Personal Notes on

Thermal Physics(PHY294)

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Abstract

This note is documented based on the textbook "Thermal Physics" by Daniel Schroeder, which is used to instruct second half of PHY294: Quantum mechanics and Thermal Physics.

Contents

1 Energy in Thermal Physics

1.1 Definition

Some definitions to know before hand are

- Thermal Equilibrium: state when temperature is the same after objects contacting for a long time.

- Relaxation time: Time for a system to reach thermal equilibrium.

- Diffusive Equilibrium: molecules of each substance are free to move around but no longer have any tendency to move one way or another.

- Mechanical equilibrium: large scale motion equilibrium.

- Temperature: measure of the tendency of an object to give up energy to its surrounding.

1.2 Ideal Gas

The ideal gas law states

$$PV = nRT$$

where R = 8.314 J/mol ·K which is only valid in low density when the average space between gas molecules is much larger than the size of a molecule. Some associates conclusions are

- Average Kinetic Energy:

$$\frac{1}{2}kT = \overline{\frac{1}{2}mv_x^2}$$

  summing three directions

$$\overline{K} = \frac{3}{2}kT$$

1.3 Equipartition of Energy

Definition: **Degree of Freedom**: different forms of energy which the formula is a quadratic function of a coordinate or velocity component.

Theorem: **Equipartition Theorem**: At temperature T, the average energy of any quadratic degree of freedom is $\frac{1}{2}kT$

Based on the theorem, suppose a system containing N molecules and each with f degrees of freedom. The total thermal energy(or just energy) is

$$U_{thermal} = N \cdot f \cdot \frac{1}{2}kT$$

For solid the vibration of solids count as 2 degrees of freedom for each direction. In solid, since it vibrates in three perpendicular directions then it counts as 6 degrees of freedom. A simple equation to find the degree of freedom is 3n, where n stands for the number of atom in the structure. In general for a monoatomic atom the total energy is:

$$U = 3 \cdot \frac{1}{2}kT + 0 \cdot \frac{1}{2}kT + 0 \cdot kT$$

1.4 Heat and Work

- **Heat:** Any spontaneous flow of energy from oen object to another causes by difference in temperature.

The total energy change can be summarized by the First Law of Thermodynamics

$$\Delta U = Q + W$$

three types of energy transfers are Conduction, Convection, and Radiation.

1.5   Work

work done can be summerized by

$$W = -\int_{V_i}^{V_f} P(V)dV \quad \text{(quasistatic)}$$

and quasistatic stands for the gas continually equilibrate to the changing conditions.

Isothermal Compression

it is a slow process that temperature doesn't change, such that

$$W = -\int_{V_i}^{V_f} P\, dV = -NkT \int_{V_i}^{V_f} \frac{1}{V}\, dV$$

$$= -NkT(\ln V_f - \ln V_i) = NkT \ln \frac{V_i}{V_f}.$$

Adiabetic Compression

It is an extremely fast process such that heat doesn't change, such that

$$V_f T_f^{f/2} = V_i T_i^{f/2}$$

eliminating T on both sides with ideal gas law gives

$$V^\gamma P = constant$$

where γ is the adiabatic exponent for (f + 2) / f

1.6   Heat Capacities

The Heat capacity is the heat needed per degree of temperature.

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}$$

IsoVolumetric

This is the case when the volume doesn't change so there's no work

$$C_v = \left(\frac{\Delta U}{\Delta T}\right)_V$$

by the equipartition theorem

$$C_v = \frac{Nfk}{2}$$

which gives a direct method to measure the number of degrees of freedom in an object, called the **Rule of Dulong and Petit**

Isobaric

When pressure is constant, such that

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

The second term is the additional heat to compensate for the energy lost as work, which is usually small for liquid and solid, and similarly.

$$C_P = \frac{Nk}{P}$$

Yet, the heat capacities increase at higher temperature. Also,

$$C_P = C_V + Nk = C_V + nR$$

Latent Heat

It is a measurement for the phase transformation, where the capacity is then infinite.

