Phys 362 2020

Lecture 16

Friday: (3 April) HW 14 due.

Thurs: Read 4.3

Statistical description of thermal systems

We aim to describe a bulk collection of particles in terms of macrostates (bulk states) and the associated microstates (arrangements of the individual constituents) and use statistics to determine the likelihood of bulk states.

We can illustrate this for a collection of N spin-½ particles:

Macroscopic state (bulk)
~ number of particles with spin up N_+

Microscopic state (detailed arrangement)
~ arrangement of spins of individual particles.

List macrostates e.g.

$N_+ = 0, 1, 2, \ldots, N$

For each macrostate list possible microstates e.g.

$N_+ = 1$ $\quad \uparrow\downarrow\downarrow\cdots\downarrow \;\; \downarrow\uparrow\downarrow\cdots\downarrow \;\; \downarrow\downarrow\uparrow\downarrow\cdots\downarrow \;\ldots$

Calculate macrostate probabilities:

$$\text{prob}(N_+) = \binom{N}{N_+} p^{N_+} q^{N-N_+}$$

Provide single particle probabilities

$\text{prob}(\uparrow) = p$

$\text{prob}(\downarrow) = q = 1-p$

A key quantity here is the number of microstates per macrostate. This is

> The multiplicity of a macrostate, Ω is the number of microstates that represent the macrostate.

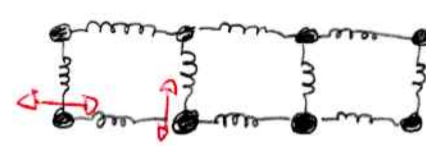
In various situations we will need to determine the multiplicity. For an ensemble of N spin-½ systems the multiplicity of the macrostate N_+ is

$$\Omega(N_+) = \binom{N}{N_+} = \frac{N!}{N_+!\,(N-N_+)!}$$

Einstein solids

This type of analysis of a bulk system will be interesting when we consider two systems which can exchange energy subject to the constraint that the total energy of the combination is constant. We will use the statistical approach to address questions about which way energy flows between the systems.

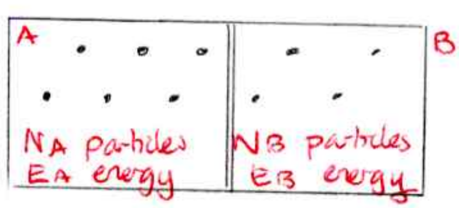
One specific system that illustrates this well is a collection of quantum harmonic oscillators. An example would be a solid whose nuclei are arranged in a lattice. Each nucleus can oscillate about an equilibrium.



We suppose that the oscillators are identical but distinguishable. This constitutes an Einstein solid. We will

1) develop a formalism for analyzing an individual Einstein solid statistically using microstates and macrostates
2) consider two interacting Einstein solids

Initially



e.g. $E_A = 80\text{J}$ $\quad E_B = 80\text{J}$

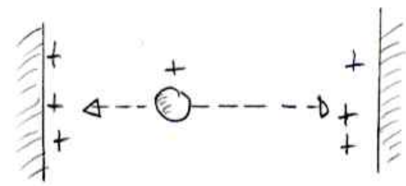
$N_A = 100 \quad N_B = 50$

a) which way does energy flow?

b) in equilibrium how does energy per particle for A : E_A/N_A compare to energy per particle for B: E_B/N_B

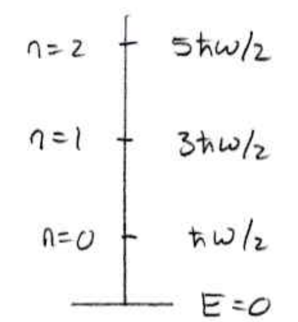
We need to review the key features of quantum harmonic oscillators. We start with a single quantum harmonic oscillator. The key results are:

1) the oscillator has an angular frequency of oscillation, ω, which depends on the physics of the system.



