

# 1 Statistical description of systems of particles

## 1.1 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.

## 1.2 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  $E_r$

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

- 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

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