

# Physics 463: Statistical Mechanics and Thermodynamics

Lectures: Chong Zu  
Notes and Homework: Junseo Shin

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# 1 Intro to statistical methods

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- Goal: Study systems consist of many particles (magnitude of moles) that interact with each other.
- Stat Mech bridges the gap between the Macroscopic and Microscopic Description of a system.

Macroscopic Description  $> \mu\text{m}$ :

- Temperature, Pressure, Volume Entropy, etc.

Microscopic Description  $\text{\AA}$ :

## Worksheet

- (1) Avogadro's number:  $N_A = 6.022 \times 10^{23}$  e.g. in 12g of carbon-12, there are  $N_A$  atoms!  
 1 mole of air : 22.4 L at 273 K, 1 atm.  
 e.g. Say a room is 5m x 5m x 8m = 200 m<sup>3</sup> =  $200 \times 10^3$  L, how many moles of air are in the room?  
 $\sim 10000 N_A$

- (2)  $k_B = 1.38 \times 10^{-23}$  J/K  
 Physical Meaning:  $k_B T$  will roughly gives us the energy in one atom

- (3) On a number line with 1 and  $+\infty$ , where is  $N_A$ ?  
 In mathematics, we would place  $N_A$  closer to 1, but in physics we would place it closer to  $+\infty$  because this number is huge in the context of physics.

- (4) In the physics convention, we use  $\theta$  as the polar angle and  $\phi$  as the azimuthal angle. So a volume element in a sphere is

$$r^2 \sin \theta dr d\theta d\phi$$

Thus the volume of a sphere is

$$V = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_0^R r^2 \sin \theta dr d\theta d\phi = \frac{4}{3} \pi R^3$$

- (5) The ideal gas law comes in two forms:

$$PV = N k_B T$$

$$PV = nRT$$

where  $n = \frac{N}{N_A}$ , and  $N$  is the number of particles in the system.

- (6) The container with gas confined to half a container at  $t = 0$  releases the gas to fill the whole container at  $t > 0$ . What is the change in entropy?

The equation for the change in entropy is

$$dS = \frac{dQ}{T}$$

but this doesn't tell us much...

**Basic Statistical Concepts** : “statistical ensemble”

Example: Fair coin toss (50/50)  $N$  times. The expected value of heads is  $N/2$ . Repeating this many times gives a Gaussian distribution centered at  $N/2$ .

**Random walk in 1D** Starting at  $x = 0$ , we have a probability  $p$  to move one unit to the right and probability  $(1 - p) = q$  to move left.

For a ‘trajectory’

- $n_L$ : # of steps left
- $n_R$ : # of steps right
- $N = n_L + n_R$
- Displacement:  $x = n_R - n_L$

Each step is independent: “no memory”, “Markovian/Markov process”

The probability of a specific trajectory is

$$p \cdot p \cdots p \cdot q \cdots q = p^{n_R} q^{n_L}$$

How many ways this  $(n_R, n_L)$  can be arranged?

$$\binom{N}{n_R} = \frac{N!}{n_R! n_L!}$$

So the probability of taking  $n_R$  steps to the right is

$$W_N(n_R) = \frac{N!}{n_R! n_L!} p^{n_R} q^{n_L}$$

## Finishing the Random Walk

$$W_N(n_R) = \frac{N!}{n_R!n_L!} p^{n_R} q^{n_L}$$

is indeed the “Binomial distribution”.

The mean displacement (or expected value) is

$$\bar{m} = \bar{n}_R - \bar{n}_L = pN - qN = N(p - q)$$

How do we define variance/dispersion?

$$\begin{aligned} \overline{(\Delta n_R)^2} &= \overline{(n_R - \bar{n}_R)^2} = \overline{n_R^2 - 2n_R\bar{n}_R + \bar{n}_R^2} \\ &= \overline{n_R^2} - 2\bar{n}_R^2 + \bar{n}_R^2 \\ &= \overline{n_R^2} - \bar{n}_R^2 = Npq \end{aligned}$$

So the deviation or width is roughly  $\sim \sqrt{Npq}$

For large  $N$ , the distribution can be approximated a continuous:

$$\left. \frac{dW(n_R)}{dn_R} \right|_{\bar{n}_R} = 0$$

or equivalently

$$\left. \frac{d \ln W(n_R)}{dn_R} \right|_{\bar{n}_R} = 0$$

And using

$$n_R \equiv \bar{n}_R + \xi$$

where  $\xi$  is the deviation from the mean.