2) the possible energies of the oscillator are $\frac{1}{2}\hbar\omega$, $\frac{3}{2}\hbar\omega$, $\frac{5}{2}\hbar\omega$, ... and in general

$$E_n = \hbar\omega(n + \tfrac{1}{2}) \qquad n = 0, 1, 2, 3, \ldots$$



3) at any instant each oscillator is in an exact energy state. We can describe its state by an integer "n".

So the model is

N distinguishable identical oscillators all with same frequency, ω

1 2 3 ... N

→ Energy of any single oscillator in state "n" is

$$E_n = \hbar\omega(n + \tfrac{1}{2})$$

↓

Describe microstate by listing "n" for each oscillator

state of oscillator 1 → $n_{(1)}$

" " " 2 → $n_{(2)}$

" " " 3 → $n_{(3)}$

⋮

" " " N → $n_{(N)}$

From a bulk perspective, we describe the collection of oscillators in terms of its overall energy. Thus a macrostate is described by the total energy of the system. Then the total energy is

$$E = \underbrace{E(1)}_{\text{energy of } 1} + E(2) + \cdots + \underbrace{E(N)}_{\text{energy of oscillator } N}$$

$$= \hbar\omega\left[n(1) + \tfrac{1}{2}\right] + \hbar\omega\left[n(2) + \tfrac{1}{2}\right] + \cdots + \hbar\omega\left[n(N) + \tfrac{1}{2}\right]$$

$$= \hbar\omega\left[n(1) + n(2) + \cdots + n(N)\right] + \underbrace{\hbar\omega\, N/2}_{\text{for fixed } N \text{ this is fixed}}$$

Now we assume that from a bulk state perspective we cannot determine the value of n for any given oscillator. So the following microstates represent the same macrostate.

1 2 3

$n(1) = 4 \quad n(2) = 0 \quad n(3) = 0$

1 2 3

$n(1) = 0 \quad n(2) = 3 \quad n(3) = 1$

We define the number of energy units as:

$$\boxed{q = n(1) + n(2) + n(3) + \cdots + n(N)}$$

Therefore a complete description of a macrostate consists of specifying N (usually fixed) and q.

Macrostate N, q $\longrightarrow$ Energy $E = \hbar\omega q + \hbar\omega N/2$

1 Einstein solid microstates and macrostates

Consider an Einstein solid with four particles.

a) List all possible macrostates and their energies.

b) For each macrostate that corresponds to one of the three lowest energies, list all possible microstates.

c) Determine the multiplicity of each macrostate.

d) Check that the multiplicity for these is also given by

$$\Omega(N,q) = \binom{N+q-1}{q}.$$

Answer: a) The macrostates are described by the total number of energy units:

$q = 0, 1, 2, 3, 4, 5, \ldots$

In each case $E = \hbar\omega\,(q + N/2) = \hbar\omega\,(q+2)$

q	E
0	$2\hbar\omega$
1	$3\hbar\omega$
2	$4\hbar\omega$
3	$5\hbar\omega$
4	$6\hbar\omega$
5	$7\hbar\omega$

b), c)

q	$n(1)$	$n(2)$	$n(3)$	$n(4)$	multiplicity
0	0	0	0	0	1
1	0	0	0	1	4
	0	0	1	0	
	0	1	0	0	
	1	0	0	0	
2	0	0	0	2	10
	0	0	2	0	
	0	2	0	0	
	2	0	0	0	
	0	0	1	1	
	0	1	0	1	
	1	0	0	1	
	0	1	1	0	
	1	0	1	0	
	1	1	0	0	

d)