Enthalpy

The total energy in a system is called the Enthalpy

$$H = U + PV$$

and

$$\Delta H = \Delta U + P\Delta V = Q + W_{Other}$$

stating that the change in enthalpy is only caused by heat and other forms of work, not by compression work (during constant-pressure processes).

2 Second Law of Thermodynamics

2.1 Two-State Systems

- **Microstate:** A combination out of all combinations of states

- **Macrostate:** A description of the states(i.e. how many heads or tails there are)

- **Multiplicity:** The number of microstates corresponding to a given macrostate. Denoted as Ω

The number of possible combinations of n object from N objects is:

$$\Omega(N, n) = \frac{N!}{n! \cdot (N-n)!}$$

Postulates

The main statement for both Thermodynamics(TD) and Statistical Mechanics(SM) is that
In a closed/isolated system all accessible microstates are equally likely in Thermodynamics equilibrium. This is so called the main postulate of SM

Two State Paramagnet

A **Paramagnet** is a material in which the particles act like tiny compass needles that tend to align parallel to any externally applied magnetic field. A **Ferromagnet** is a magnet that magnetize even without any externally applied field. Each magnetic particle is called **dipole**. For the simple cases, only two directions of the magnetic dipole is allowed, up or down(denoted as $N_\uparrow$ and $N_\downarrow$. The total number of dipoles is then $N = N_\uparrow + N_\downarrow$. The multiplicity of any macrostate is given by

$$\Omega(N_\uparrow) = \frac{N!}{N_\uparrow! N_\downarrow!}$$

This combination determines the total energy of a system.

$$\underbrace{E_i}_{\text{potential energy}} = - \underbrace{\vec{\mu}}_{\text{magnetic moment}} \cdot \underbrace{\vec{B}}_{\text{magnetic field}} = -\mu S_i B$$

where S_i is a general term for the spin direction(1 for up and -1 for down), and $\mu_e = \dfrac{e\hbar}{2 m_e c}$. So the total energy of a system goes to

$$U = \sum_{i=1}^{N} E_i = -\mu B \mathbf{S}$$

where $\mathbf{S}$ in this case is the total spin specifies macrostate. Yet, there are total of $\mathbf{N+1}$ possible distinct macrostates of a N spin system with 2^N microstates. A few equations to note

- Macrostates:
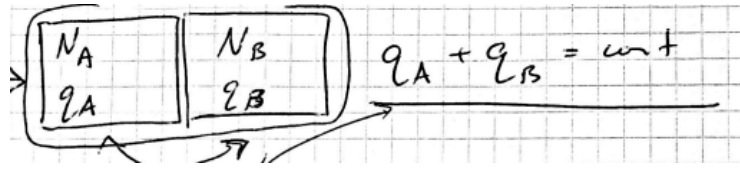
$$S = N_\uparrow - N_\downarrow = -N + 2N_\uparrow$$

- Multiplicity: same as the equation before but the definition is that it is the number of microstates of the N-spin system st. the total number of up spins is $N_\uparrow$

2.2 Einstein model of Solid

A harmonic oscillator can be used to simulate the vibration of atoms in a solid.

- Each atom has 3 directions of oscillation so N = 3n simple harmonic oscillators where n stands for the number of atoms.

- EMS Microstate: Each microstate is noted by $(n_1, n_2, n_3 .... n_N)$ where $n_i = 0, 1, ... \infty$. Each microstate is a collection of N non-negative integers(# of quantum excited states in each of the N SHOs).

- EMS Macrostate: the total energy "q" is denoted by7

$$q = n_1 + n_2 ... n_N$$

- Multiplicity: The multiplicity function of EMS is ways of finding q balls in N boxes:

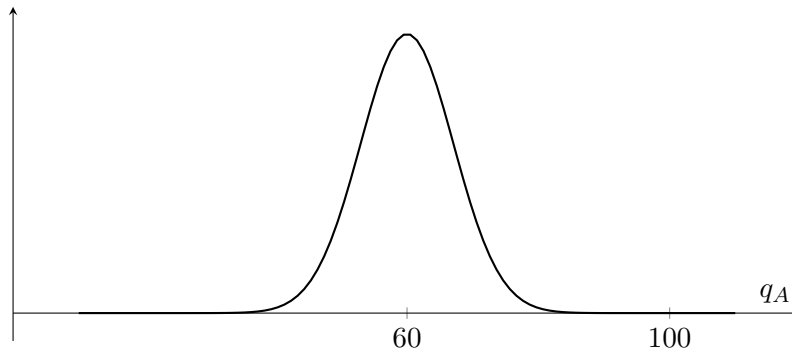$$\Omega(N, q) = \frac{(N - 1 + q)!}{(N - 1)! q!}$$

which stands for the function of macrostate with q quanta of EMS with N oscillators.