So now we can Taylor expand  $\ln W$ :

$$\ln W(n_R) = \ln W(\bar{n}_R) + \cancel{\left. \frac{d \ln W(n_R)}{dn_R} \right|_{\bar{n}_R} (n_R - \bar{n}_R)} + \frac{1}{2} B_2 \xi^2 + \dots$$

where

$$W(n_R) \equiv W_{max} e^{-\frac{1}{2} B_2 \xi^2}, \quad B_2 = \frac{1}{Npq}$$

This yields the Gaussian distribution approximation.

$$P(m) = W(n_R) = (2\pi Npq)^{-1/2} e^{-\frac{[m - N(p-q)]^2}{8Npq}}$$

## Worksheet

1. If a coin is flipped 400 times, what's the probability of getting 215 heads?

$$N = 215 + 185 = 400, \quad p = 0.5, \quad q = 0.5, \quad m = 215 - 185 = 30$$

Plugging in the numbers gives  $P(30) = 1.295\%$

## 2 Statistical description of systems of particles

### 2.1 Statistical formulation

#### Essential ingredients:

1. state of the system:
  - single spin-1/2 particle.  $\uparrow, \downarrow$
  - a bunch of spin-1/2 particles.  $\uparrow\uparrow\downarrow \dots$
  - a simple 1D Harmonic Oscillator:  $E = (n + 1/2)\hbar\omega$ , with states  $|n\rangle$
  - a bunch of 1D HO:  $|n_1, n_2, \dots, n_N\rangle$
2. Statistical ensemble: Instead of a simple experiments, we consider an ensemble of many exps.
3. Basic postulate about a priori probabilities (relative prob of finding the system in any of its accessible states)
4. Calculate probabilities

**Example:** 3 spin-1/2

State	Spin	Energy	$\Omega(E)$	$y_k = \uparrow, \downarrow$ $\Omega(-\mu H, \uparrow)$
$\uparrow\uparrow\uparrow$	3/2	$-3\mu H$	1	
$\uparrow\uparrow\downarrow$	1/2	$-\mu H$	3	
$\uparrow\downarrow\uparrow$				
$\downarrow\uparrow\uparrow$				
$\uparrow\downarrow\downarrow$	-1/2	$\mu H$	3	
$\downarrow\uparrow\downarrow$				
$\downarrow\downarrow\uparrow$				
$\downarrow\downarrow\downarrow$	-3/2	$3\mu H$	1	

Table 1: Energy levels of 3 spin-1/2 particles

System: *isolated*: energy cannot change *equilibrium*: prob of finding the system in any one accessible state is constant in time

#### A fundamental postulate:

An isolated system in equilibrium is equally likely to be in any of its accessible states

In calculating probabilities, e.g., isolated system with energy in range  $[E, E + \delta E]$

$\Omega(E)$ : total number of states of the system in this range

$\Omega(E, y_k)$ : in this energy range and some other property  $y_k$  where the probability of having this property is

$$P(y_k) = \frac{\Omega(E, y_k)}{\Omega(E)}$$

#### Density of states (DOS)

$$\Omega(E) = w(E)dE, \quad w(E) \sim E$$

where  $w(E)$  is the density of states.

## 2.2 Interactions between macroscopic systems

In general: specify some macroscopic measurable parameters  $x_1, x_2, \dots, x_n$

- Microstate: A particular quantum state:  $\gamma$  of the system with energy  $E_\gamma$

$$E_\gamma = E_\gamma(x_1, x_2, \dots, x_n)$$

- Macrostate (Macroscopic state): Specify external parameters and any other conditions, and includes all the possible microstates—e.g., from Table above the macrostate of  $-\mu H$  has 3 microstates. “Microstate” is one particular specific state consistent with the macrostate.

Consider two macro systems  $A, A'$ ; they can interact with each other to exchange energy.

Q: what are the different ways to exchange  $E$ ? HEAT, WORK. e.g. If  $A, A'$  are in a box separated by a wall, then the wall moving due to pressure exchanges energy as work. If the wall cannot move, then there is no work exchanged. [insert image of two boxes with a wall]

### Two Cases:

- *thermal interaction*: If all the external parameters are fixed

$$\Delta E = Q, \quad \Delta E' = Q'$$

where  $Q, Q'$  are the heat absorbed by each macrosystem, and the energy of the whole system is unchanged, i.e.,

$$\Delta E + \Delta E' = 0 \implies Q + Q' = 0, \quad Q = -Q'$$

- *mechanical interaction* (thermal isolation): no heat exchange “adiabatic”. I do work, negative work is done!

**Example:** Beaker of water,  $A$ , and a wheel attached to a pulley with a weight,  $A'$  (2.7 Example 2). The work done by the pulley decreases the energy of system  $A'$  by  $ws$  (weight times distance).

