

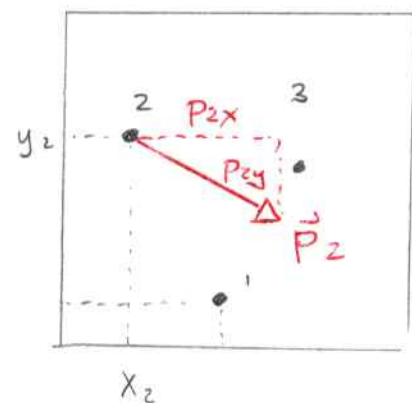
Thurs: Read 4.4, 4.5

Fri: HW by 8pm 11:30pm

Statistical physics for systems of particles with position and momentum

We now consider situations where the microscopic description of the system involves continuous variables. Specifically we consider particles, each of whose states is described by its position and momentum. The model we consider is a gas consisting of classical particles. We assume

- 1) there are  $N$  distinguishable molecules, each with mass  $m$ .
- 2) the molecules do not interact with each other
- 3) the region that could be occupied by these has volume  $V$
- 4) the energy of the entire ensemble of molecules is  $E$



We need to describe macrostates and microstates. First a macrostate will be

macrostate  $\rightarrow$  specify  $E, V, N$

Then a microstate is described by listing all the positions and momenta:

particle	position	momentum
1	$x_1, y_1, z_1$	$p_{1x}, p_{1y}, p_{1z}$
2	$x_2, y_2, z_2$	$p_{2x}, p_{2y}, p_{2z}$
$\vdots$	$\vdots$	$\vdots$

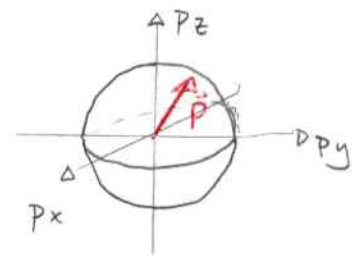
} one microstate

The connection between this microstate and the macrostate that it represents arises via

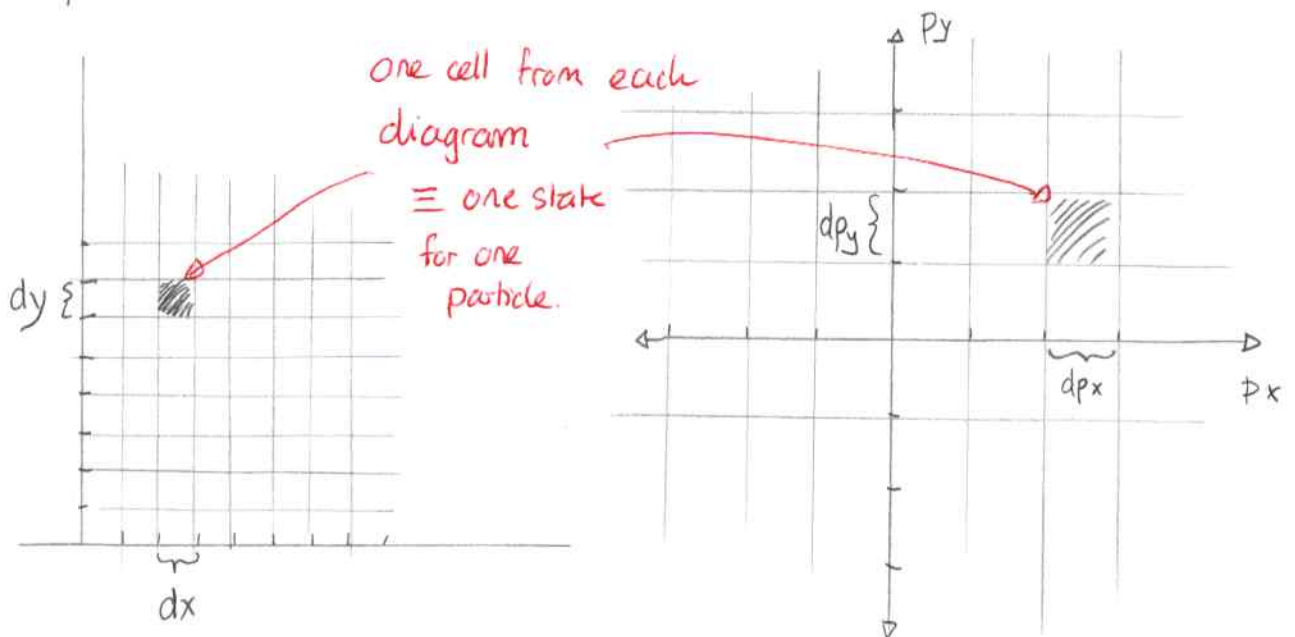
$$E = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} = \frac{1}{2m} \left\{ p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 + \dots \right\}$$