$\Omega = \binom{3}{0} = 1$

$\Omega = \binom{4}{1} = 4$

$\Omega = \binom{5}{2} = \frac{5!}{3!\,2!} = 10$

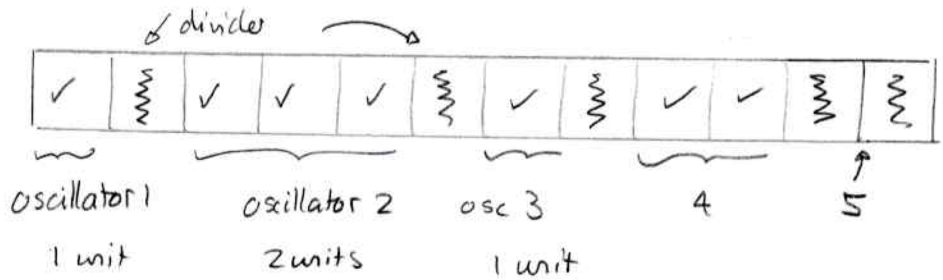
In general one can show:

> For an Einstein solid with N oscillators the macrostate with q energy units has multiplicity
>
> $$\Omega(N,q) = \binom{N+q-1}{q} = \frac{(N+q-1)!}{q!\,(N-1)!}$$

To prove consider allocating q energy units as follows:

* list q boxes each with an energy unit
* include $N-1$ divider boxes to separate oscillators.

e.g. $N = 6 \Rightarrow 5$ dividers (boxes) $\quad$ $q = 7 \Rightarrow 7$ energy boxes. $\Big\}$ 12 boxes



We only need to choose the q boxes that contain one energy unit each out of the $N-1+q$ total boxes. There are

$$\binom{N+q-1}{q}$$

such choices

Interacting Einstein solids

The question:

"Given an Einstein solid with N oscillators and energy E, what is the most probable macrostate?"

has a trivial answer since, with a given E, the energy number, q, is determined via

$$E = \hbar\omega\,(q + N/2)$$

There is only one possible macrostate.

Rather we consider two Einstein solids, which are labelled A and B. The total energy is

$$E = E_A + E_B$$

system A	system B
N_A particles	N_B particles
macrostate q_A	macrostate q_B
energy E_A	energy E_B

We assume that the total energy is fixed. Then.

$$E_A = \hbar\omega\,(q_A + N_A/2)$$

$$E_B = \hbar\omega\,(q_B + N_B/2)$$

$$\Rightarrow \quad E = \hbar\omega\left(q_A + q_B + \frac{N_A + N_B}{2}\right)$$

is fixed. Define the total number of energy units

$$q = q_A + q_B$$

This must be fixed. So we can describe the system macrostates via:

Fixed N_A, N_B
$q = q_A + q_B$

Variable q_A, q_B

$\longrightarrow$ label macrostate using N_A, N_B, q_A, q_B

The question then is:

"Given fixed particle numbers (N_A, N_B) and fixed total number of energy units q, which macrostate is most likely?"

A macrostate is described by q_A, q_B so that $q = q_A + q_B$ is fixed.

We assume that the systems can exchange energy units freely and

$$\boxed{\text{Each microstate that gives the same total energy is equally likely.}}$$

Letting $\Omega(N_A, N_B, q, q_A)$ be the multiplicity of a macrostate we get

$$\boxed{\mathrm{Prob}(N_A, N_B, q, q_A) = \frac{\Omega(N_A, N_B, q, q_A)}{\text{total \# microstates.}}}$$

The key computational result is

$$\boxed{\Omega(N_A, N_B, q, q_A) = \Omega_A(N_A, q_A)\,\Omega_B(N_B, \underbrace{q_B}_{q-q_A})}$$

2 Interacting Einstein solids

One Einstein solid, A, consists of 3 oscillators and another, B, consists of 2 oscillators. The total number of energy units is 10.

a) List all macrostates using giving q_A and q_B for each.

b) Determine the multiplicity of each macrostate.

c) Which is the most likely macrostate? For this state determine the energy per oscillator for each subsystem. How do these compare?

d) Suppose that each subsystem initially had 5 energy units. Determine the energy per oscillator for each subsystem at this stage. If the systems are allowed to interact and exchange energy which way does the energy flow as they reach the most likely macrostate?

