

Notes on Physics 415:
Statistical and Thermal Physics
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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 $n_2 = \left(\frac{N-m}{2}\right)$:

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

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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 conditoin

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

- 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 $[x, x + dx]$.

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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 indep. 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 $\Phi = -T \ln Z$, 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:

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

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

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

- 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: $\overline{v_z^2} = T/m \Rightarrow \bar{p} = nT \Rightarrow pV = NT$