Statistical physics then requires that we obtain the multiplicity  $\Omega(E, V, N)$  for each macrostate. The immediate issue is that the continuous nature of the microstate means that there are infinitely many microstates for each macrostate.

We can see this via momentum for a single particle, whose vector can be drawn in three dimensional space. Taking a single spherical surface in this space, every vector on this surface gives the same energy contribution, so represents the same macrostate. But there are infinitely many such vectors. So  $\Omega = \infty$ .



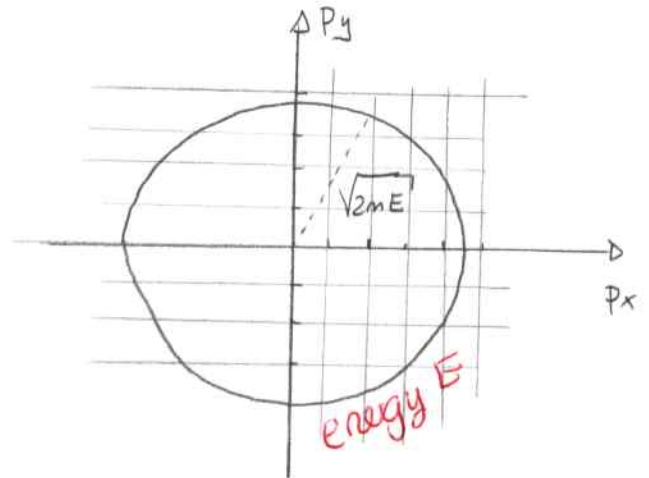
We present an alternative analysis that uses the fundamental ideas of statistical physics and avoids these issues. To start we could represent the possible states for each individual particle via a discretization of the space of states. We illustrate this in two dimensions:



This type of discretization will allow us to count microstates. We can then shrink the cell size to obtain an increasingly accurate count. We will see that certain crucial statistical and thermal physics conclusions are independent of the cell size. Note that the energy only depends on momentum.

Therefore the crucial task will be to compute the number of momentum states giving one particular energy. For a single particle in two dimensions:

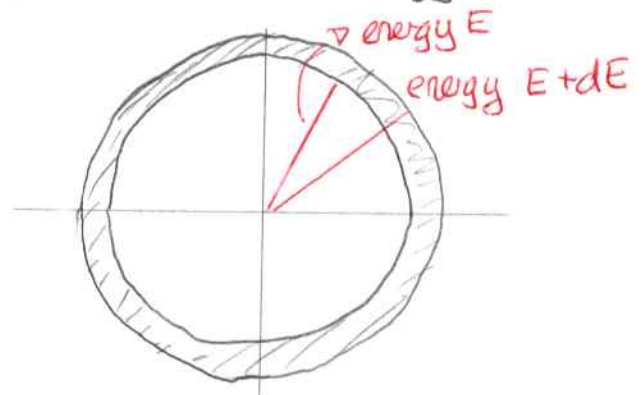
$$E = \frac{1}{2m}(p_x^2 + p_y^2) \Rightarrow p_x^2 + p_y^2 =$$



and all such states lie on a circle with radius  $\sqrt{2mE}$  in the  $p_x, p_y$  diagram. So for a macrostate with given energy  $E$  we would need to count the number of cells that give this energy. Again this is imprecise, even for small cells since they all "partly" intersect with the energy circle.