Answer: a) The energy is distributed so that $q_A + q_B = 10$

q_A	q_B	$\Omega_A(q_A)$	$\Omega_B(q_B)$	$\Omega = \Omega_A \Omega_B$
0	10	1	11	11
1	9	3	10	30
2	8	6	9	54
3	7	10	8	80
4	6	15	7	105
5	5	21	6	126
6	4	28	5	140
7	3	36	4	144
8	2	45	3	135
9	1	55	2	110
10	0	66	1	66

In each case $\Omega_A = \binom{N_A + q_A - 1}{q_A} = \binom{3 + q_A - 1}{q_A}$

$$= \binom{2+q_A}{q_A} = \frac{(2+q_A)!}{q_A!\,2!} = \frac{(2+q_A)(1+q_A)}{2}$$

Then $\Omega_B = \binom{N_B+q_B-1}{q_B} = \binom{2+q_B-1}{q_B} = \binom{q_B+1}{q_B}$

$$= \frac{(q_B+1)!}{1!\ q_B!} = q_B+1$$

c) The state with the largest multiplicity:

$q_A = 7 \qquad q_B = 3$

For A energy per oscillator is $\frac{7}{3} = 2.3$ } similar.
For B " " " " $3/2 = 1.5$

Note that

$q_A = 6 \qquad q_B = 4$

is almost as likely. Here

For A energy per oscillator is $6/3 = 2.0$ } same.
For B " " " " $4/2 = 2.0$

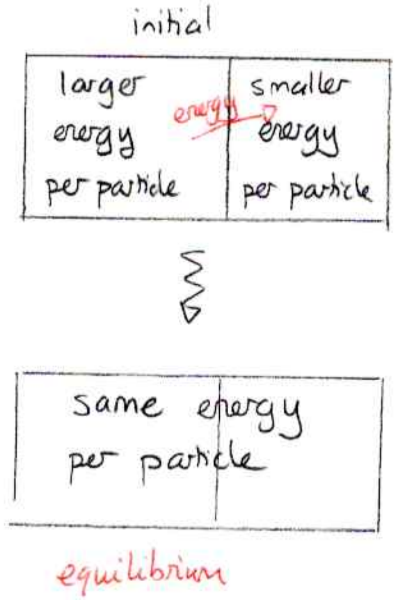
d) Initially for A energy per oscillator is $5/3 = 1.67$
" " B " " " " $5/2 = 2.5$

Appears to flow from B to A.

$\Rightarrow$ energy flows from system with larger energy per oscillator

This illustrates the following:

Consider two systems which can exchange energy. Statistical models indicate that the flow of energy is from the system with a larger energy per particle to that with a smaller energy per particle.



System size and statistics

We can plot the probability distribution for the macrostates versus q_A. For small numbers there is a broad range of equally likely macrostates. As the numbers increase the statistics become more convincing. Consider examples that differ by the same factor:

	N_A	N_B	q	peak q_A	range around peak summing to prob 0.50	range as fraction of q
	3	2	10	7	$5 \le q_A \le 8$	$0.50 \le \frac{q_A}{q} \le 0.80$
×4	12	8	40	25	$21 \le q_A \le 28$	$0.53 \le \frac{q_A}{q} \le 0.70$
×10	30	20	100	61	$55 \le q_A \le 66$	$0.55 \le \frac{q_A}{q} \le 0.66$