**In general** energy can be exchanged both as Heat and Work.

$$Q \equiv \Delta E - \mathcal{W}$$

where  $\mathcal{W}$  is the work done to the system. And

$$W = \mathcal{W}$$

is the work done by the system, i.e.,

$$Q \equiv \Delta \bar{E} + W$$

**Case of small amounts interaction:** Infinitesimal changes

$$dQ = d\bar{E} + dW$$

where the bar through the differential indicates the process as path dependent.

### Worksheet

- (1) For the infinitesimal quantity

$$dG = \alpha dx + \beta \frac{x}{y} dy$$

it is path dependent:



**General interaction process:** energy is exchanged both as heat and work

$$Q = \Delta E + W$$

where  $Q$  is the heat added to the system (positive  $\Delta E$  adds energy) and  $W$  is the work done by the system

**Very very small work/heat:** infinitesimal

$$dQ = d\bar{E} + dW$$

where  $d$  is an exact differential (path independent) and  $d\bar{}$  is an inexact differential (path dependent).

**Math:** multivariable differential

A differential form is exact if its equal to the general differential  $dF$  for some function  $F(x, y)$

e.g.  $A(x, y)dx + B(x, y)dy = dF(x, y)$

From last times worksheet:

$$\frac{a}{x}dx + \frac{b}{y}dy = d(a \ln x + b \ln y)$$

**How to check if its exact?** Assume  $F$  exists:

$$dF(x, y) : \text{ is exact } \iff \left( \frac{\partial A}{\partial y} \right)_x = \left( \frac{\partial B}{\partial x} \right)_y$$

where  $\iff$  means iff or if and only if. e.g. from the worksheet:

$$dG = a dx + b \frac{x}{y} dy, \quad A = a, \quad B = b \frac{x}{y}$$

so

$$\frac{\partial A}{\partial y} = 0, \quad \frac{\partial B}{\partial x} = \frac{b}{y}$$

thus it is inexact.

**Quasi-static process:** A system interacts with other systems in a process that is so slow that  $A$  remains arbitrarily close to equilibrium at all stages!

e.g. a piston pushing very slowly in a cylinder; when the system is not in equilibrium, then the ideal gas law  $pV = nRT$  does not hold.

“relaxational time  $\tau$ ”: time system requires to reach equilibrium if it experiences a sudden change.

Recall we denote the external parameters of an isolated system

$$x_1, x_2, \dots, x_n$$

and the energy of a microstate  $r$

$$E_r = E_r(x_1, x_2, \dots, x_n)$$

When we start to change the external parameter, energy of state  $r$  will change:

$$x_\alpha \rightarrow x_\alpha + dx_\alpha$$

and the change in energy is

$$dE_r = \sum_{\alpha=1}^n \frac{\partial E_r}{\partial x_\alpha} dx_\alpha$$

Now in isolated case  $dQ = 0$  so

$$\begin{aligned} dE_r + dW_r &= 0 \\ \implies dW_r &= -dE_r = - \sum_{\alpha=1}^n \left( \frac{\partial E_r}{\partial x_\alpha} \right) dx_\alpha \end{aligned}$$



where

$$X_{\alpha,r} = -\frac{\partial E_r}{\partial x_\alpha}$$

is the “generalized force”— e.g. if  $x$  is a distance, then  $X$  is a force; if  $x$  is a volume, then  $X$  is a pressure.

NOTE all discussion above are for : state  $r$

Consider an ensemble: in a quasi static process,  $X_{\alpha,r}$  has definite value, so

$$dW = \sum_{\alpha} \bar{X}_{\alpha,r} dx_{\alpha}$$

where  $\bar{X}_{\alpha,r}$  is mean of the generalized force.

**Example:** Cylindrical chamber in state  $r$  (height  $s$ , circular area  $A$ , pressure  $P_r$ ) with a piston pushing in  $ds$

Force on the piston:  $P_r A$

Volume:  $V = AS$

Thus work done is

$$\begin{aligned} dW &= F ds = (P_r A) ds \\ &= P_r dV \end{aligned}$$

and

$$dE_r = -dW_r = -P_r dV, \quad P_r = -\frac{\partial E_r}{\partial V}$$

## Worksheet

1. The mean pressure  $p$  of thermally insulated gas varies with volume  $V$  by

$$pV^\gamma = K$$

where  $K$  and  $\gamma$  are constants. Find work from  $p_i, V_i$  to  $p_f, V_f$ .

$$\begin{aligned} \int dW &= \int_{V_i}^{V_f} p dV \\ &= \int_{V_i}^{V_f} \frac{K}{V^\gamma} dV \\ W &= \left. \frac{KV^{1-\gamma}}{1-\gamma} \right|_{V_i}^{V_f} \end{aligned}$$

And since  $p_i V_i^\gamma = p_f V_f^\gamma = K$ , then

$$\begin{aligned} W &= \frac{K}{1-\gamma} (V_f^{1-\gamma} - V_i^{1-\gamma}) \\ &= \frac{1}{1-\gamma} (p_f V_f - p_i V_i) \end{aligned}$$

### 3 Statistical thermodynamics

#### Irreversibility and attainment of equilibrium

##### 3.1 Equilibrium conditions and constraints

Equilibrium condition: The system is equally likely to be found in any accessible states.

