c_v dT$

- Similarly, Const. p: $\delta Q|_p = C_p dT = \nu c_p dT$. A general relation is

$$c_p = c_v + R \quad (49)$$

- adiabatic Index

Using $E = \frac{3}{2}\nu RT$; $c_v = \frac{1}{\nu} \left(\frac{\partial E}{\partial T} \right)_V$, we have

$$c_v = \frac{3}{2}R; c_p = c_v + R = \frac{5}{2}R. \quad (50)$$

So that adiabatic index $\gamma \equiv c_p/c_v = 5/3$

Ideal Gas in Various Process

- Isothermal: cons. T. $\Rightarrow pV = C$.
- Adiabatic: no heat transfer.

By first law:

$$\delta Q = dE + \delta W = 0 \Rightarrow 0 = \nu c_v dT + p dV. \quad (51)$$

using eqn of state : $pV = \nu RT$:

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0 \quad (52)$$

Since $c_v = \frac{3}{2}$ is constant, integrate the above gives

$$\gamma \ln V + \ln p = C \Rightarrow pV^\gamma = C. \quad (53)$$

13 Summary of Thermal laws

- Fundamental Relation $dE = T dS - p dV$.
- First Law: $dE = \delta Q - \delta W$.
- Second Law: $\delta Q = T dS$ for quasistatic.
- Ideal Gas Law Writing $N = \nu N_A$, we have

$$pV = \nu RT, \quad R \equiv N_A k_B \quad (54)$$

14 Response function

- Heat Capacities: $\delta Q|_x = C_x dT$
 - for $\delta Q|_V = (dE + \delta W)|_V \Rightarrow C_V = \left(\frac{\partial E}{\partial T} \right)_V$.
 - for $\delta Q|_p = (dE + \delta W)|_p \Rightarrow C_p = \left(\frac{\partial E}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p$.

Useful so that combined with $dS = \frac{\delta Q}{T} = \frac{C_V}{T} dT$:

$$S(x, T_2) = S(x, T_1) + \int_{T_1}^{T_2} \frac{C_x}{T} dT \quad (55)$$

- Compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (56)$$

- Expansivity:

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (57)$$

15 Thermodynamic Potentials

energy E , $E(S, V)$, $dE = T dS - p dV$

enthalpy $H = E + pV$, $H(S, p)$, $dH = T dS + V dP$

Helmholtz $F = E - TS$, $F(T, V)$, $dF = -S dT - p dV$

Gibbs $G = E - TS + pV$, $G(T, p)$, $dG = -S dT + V dp$

16 Maxwell Relations

$$\begin{aligned} \left(\frac{\partial T}{\partial V} \right)_S &= - \left(\frac{\partial p}{\partial S} \right)_V, & \left(\frac{\partial S}{\partial V} \right)_T &= \left(\frac{\partial P}{\partial T} \right)_S \\ \left(\frac{\partial T}{\partial p} \right)_S &= \left(\frac{\partial V}{\partial S} \right)_p, & \left(\frac{\partial S}{\partial p} \right)_T &= - \left(\frac{\partial V}{\partial T} \right)_p \end{aligned} \quad (58)$$

Used to obtain general relation between Specific heat: let

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{(\partial T)_P} \right); \quad \kappa \equiv - \frac{1}{V} \left(\frac{\partial V}{(\partial P)_T} \right). \quad (59)$$

Recall

$$\delta Q|_x = C_x dT, \quad C_x = T \left(\frac{\partial S}{\partial T} \right)_x \quad (60)$$

and thus $C_p - C_v = VT\alpha^2/\kappa$

- 3rd law : $S \rightarrow 0$ as $T \rightarrow 0$. Implies

$$C_v \rightarrow 0; \quad C_p \rightarrow 0; \quad \alpha \rightarrow 0; \quad \frac{C_p - C_v}{C_v} \rightarrow 0 \quad (61)$$

17 Entropy and Internal Energy : Take (T, V) as indp. var.

- Seek $S(T, V), E(T, V)$.

$$dS = \frac{C_v}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV, \quad (62)$$

where

$$\left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{\partial^2 p}{\partial T^2} \right)_V \quad (63)$$

then

$$C_v(T, V) = C_v(T, V_0) + \int_{V_0}^V T \left(\frac{\partial^2 p(T, V')}{\partial T^2} \right)_V dV'. \quad (64)$$

So

$$\begin{aligned}
& S(T, V) - S(T_0, V_0) \\
&= \int_{T_0}^T \frac{C_v(T', V)}{T'} dT' + \int_{V_0}^V \left(\frac{\partial p(T_0, V')}{\partial T} \right)_V dV'
\end{aligned} \tag{65}$$