- Energy: q is only a number of quanta the total energy is actually

$$U = \hbar \omega q$$

Thermal Contact of two systems

Consider two initially isolated systems contacting each other. after thermal equilibrium is achieved $q'_A + q'_B = q_A + q_B$. However, there are many ways $q_A \& q_B$ sums to q. Therefore, we need to find the values of combination that have the highest multiplicity. By bashing all the terms, we would get such a diagram

where given $q = 100$, $q_A = 60$ has the highest multiplicity. Note that

$$\frac{q'_A}{q'_B} = \frac{N_A}{N_B}$$

So when two systems are put together, the configuration will maximize Ω_{total}. Given this information, the probability that combined system will have E/2 - Δ in solid 1 and E/2 + Δ in solid 2 is

$$P(E, \Delta) = \frac{\Omega_1 \left(\frac{E}{2} - \Delta \right) \Omega_2 \left(\frac{E}{2} + \Delta \right)}{\Omega_{1+2}(E)}$$

where

$$\Omega_{1+2}(E) = \sum_{\Delta'} \Omega_1 \left(\frac{E}{2} - \Delta' \right) \Omega_2 \left(\frac{E}{2} + \Delta' \right)$$
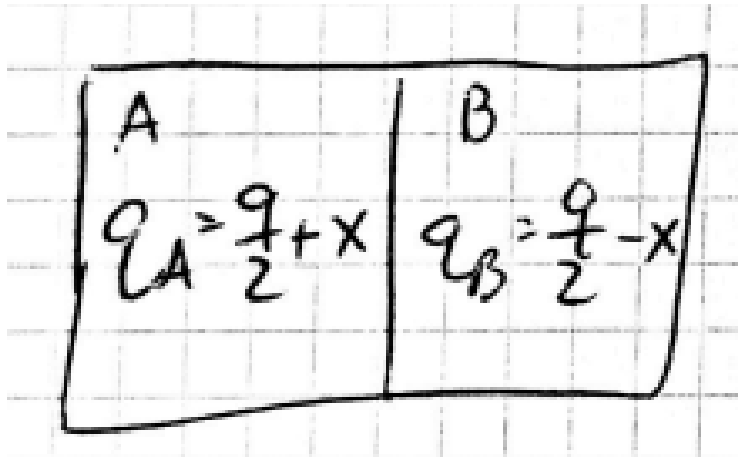
so we need to maximize the numerator, which can be done through some simple calculus s.t.

$$\left\{ \frac{\partial}{\partial \Delta} \left(\Omega_1 \left(\frac{E}{2} - \Delta \right) \Omega_2 \left(\frac{E}{2} + \Delta \right) \right) = 0 \right\}$$

and we get

$$\frac{\partial \ln \Omega_1(E'_1)}{\partial E'_1} = \frac{\partial \ln \Omega_2(E'_2)}{\partial E'_2}$$

This introduce some statistical definitions

- Temperature:

$$\frac{1}{T} = \frac{\partial}{\partial E}\left(k \ln \Omega(E)\right)$$

- Entropy:

$$S(E) = k \ln(\Omega(E))$$

where k stands for the boltzman constant. And

$$\frac{1}{T} = \frac{\partial}{\partial E} S(E)$$

- Stirling's Formula:

$$\ln(n!) \approx \ln\left(n^n e^{-n}\sqrt{2\pi n}\right) = n(\ln n - 1) + \frac{1}{2}\ln(2\pi n)$$

By using all the definitions above we can show that for $N \gg 1, q \gg N$ we have at **High temperature Limit**

-
$$\Omega(N, q) \approx \left(\frac{qe}{N}\right)^N$$

-
$$S = kN \ln\left(\frac{qe}{N}\right)$$

-
$$\frac{1}{T} = \frac{\partial S}{\partial(\hbar\omega q)} = \frac{kN}{\hbar\omega q}$$

where

$$kT = \text{average energy per oscillator}$$

and $q \gg N \Leftrightarrow kT \gg \hbar\omega$ which is the high temperature situation of the system.