The mostly likely value $q_A/q \to 0.60$

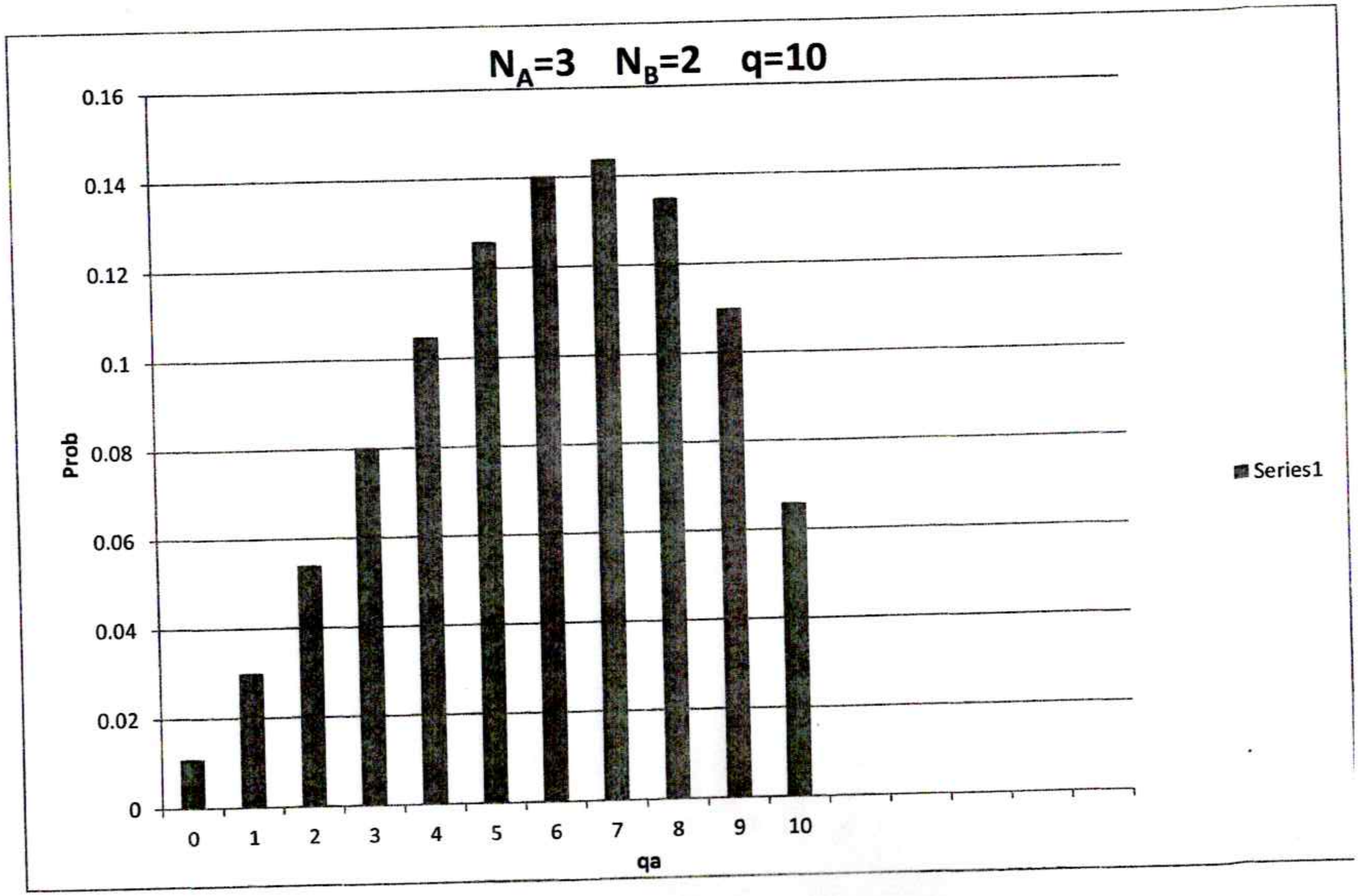
We note that $q_A/q = N_A/N \Rightarrow \frac{q_A}{N_A} = q/N$