Similarly, for energy:

$$dE = C_v dT + \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] dV \tag{66}$$

and so

$$\frac{\partial E}{(\partial T)_V} = C_v, \quad \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p \tag{67}$$

then, by integration,

$$\begin{aligned}
& E(T, V) - E(T_0, V_0) \\
&= \int_{T_0}^T C_v(T', V) dT' + \int_{V_0}^V \left[T_0 \left(\frac{\partial p(T_0, V')}{\partial T} \right)_V - p(T_0, V') \right] dV'
\end{aligned} \tag{68}$$

18 Free Expansion: Start from T_1, V_1 and $V_1 \rightarrow V_2$:

$\Delta E = Q - W = 0$; for ideal gas: $E(T_1) = E(T_2) \Rightarrow T_1 = T_2$.

In general, temp change:

$$\begin{aligned}
& \left(\frac{\partial T}{\partial V} \right)_E = \frac{1}{C_V} \left(p - \frac{T\alpha}{\kappa} \right) \\
& T_2 = T_1 + \int_{V_1}^{V_2} dV \left(\frac{\partial T}{\partial V} \right)_E
\end{aligned} \tag{69}$$

Entropy change:

$$\begin{aligned}
& \left(\frac{\partial S}{\partial V} \right)_E = \frac{p}{T} > 0. \\
& S_2 = S_1 + \int_{V_1}^{V_2} dV \left(\frac{\partial S}{\partial V} \right)_E
\end{aligned} \tag{70}$$

- for ideal gas: $\Delta S = N \ln \left(\frac{V_2}{V_1} \right)$
- for van der Waals with Eqn of State $(p + a/v^2)(v - b) = RT$, where $v = V/\nu$ molar vol:

$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{R}{v - b}; \quad \left(\frac{\partial T}{\partial V} \right)_E = -\frac{a\nu^2}{C_V V^2} \tag{71}$$

and it can be shown:

$$\Delta T = \frac{a\nu^2}{C_V} \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \tag{72}$$

19 Joule-Thomson Process: start p_1, T_1 ; $p_1 \rightarrow p_2$ and so $T_1 = T_2$

$$\Delta E = -W = p_1 V_1 - p_2 V_2 \Rightarrow H_1 = H_2 \tag{73}$$

- ideal gas:

$$H = E + pV = E(T) + \nu RT \Rightarrow H(T_1) = H(T_2) \Rightarrow T_1 = T_2$$

- In general:

$$\mu \equiv \left(\frac{\partial T}{\partial p} \right)_H = \frac{V}{C_p} (T\alpha - 1). \quad (74)$$

and also

$$\begin{aligned} dH &= T dS + V dp = 0 \\ \Rightarrow \left(\frac{\partial S}{\partial p} \right)_H &= -\frac{V}{T} \\ \Rightarrow \Delta S &= \left(\frac{\partial S}{\partial p} \right)_H \Delta p = -\frac{V}{T} \Delta p \end{aligned} \quad (75)$$

20 Heat Engines and Refrigerators

- heat absorbed by bath: $Q = T \Delta S$.

20.1 Heat engine

- ▶ Perfect heat engine: convert all heat to work:

$$\Delta S_{\text{ttl}} = -q/T = -w/T < 0.$$

- ▶ Real heat Engine: absorb q_1 , emits q_2 , produce work $w = q_1 - q_2$: $\Delta S = -q_1/T_1 + q_2/T_2 \geq 0$
- ▶ efficiency $\eta \equiv w/q_1 \leq (1 - T_2/T_1)$.
- ▶ Carnot Engine: $\Delta S = 0 \Rightarrow \eta_{\text{max}} = (T_1 - T_2)/T_1$

20.2 fridge

- ▶ Perfect fridge: Does no work in refrigeration $\Delta S = q_1/T_1 - q_2/T_2$
- ▶ real fridge: absorbs q_2 from cold bath, emits q_1 to hot bath, with work $w = q_1 - q_2$.
- ▶ coefficient of performance $\eta = q_2/w \leq T_2/(T_1 - T_2)$

21 Cononical Ensemble: fix T, N, V.

$$P_r = \frac{\exp\left(-\frac{E_r}{T}\right)}{Z}; \quad Z \equiv \sum_r \exp\left(-\frac{E_r}{T}\right) \quad (76)$$

$$\text{Observables: } \overline{O} = \sum_r \frac{\exp\{-\beta E_r\}}{Z} O_r$$

$$\text{In classical case: } P(E) = \frac{\Omega(E) \exp(-\beta E)}{Z}$$

- Maxwell velocity distribution: Consider a classical monatomic gas. Take A = single gas particle and A' remaining molecules, acting as heat reservoir. at temp. T. Distribution of velocity:

$$f(\vec{v}) = \left(\frac{m}{2\pi T} \right)^{\frac{3}{2}} \exp\left(-\frac{m\vec{v}^2}{2T}\right) \quad (77)$$