“accessible states”: some specific conditions/constraints of system, these limit the number of states the system can be possibly found.

Furthermore, how does the change of constraints change the number of accessible states?

##### Examples:

- Box divided (partition) into two equal parts: left half is filled with gas, and the right half is empty. After removing the partition (constraint), the gas spreads, but the probability of the gas being in the left half is much smaller,  $\frac{1}{2^N}$ . Rather, we would expect an equal number of particles on each side for  $N \rightarrow N_A$ .
- Box with insulating wall constrained to move: If the barrier freely moves, we would expect the pressures to equalize  $P = P'$
- Box with noninsulating wall (can't move): We would expect temperature to be equal  $T = T'$

After the states reach equilibrium, if we added the constraint back in, the system would not go back to the original state! (irreversible process)

##### But what is temperature???

- Kinetic energy? Heat transfer?
- Perhaps macroscopically: flow of heat from one system to another by touch (thermal contact)

##### 3.2 Distribution of energy between systems via heat

Consider two systems  $A$  and  $A'$ :

- $A$ : Energy  $E$ , Number of states  $\Omega(E)$
- $A'$ : Energy  $E'$ , Number of states  $\Omega(E')$

where  $\Omega(E)$  is the # of states in  $A$  with energy range  $(E, E + \delta E)$

The total combined system  $A^{(0)}$ , with number of states  $\Omega^{(0)}$ , has a constant total energy,

$$E^{(0)} = E + E' = \text{constant}$$

where we define:  $\Omega^{(0)}(E)$ : # of states accessible to  $A^{(0)}$  when the subsystem  $A$  has energy  $(E, E + \delta E)$ .

When  $A^{(0)}$  is in equilibrium the probability is proportional to the number of accessible states:

$$P(E) \propto \Omega^{(0)}(E), \quad \text{or} \quad P(E) = \frac{\Omega^{(0)}(E)}{\sum_E \Omega^{(0)}(E)} = C \Omega^{(0)}(E)$$

where  $C$  is a constant.

##### Multiplicity

$$\Omega^{(0)}(E) = \Omega(E) \Omega'(E^{(0)} - E)$$

Now, the probability  $P(E)$  with  $E$  is

$$P(E) = C \Omega(E) \Omega'(E^{(0)} - E)$$

Graphically, we would expect  $E$  vs.  $\Omega(E)$  to increase (as  $E$  increases,  $\Omega(E)$  increases), and same with  $E'$  vs.  $\Omega'(E')$ . But  $E$  vs.  $\Omega'(E^{(0)} - E)$  would decrease. In addition, the probability  $P(E)$  as a function of  $E$  would have a sharp peak near the equilibrium  $\tilde{E}$ .

**Finding maximum** Take the derivative (of the log because multiplication becomes addition):

$$\frac{\partial \ln P(E)}{\partial E} = 0, \quad \ln P(E) = \ln C + \ln \Omega(E) + \ln \Omega'(E^{(0)} - E)$$

hence

$$\frac{\partial \ln P(E)}{\partial E} = \frac{\partial \ln(\Omega(E))}{\partial E} - \frac{\partial \ln(\Omega'(E'))}{\partial E'} = 0$$

**Thermodynamic beta (Wikipedia)** Define  $\beta$ :

$$\beta = \frac{\partial \ln \Omega(E)}{\partial E}$$

where at equilibrium,  $\beta(\tilde{E}) = \beta'(\tilde{E}')$

Then we introduce a *dimensionless* parameter  $T$  such that

$$\boxed{kT = \frac{1}{\beta}}$$

where  $k$  ( $k_B$  everywhere else) is the Boltzmann constant. Therefore, temperature characterizes the variation of density of state with energy.