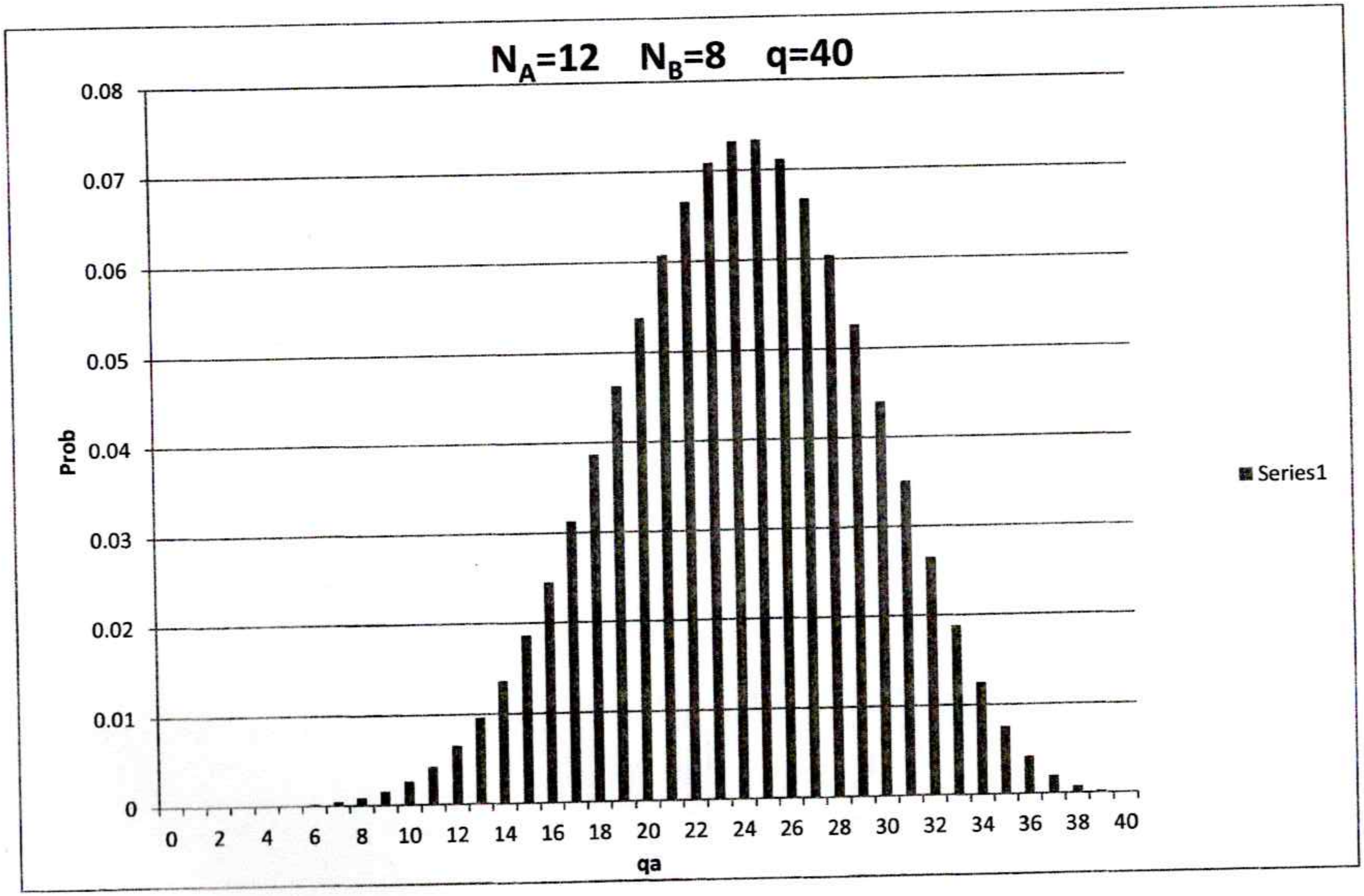
Similarly $\frac{q_B}{N_B} \to q/N$

Thus

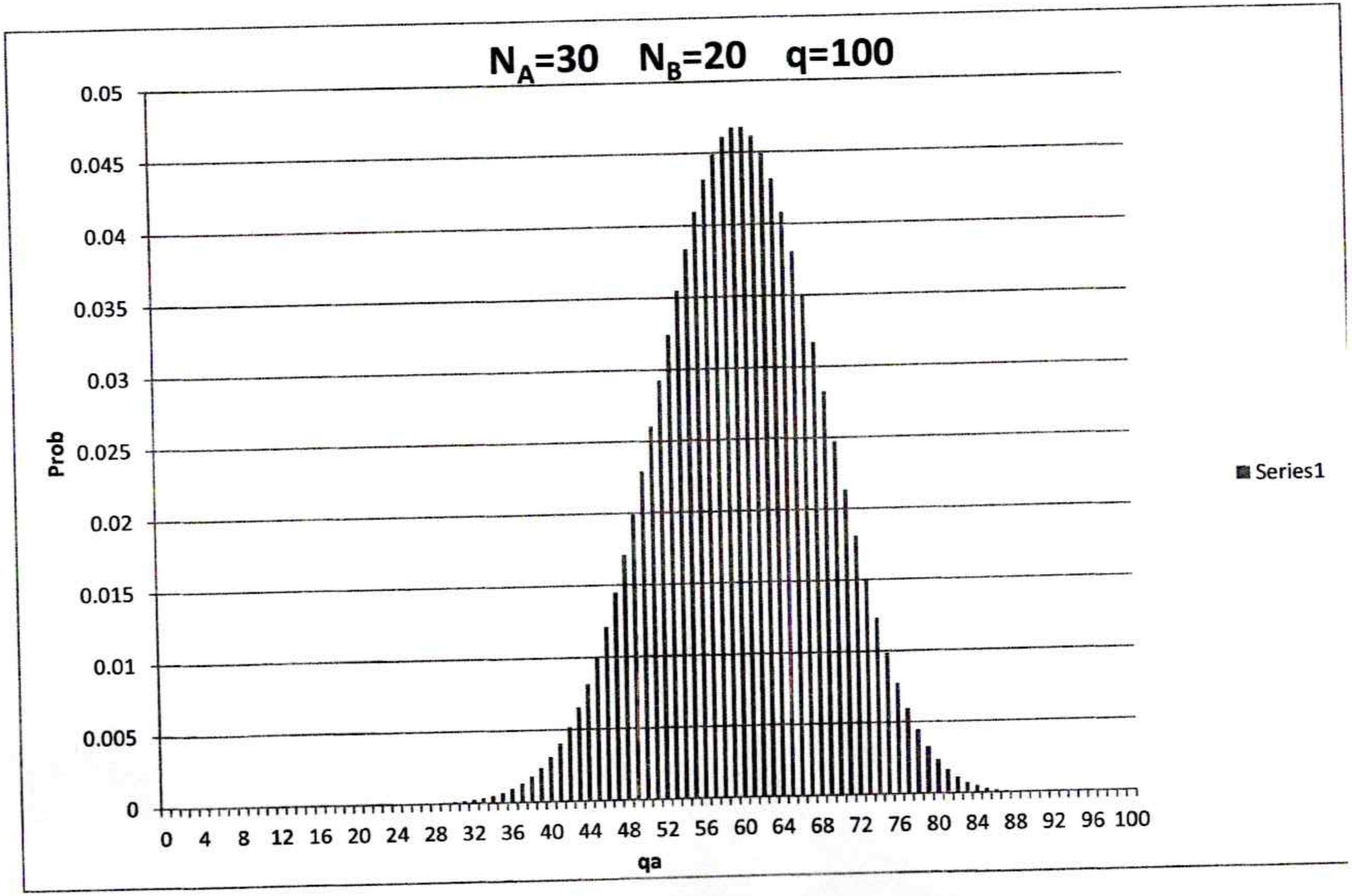
$$\frac{q_A}{N_A} \rightarrow \frac{q_B}{N_B} = \frac{q}{N}$$

and the energy per particle is the same for each.


N_A=3 N_B=2 q=10
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Prob
0 1 2 3 4 5 6 7 8 9 10
qa
Series1



N_A=12 N_B=8 q=40
Prob
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
qa
Series1



N_A=30 N_B=20 q=100
Prob
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0 4 8 12 16 20 24 28 32 36 40 44 48 52 56 60 64 68 72 76 80 84 88 92 96 100
qa
Series1