- Free energy : $F = -T \ln Z$

21.1 Ex: spin in H-field

$$E_r = E_{\pm} = \mp \mu H$$

$$P_r = \frac{\exp[\pm \beta \mu H]}{\exp[\beta \mu H] + \exp[-\beta \mu H]} = \frac{\exp[\pm \beta \mu H]}{2 \cosh(\beta \mu H)} \quad (78)$$

$$\text{avg momentum: } \bar{\mu} = \sum_{r=\pm} P_r \mu_r = \mu \tanh(\beta \mu H)$$

$$\overline{M} = n\overline{\mu} = n\mu \tanh(\mu H/T) \text{ when } \mu H \ll T, \overline{M} \approx (n\mu^2 H)/T \equiv \chi H$$

21.2 Properties of Z , and thermo potential

- avg energy $\overline{E} = -\partial_{\beta} \ln Z = -T^2 \partial_T (F/T)$;
- avg momentum for spin 1/2: $\overline{\mu} = +T \partial_H \ln Z$
- energy dispersion: $\overline{\Delta E^2} = T^2 \partial_T \overline{E} = T^2 C_v$
- $S \equiv -\sum_r P_r \ln P_r = -\partial_T (T \ln Z) = -\partial_T F$;
- $F = E - TS = -T \ln Z = -T \ln \left(\sum_r \exp[-E_r/T] \right)$

22 Fundamental Relation:

$$dF = -S dT - p dV.$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V; \quad p = -\left(\frac{\partial F}{\partial V}\right)_T \quad (79)$$

- Second law for CE: $F = \min$ in equil.
- first law in CE: quasistatic change gives $d\overline{E} = \sum_r E_r dP_r + \sum_r P_r dE_r$
- $\delta Q \equiv \sum_r E_r dP_r = T dS$.
- $\delta W \equiv -\sum_r P_r dE_r$

23 Grand Canonical Ensemble

- Chemical potential $\mu \equiv -T \left(\frac{\partial S}{\partial N} \right)_E = \left(\frac{\partial E}{\partial N} \right)_{S,V}$.
- equilibrium condition: $\mu/T = \text{const.}$
- distribution:

$$\begin{aligned} P_r &= \frac{\exp[-(E_r - \mu N_r)/T]}{\mathcal{Z}} \\ \mathcal{Z} &= \sum_r \exp[-(E_r - \mu N_r)/T] \\ &= \sum_n \exp(\mu N/T) Z(T, N) \end{aligned} \quad (80)$$

- particle fluctuation:

$$\overline{E} = \sum_r \frac{\exp[-(E_r - \mu N_r)/T]}{\mathcal{Z}} N_r = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}, \quad (81)$$

where $\Phi = -T \ln \mathcal{Z}$, Grand Potential.

24 Classical Ideal gas

$$Z' = \zeta^N; \quad \zeta = V \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \quad (82)$$

Correction:

$$\begin{aligned} Z &= Z'/N! \\ \Rightarrow F &= -NT \ln \left[\frac{eV}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \right] \end{aligned} \quad (83)$$

25 Thermal Classical Limit

$\lambda = \sqrt{(2\pi\hbar^2)/(mT)}$ and then

$$\zeta = \frac{V}{\lambda^3} \Rightarrow Z = \frac{1}{N!} \zeta \int \prod_{i=1}^N \frac{\exp[-\beta U(q)]}{V} d^3 \vec{q} \quad (84)$$

26 Equipartition theroem

Each Quadratic term in Energy ($q \vee p$) contributes $\frac{1}{2}T$ to the avg energy, and $\frac{1}{2}$ to heat capacity.

- **Ex: harmonic Oscillator:** $E = p^2/2m + \frac{1}{2}kq^2$. Two quad term gives $\bar{E} = 2 * \frac{1}{2}T = T$,

where kenitic: $\bar{K} = \frac{p^2}{2}m = \frac{\bar{E}}{2}$; potential energy: $\bar{U} = \frac{1}{2}kq^2 = \frac{\bar{E}}{2}$.