**Entropy** From temperature and defining entropy  $S(E)$ :

$$\begin{aligned} \frac{1}{T} = k\beta &= \frac{\partial k \ln \Omega(E)}{\partial E}, \quad S(E) = k \ln \Omega(E) \\ &= \frac{\partial S}{\partial E} \end{aligned}$$

### Worksheet

1. # of energy levels  $\Phi_1(\epsilon) \leq \frac{\epsilon}{\Delta\epsilon} = C\epsilon$
2. Average energy per molecule is  $\epsilon = E/f$  ( $f$  molecules)

$$\Phi(E) = (\Phi_1(\epsilon))^f$$

3.

$$\begin{aligned} \Omega(E) &= \Phi(E + \delta E) - \Phi(E) \\ &= \frac{\partial \Phi(E)}{\partial E} \delta E, = \Phi_1^{f-1} \frac{\partial \Phi_1}{\partial \epsilon} \delta E \end{aligned}$$

4. If  $f$  is very large

$$\begin{aligned} \ln \Omega &= (f-1) \ln \Omega(\epsilon) + \dots \\ &\approx f \ln \Omega(\epsilon) \end{aligned}$$

5. So

$$\Omega \propto \phi_1(\epsilon)^f \propto E^f$$

**Review of last time:** What is temperature?

For two systems  $A$  and  $A'$  that present heat exchange:

- $E^{(0)} = E + E'$ : total energy is constant
- At thermal equilibrium, the temperature of the systems are the same.
- $P(E) \propto \Omega^{(0)}(E)$ : probability of finding system  $A$  to have energy  $E$  is proportional to the number of accessible states in the total system  $A^0$ .
- $\Omega^{(0)}(E) = \Omega(E)\Omega'(E^{(0)} - E)$ : multiplicity
- To find the maximum, take the derivative to zero:

$$\begin{aligned} \frac{\partial \ln P(E)}{\partial E} &= 0 \\ \Rightarrow \frac{\partial \ln \Omega(E)}{\partial E} &= \frac{\partial \ln \Omega'(E^{(0)} - E)}{\partial E'} \end{aligned}$$

where

$$\beta = \frac{\partial \ln \Omega(E)}{\partial E} \quad \text{and} \quad kT = \frac{1}{\beta}$$

and at equilibrium,  $\beta(\tilde{E}) = \beta'(\tilde{E}')$  Finally, we define entropy  $S(E)$  as

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

where  $S + S' = \text{maximum at equilibrium}$

[insert figure graph of  $P(E), \Omega(E), \Omega'(E')$ ]

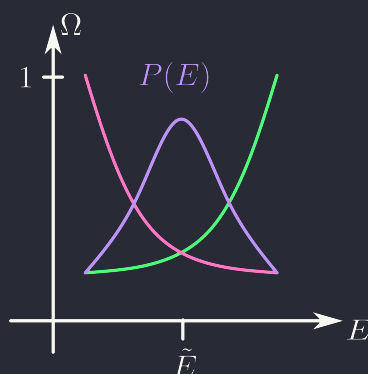


Figure 3.1: Graph of  $P(E), \Omega(E)$  (green),  $\Omega'(E')$

**What is  $kT$ ?**

We replace  $\Omega \sim E^f$  so

$$\begin{aligned} \frac{1}{kT} = \beta &= \frac{\partial \ln \Omega}{\partial E} \approx f \frac{\partial \ln E}{\partial E} = \frac{f}{E} \\ \Rightarrow kT &\approx \frac{\bar{E}}{f} \end{aligned}$$

so  $kT$  roughly represents energy per atom. Or

$kT$  is a measure of the mean energy above the ground state per atom

- In the hydrogen atom, if  $kT \geq \Delta$  (energy difference between the ground state and the first excited state), then the atom can be excited.

- Room temperature (300 K) is roughly  $kT \approx 1/40 \text{ eV} = 25 \text{ meV}$
- A superconducting qubit of energy (usually in GHz)  $25 \mu\text{eV}$  uses temperature in the magnitude of 15 mK: Backwards calculation: Going from 300K to 25 meV means we need to go to 0.3 K, but 0.03 K for the precision, to be in the range of the qubit.

### 3.3 Approach to equilibrium

Given  $A, A'$  we have average initial energy  $\bar{E}_i, \bar{E}'_i$ : At equilibrium

$$\begin{aligned}\bar{E}_f &= \tilde{E} \\ \bar{E}'_f &= \tilde{E}' = E^{(0)} - \tilde{E}\end{aligned}$$

The heat exchange is

$$\begin{aligned}Q &= \bar{E}_f - \bar{E}_i \\ Q' &= \bar{E}'_f - \bar{E}'_i\end{aligned}$$

where the total heat is constant,  $Q + Q' = 0$ .

- The system that absorbs heat is “colder”
- The system that releases (gives off) heat is “hotter”

### 3.4 Temperature

Properties of  $T$ :

- If the two systems have same  $T$ , they will remain in equilibrium when brought together.
- Zeroth Law of Thermodynamics: If two systems are in thermal equilibrium with a 3rd system, then they must be in equilibrium with each other.

This allows us to use a test system as a “thermometer”: a small system that has a macroscopic parameter that varies when brought into contact with another system.

### 3.5 Heat Reservoir

A heat reservoir  $A'$  with temp  $T'$  transfers heat to a smaller system  $A$  with temp  $T$ :

- $T \rightarrow T'$
- $T'$  does not change!