-
$$\Omega_{total}(q_A, q_B; N, N) \approx \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N$$

- Two Oscillator Contact: where the total multiplicity is

$$\left(\frac{e^2}{N^2}\right)^N \left(\frac{q}{2} - x\right)^N \left(\frac{q}{2} + x\right)^N = \left(\frac{e^2}{N^2}\right)^N \left((\frac{q}{2})^2 - x^2\right)^N$$

Note: we assume two solids having the same amount of atom N
Under high temperature situation:

$$= \left(\frac{e^2}{N^2}\right)^N (\frac{q^2}{4})^N \left(1 - (\frac{2x}{q})^2\right)^N$$

$$= \Omega_{\text{total}}(q, 0; N, N) \times \left(1 - \left(\frac{2x}{q}\right)^2\right)^N$$

$$= \left(\frac{e^2}{N^2}\right)^N \left(\frac{q^2}{q^2}\right)^N \times \left(1 - \left(\frac{2x}{q}\right)^2\right)^N$$

where

$$\Omega_{\text{total}}(q, 0; N, N) = \Omega_{max}$$

This leads to the final expression:

$$\frac{\Omega_{\text{total}}(q, x; N, N)}{\Omega_{\max}} = e^{-N\left(\frac{2x}{q}\right)^2} = \frac{\text{Probability to have x != 0}}{\text{Probability to have x = 0}}$$

$$\begin{cases} N \gg 1, \text{ a given in SM} \\ \dfrac{q}{2} + x \gg N, \text{ lots of quanta per oscillator} \\ \qquad \text{(high-}T \text{ limit)} \\ x \ll \dfrac{q}{2}, \text{ small imbalance between A \& B} \end{cases}$$

Also

$$\frac{x}{q/2} = (\text{fractional energy imbalance between A \& B})$$

with the final function, we can conclude that

> **Idea**:
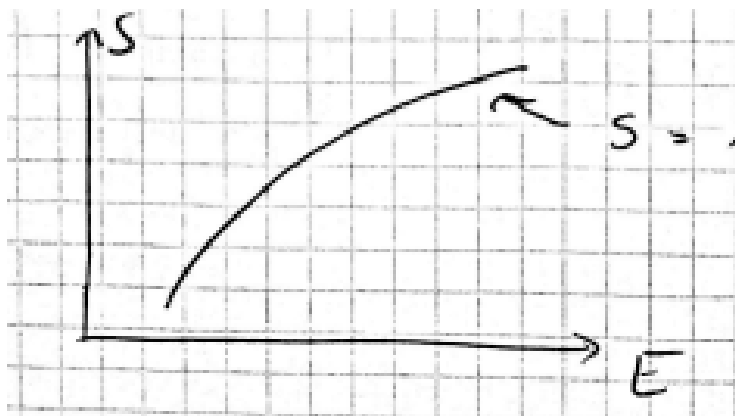> - Probability of any nonzero fractional energy imbalance scales as $\dfrac{1}{\sqrt{N}}$ as $N \to \infty$
> - a closed system in TD equilibrium is most likely to be found in the state of highest entropy.
> - The entropy of a closed system always increases (2nd law of TD)

Entropy and Temperature

recall that we defined entropy as $N \to \infty$

$$S \approx kN \log\left(\frac{qe}{N}\right) = kN \log\left(\frac{Ee}{\hbar\omega N}\right)$$

Also

$$\frac{\partial S}{\partial E} > 0, i.e. T > 0$$

- for all "normal systems in TD equilibrium."
- For a normal system S(E) also have negative 2nd derivative, like a linear term plus an upside-down parabola.

- Also as E increases, T increases.

- This also means that heat capacities of TD systesm: $C_v > 0$ for stable systems in TD equilibrium.