Further, partition function yields:

$$Z = \sum_n e^{-\beta E_n} = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}} \quad (85)$$

$$\bar{E} = -\partial_\beta \ln(Z) = \hbar \omega \left(\frac{1}{2} + \frac{1}{e^{-\beta \hbar \omega} - 1} \right) \quad (86)$$

$$C = \frac{\partial \bar{E}}{\partial T} = \left(\frac{\hbar \omega}{T} \right)^2 \frac{\exp[\hbar \omega / T]}{\exp[\hbar \omega / T] - 1} \quad (87)$$

- Thermal limits:

$$T \gg \hbar \omega : \bar{E} \rightarrow T; C \rightarrow 1. \quad (88)$$

–

$$T \ll \hbar \omega : \bar{E} \rightarrow \hbar \omega / 2; C \rightarrow \left(\frac{\hbar \omega}{T} \right)^2 \exp[-\hbar \omega / T] \quad (89)$$

27 Solid Lattice

$$\bar{E} = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2} m \omega_i^2 q_i^2 \right) = 3NT = 3\nu RT. \quad (90)$$

$$C_v = \left(\frac{\partial \bar{E}}{(\partial T)_V} \right) = 3\nu R.$$

at low temp, assume $\omega_i = \omega = \text{const}$. Let $\theta_E \equiv \hbar \omega$.

$$\begin{aligned} \bar{E} &= 3N\theta_E \left(\frac{1}{2} + \frac{1}{\exp[\beta \theta_E] - 1} \right) \\ C_V &= \left(\frac{\partial \bar{E}}{(\partial T)_V} \right) = 3N \left(\frac{\theta_E}{T} \right)^2 \frac{\exp[\beta \theta_E]}{(\exp[\beta \theta_E] - 1)^2} \end{aligned} \quad (91)$$

Thermal limits:

- $T \gg \theta_E : C_V = 3R$.
- $T \ll \theta_E : C_V = 3R(\theta_E/T)^2 \exp[-\theta_E/T]$

28 Paramagnetism

- $\vec{\mu} = g\mu_B \vec{v}$; $\mathcal{E} = -\vec{\mu} \cdot \vec{H} \Rightarrow \mathcal{E}_m = -g\mu_B H_m$

$$\begin{aligned} Z &= \sum_{m=-J}^{+J} \exp[-\beta g \mathcal{E}_m] = \frac{\sinh[(J + \frac{1}{2})\eta]}{\sinh(\frac{\eta}{2})}, \\ \eta &\equiv \frac{g\mu_B H}{T}. \end{aligned} \quad (92)$$

- avg. momentum:

$$\overline{\mu_z} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} = g\mu_B J B_J(\eta), \quad (93)$$

where $J B_J(\eta) \equiv (J + \frac{1}{2}) \coth[(J + \frac{1}{2})\eta] - \frac{1}{2} \coth(\eta/2)$.

- Magnetization: $\overline{M_z} = n\overline{\mu_z} = ng\mu_B J B_J(\eta)$.
 - Thermal limits:

$$\begin{aligned} \eta \ll 1 : \quad \overline{M_z} &= \frac{n(g\mu_B)^2 J(J+1)}{3T} H \equiv \chi H. \\ \eta \gg 1 : \quad \overline{M_z} &= ng\mu_B J. \end{aligned} \quad (94)$$

29 Kinetic Theory

- maxwell velocity distribution:

$$f(\vec{v}) = \left(\frac{m}{2\pi T} \right)^{3/2} \exp[-(m\vec{v}^2)/(2T)] \quad (95)$$

- distribution for speed $v = |\vec{v}|$:

$$F(v) dv = 4\pi \left(\frac{m}{2\pi T} \right)^{3/2} v^2 \exp[-(mv^2)/(2T)] dv \quad (96)$$

- mean speed: $\bar{v} = \sqrt{8/\pi} \sqrt{T/m}$
- RMS speed: $v_{\text{RMS}} = \sqrt{3} \sqrt{T/m}$
- most probable speed: $\tilde{v} = \sqrt{2} \sqrt{T/m}$

29.1 Examples:

- Number of particle striking a surface = $n(v_z dt dA)$, $n = N/V$
- total particle flux:

$$\Phi_0 = \int d^3\vec{v} \Phi(\vec{v}) = \frac{1}{4} n \bar{v} \quad (97)$$

write $\bar{v} = \sqrt{8T/\pi m} \Rightarrow \Phi_0 = \frac{1}{4} n \sqrt{8T/\pi m}$. With $p = nT$: $\Phi_0 = p/\sqrt{2\pi m T}$ for ideal gas.

- effusion: $I = \Phi_0 * A = pA/\sqrt{2\pi m T}$
- Elastic collision force: $F = mn\overline{v_z^2} dA$.
 - $\bar{p} = \frac{F}{dA} = mn\overline{v_z^2}$
 - for ideal gas: $\overline{v_z^2} = T/m \Rightarrow \bar{p} = nT \Rightarrow pV = NT$