Using the parameter  $\beta' = \beta'(E')$  (where it is inversely related to temp),

$$\left| \frac{\partial \beta'}{\partial E'} Q' \right| \ll \beta'$$

which pretty much tells us that  $\Delta \beta' \ll \beta'$ , so the temperature of the reservoir does not change.

The change of the density of states of the reservoir is

$$\ln \Omega'(E' + Q') - \ln \Omega'(E')$$

where the Taylor expansion gives us

$$= \frac{\partial \ln \Omega'}{\partial E'} Q' = \beta' Q'$$

This is proportional to the change of entropy:

$$\begin{aligned}\Delta S' &= k(\ln \Omega'(E' + Q) - \ln \Omega'(E')) \\ \beta' Q' k &= \frac{Q'}{T'}\end{aligned}$$

Simply,

$$\Delta S' = \frac{Q'}{T'} \quad (\text{for a heat reservoir})$$

If one assumes an infinitesimal amount of heat  $dQ$

$$dS' = \frac{dQ'}{T'}$$

which is the 2nd law of thermodynamics.

The first law of thermodynamics is (as we discovered)

$$dE + dW = dQ$$

### 3.6 Dependence on Density of States (DoS) on external parameters

$\Omega(E, x)$  where  $x$  is an external parameter. The change of energy is

$$\frac{\partial E}{\partial x} dx \quad \text{where} \quad X = -\frac{\partial E}{\partial x} \quad \text{“generalized force”}$$

## Review

$$\frac{\partial \ln \Omega(E)}{\partial E} = \beta = \frac{1}{kT}$$

$$ds = \frac{dQ}{T}, \quad S = k \ln \Omega$$

## 3.7 Density of states on external parameters

When a parameter  $x \rightarrow x + dx$  the energy of each microstate  $r$  changes by

$$\frac{\partial E_r}{\partial x} dx$$

where

$$X = -\frac{\partial E_r}{\partial x}$$

is the generalized force.

- $\Omega(E, x)$ : external parameter  $x$  for the # of states in  $[E, E + \delta E]$ .
- $\Omega_Y(E, x)$ : # of states in  $[E, E + \delta E]$  with  $Y = \frac{\partial E_r}{\partial x}$  in  $[Y, Y + \delta Y]$

The total number of states is now

$$\Omega(E, x) = \sum_Y \Omega_Y(E, x)$$

Consider energy  $E$  when  $x \rightarrow x + dx$ :

some states  $r$  originally with energy  $< E$  Can now acquire energy  $> E$ :

- $\sigma(E)$ : # of state of originally
- $\sigma_Y(E)$ : # of states ... with  $Y = \frac{\partial E_r}{\partial x}$  in  $[Y, Y + \delta Y]$

For a given  $E, Y$ ; the work done is the generalized force times the change in the parameter  $Y dx$  which is like the width of the rectangle below the energy  $E$ .

Above the energy  $[E, E + \delta E]$  we can treat the total area as the total # of states  $\Omega_Y(E, x)$ , and dividing by the width  $\delta E$  kind of gives us a linear density of states per unit energy. Finally we can find  $\sigma_Y$  by getting the area

$$\sigma_Y(E) = \frac{\Omega_Y(E, x)}{\delta E} Y dx$$

and thus

$$\begin{aligned} \sigma(E, x) &= \sum_Y \sigma_Y(E, x) = \sum_Y \frac{\Omega_Y(E, x)}{\delta E} Y dx \\ &= \frac{\Omega(E, x)}{\delta E} \bar{Y} dx \\ \bar{Y} &= \frac{1}{\Omega(E, x)} \sum_Y Y \Omega_Y(E, x) \end{aligned}$$

The change of the DoS is

$$\frac{\partial \Omega(E, x)}{\partial x} dx = \sigma(E) - \sigma(E + \delta E) = -\frac{\partial \sigma(E)}{\partial E} \delta E$$

on the RHS

$$\frac{\partial \sigma(E, x)}{\partial E} = \frac{dx}{\delta E} \frac{\partial \Omega \bar{Y}}{\partial E}$$



and thus

$$\frac{\partial \Omega(E, x)}{\partial x} = -\frac{\partial \Omega \bar{Y}}{\partial E} = -\frac{\partial \Omega}{\partial E} \bar{Y} - \Omega \frac{\partial \bar{Y}}{\partial E}$$

dividing both sides by  $\Omega$

$$\frac{1}{\Omega} \frac{\partial \Omega}{\partial x} = -\frac{1}{\Omega} \frac{\partial \Omega}{\partial E} \bar{Y} - \frac{\partial \bar{Y}}{\partial E}$$

where

$$\frac{\partial \ln \Omega}{\partial x} = \frac{1}{\Omega} \frac{\partial \Omega}{\partial x}, \quad \frac{\partial \ln \Omega}{\partial E} = \frac{1}{\Omega} \frac{\partial \Omega}{\partial E}$$

and another trick: the second term is  $\sim \bar{Y}/E$  and  $\Omega \sim E^f$  so we can drop the second term

$$\frac{\partial \ln \Omega}{\partial x} = -\frac{\partial \ln \Omega}{\partial E} \bar{Y} = \beta \bar{X}$$

**Recap:** For a system with states  $\Omega(E, x)$  we are give

$$\boxed{\frac{\partial \ln \Omega}{\partial E} = \beta}, \quad \boxed{\frac{\partial \ln \Omega}{\partial x} = \beta \bar{X}}$$

The second equation tells us that doing work will obviously increase  $\Omega$ .

**The rubber band example:** Stretching the rubber band (work done) adds energy or heat to the system.

### 3.8 Equilibrium of interacting systems

$\Omega^{(0)}(E, x)$  will be maximum at  $\tilde{E}, \tilde{x}$ .

Consider an infinitesimal quasi-static process where  $A$  and  $A'$  are brought from equilibrium to another state  $\tilde{E} + d\tilde{E}, \tilde{x} + d\tilde{x}$ .

The differential of the log Dos is (using math)

$$\begin{aligned} d \ln \Omega(E, x) &= \frac{\partial \ln \Omega}{\partial E} d\tilde{E} + \frac{\partial \ln \Omega}{\partial x} d\tilde{x} \\ &= \beta(d\tilde{E} + X d\tilde{x}) \quad X d\tilde{x} = dW \\ &= \beta dQ \\ k d \ln \Omega(E, x) &= \frac{dQ}{T} \end{aligned}$$

where  $S = k \ln \Omega$  or equivalently

$$dS = \frac{dQ}{T}$$

Case 1 : Thermally isolated and quasi-static process

$$dQ = 0 \implies \Delta S = 0$$

thus a **reversible process**

**Worksheet** A gas with  $N$  atoms confined to half a box is released to fill the whole container:  
Given

- Ideal gas:  $PV = NkT$
  - Average energy:  $\bar{E}(T) = \frac{3}{2}NkT$
- (i) Change in entropy  $S = k \ln \Omega$ : Originally we have only 1 macrostate or  $\Omega_0$  microstates, and now the total number of arrangements is  $\Omega_0 2^N$  so

$$\Delta S = k \ln \Omega_0 2^N - k \ln \Omega_0 = Nk \ln 2$$

where we have a volume independence  $\Omega \sim V^N X(E)$ .

- (ii) Defining a quasi-static process where energy doesn't change from initial to final state: We can now use

$$dS = \frac{dQ}{T}$$

and for a quasi-static process

$$\begin{aligned} dQ &= d\tilde{E} + dW \\ dQ &= dW = PdV \end{aligned}$$

So

$$\Delta S = \int ds = \int_{V_0}^{2V_0} \frac{PdV}{T} = \int_{V_0}^{2V_0} \frac{Nk}{V} dV = Nk \ln 2$$

### 3.9 Fundamental Results

#### 3.9.1 Thermodynamic laws

**0th law** If two systems are in equilibrium with a 3rd system, they're in equilibrium with each other. (allows us to compare temp of systems via thermometer)

**1st law** Energy is conserved:  $dQ = d\bar{E} + dW$

**2nd law** An equilibrium macrostate can be characterized by  $S$  (entropy), which has properties that

- a. In any thermally isolated process goes from one macrostate to another, entropy tends to increase

$$\Delta S \geq 0$$

- b. If the system is not isolated and undergoes a quasi-static process (absorbs heat),

$$dS = \frac{dQ}{T}$$

**3rd law** The entropy  $S$  of a system has the limiting properties that

$$T \rightarrow 0, \quad S \rightarrow S_0 \quad (\text{Absolute entropy})$$

**Remarks** All four laws are *macroscopic*. In the context of three parameters  $\bar{E}, S, T$ .

#### 3.9.2 Statistical calculation of thermodynamic quantities

**Statistical Relations (Microscopic nature)**

- $S = k \ln \Omega$
- $\beta = \frac{\partial \ln \Omega}{\partial E}, \quad X_\alpha = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial x_\alpha}$

For the free expansion of an idea gas:

$$\Omega \propto V^N X(E)$$

where the log of the DoS is

$$\ln \Omega = N \ln V + \ln X(E) + C$$

So from the mean pressure

$$P = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial V} = \frac{1}{\beta} \frac{\partial \ln V^N}{\partial V} = \frac{1}{\beta} \frac{N}{V} = \frac{NkT}{V}$$

$$PV = NkT$$

From the beta relation

$$\beta = \frac{\ln X(E)}{E}$$

thus it is only a function of energy and not volume  $V$ :

$$\beta(\bar{E}) = E \implies \bar{E}(T) = \bar{E}$$

**Extensive vs Intensive parameters** For macroscopic parameters  $y_1, y_2$  we have two cases:

- Case 1: Extensive if  $y_1 + y_2 = y$
- Case 2: Intensive if  $y_1 = y_2 = y$

Extensive	Intensive
Volume	T
Energy	Pressure
entropy	specific heat
mass	
heat capacity	

### 3.10 Heat capacity and specific heat

Suppose we add  $dQ$  to the system while other parameters are fixed, the system temperature raised by  $dT$

$$\text{“Heat capacity”} \quad \left( \frac{dQ}{dT} \right)_y = C_y$$

**In general** The heat capacity is defined by temperature and the parameter

$$C_y = C_y(T, y)$$

We can also relate it to the entropy change  $ds = \frac{dQ}{T}$ :

$$C_y = \left( \frac{dQ}{dT} \right)_y = T \left( \frac{ds}{dT} \right)_y$$

**Specific heat:** Intensive parameter

$$C_y = \frac{C_V}{V} \quad \text{per mole}$$

$$C_y = \frac{C_P}{\text{mass}} \quad \text{per gram}$$

or the “specific heat/heat capacity per mole/gram”

Defining some units:

- Calorie: Heat required to raise temperature of 1 g of water @ 1 atm from 14.5  $\rightarrow$  15.5  $^{\circ}\text{C}$ .
- Joule: Applied work

$$1 \text{ cal} = 4.1840 \text{ J}$$

### Worksheet

1. Increase in entropy of a cup of water as it is heated from room temp to boiling:

$$\begin{aligned} \Delta S &= \int dS = \int \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{C_P}{T} dT \\ &= C_P \ln \frac{T_2}{T_1} = C_P \ln \frac{373}{298} \end{aligned}$$

where  $q = mC_P\Delta T$

## 4 Macroscopic Parameters and their measurement

### 4.1 Work & internal energy

From the first law of thermodynamics we always talk about

$$Q = \Delta \bar{E} + W$$

Given a system, work is *easy* measure i.e. we integrate

$$W = - \int p dV$$

#### Measure of internal energy

- Thermal isolation case:  $Q = 0$

$$\Delta \bar{E} = \bar{E}_b - \bar{E}_a = -W_{ab} = \int_a^b dW$$

e.g. a thermally isolated piston goes from state  $a$  to  $b$ .

### 4.2 Heat

The heat absorbed by a system going from macrostate  $a$  to  $b$  is simply

$$Q_{ab} = (\bar{E}_b - \bar{E}_a) + W_{ab}$$

**Example** A superconducting circuit  $A$  is connected to the circuit  $B$  with a resistor.

Adding 20  $\mu\text{W}$  of heat to the system: we actually are doing work on a resistor.

#### Method of Mixers (Comparison Method)

Bring system  $A$  into contact with system  $B$  that has a known relation between its internal energy and some parameters ( $T$ ).

$$Q_A = \Delta \bar{E}_B = -Q_B$$

e.g. system  $A$  is submerged in water  $B$  and we can measure the change in internal energy of water quite easily.

### 4.3 Entropy

We define entropy  $S$

$$dS = \frac{dQ}{T}$$

and **Absolute entropy** from the 3rd law

$$T \rightarrow 0, \quad S \rightarrow S_0$$

**Example:** Tin

Two structures of a solid:

1. White tin—a metal  $\rightarrow$  stable  $> 298 \text{ K}$
2. Grey tin—semiconductor  $\rightarrow$  stable  $< 298 \text{ K}$

Thus it requires some amount of heat  $Q$  to transform from grey to white tin.

- Case 1: a mole of white tin from  $T = 0 \rightarrow T_0$  with specific heat  $C^{(w)}(T)$

$$S^{(w)}(T_0) = S^{(w)}(T = 0) + \int_0^{T_0} \frac{C^{(w)}(T)}{T} dT$$

- Case 2: Grey tin from  $0 \text{ K} \rightarrow T_0$  and then it transforms to white tin quasi-statically. It absorbs heat  $Q$  and the entropy change is

$$S^{(w)}(T_0) = S^{(g)}(T = 0) + \int_0^{T_0} \frac{C^{(g)}(T)}{T} dT + \frac{Q}{T_0}$$

where

$$S^{(g)}(T = 0) = S^{(w)}(T = 0) = S_0$$

figure of moleoftin.png



Figure 4.1: Mole of Tin