### Density of states

Rather than calculate the number of states with a precise energy, we can more reasonably try to compute the number of states with energy in the range  $E \rightarrow E + dE$ . If the grid representing the single particle states is sufficiently fine then the counting will have minimal ambiguity. We can eventually let  $dE \rightarrow 0$  and will find that it does not affect the resulting thermodynamics.



We now present mathematical techniques for managing the counting and the ensuing thermodynamics. First define

$$\Gamma(E) = \text{total number of microstates with energy in the range } 0 \rightarrow E$$

It follows that the number of states in the range  $E \rightarrow E+dE$  is

$$\Gamma(E+dE) - \Gamma(E)$$

and when  $dE$  is small enough then this gives the approximate number of states, so

$$\Omega(E) \approx \Gamma(E+dE) - \Gamma(E)$$

as  $dE \rightarrow 0$ . But

$$\Gamma(E+dE) - \Gamma(E) \cong \frac{d\Gamma}{dE} dE$$

We therefore define the density of states:

$$g(E) := \frac{d\Gamma}{dE}$$

Thus we get

$$\begin{array}{l} \text{Number of states} \\ \text{in the range } E \rightarrow E+dE \end{array} = g(E)dE \sim \Omega(E)$$

Then the entropy for the system should be

$$S(E, V, N) = k \ln[g(E)dE]$$

Does  $dE$  matter here?

## 1 Entropy and density of states

For a system with continuous degrees of freedom

$$S(E, V, N) = k \ln [g(E, V, N)dE].$$

- Determine an expression for the (thermodynamic) temperature and show that it only depends on the density of states and not  $dE$ .
- Does the way in way the state space is discretized affect the temperature as predicted by this model of statistical physics?
- Suppose that  $\Gamma(E, V, N) = AE^{\alpha N}$  where  $A$  and  $\alpha$  are independent of  $E$ . Show that for temperature and for  $\alpha N \gg 1$  there is negligible difference between using

$$S(E, V, N) = k \ln [g(E, V, N)dE]$$

and

$$S(E, V, N) = k \ln [\Gamma(E, V, N)].$$

Answer a)  $\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V, N}$

$$= \frac{\partial}{\partial E} k \ln [g(E, V, N) dE]$$

$$= \frac{\partial}{\partial E} k \ln [g(E, V, N)] + \frac{\partial}{\partial E} k \ln [dE]$$

$dE$  is independent of  $E$  so this = 0

$$= k \frac{1}{g} \frac{dg}{dE}$$

$$\Rightarrow T = \frac{g}{k} / \frac{dg}{dE} \quad \left. \vphantom{\frac{g}{k}} \right\} \text{ independent of } dE$$

- b) No. If the block sizes are halved then  $g$  would double but  $g \frac{dg}{dE}$  would stay constant

$$c) \quad g(E, V, N) = \frac{d\Gamma}{dE} = \alpha N A E^{\alpha N - 1}$$

$$\text{So } T = \frac{\alpha N A E^{\alpha N - 1}}{k} / \alpha N A (\alpha N - 1) E^{\alpha N - 2}$$

$$\Rightarrow \ln(g dE) \quad \leadsto \quad T = \frac{E}{k(\alpha N - 1)} \quad \Rightarrow \quad T \approx \frac{E}{k \alpha N}$$

Then with  $S(E, V, N) = k \ln(\Gamma)$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k \frac{1}{\Gamma} \frac{\partial \Gamma}{\partial E}$$

$$\frac{\partial \Gamma}{\partial E} = A \alpha N E^{\alpha N - 1}$$

$$\frac{1}{\Gamma} \frac{d\Gamma}{dE} = \frac{A \alpha N E^{\alpha N - 1}}{A E^{\alpha N}} = \frac{\alpha N}{E}$$

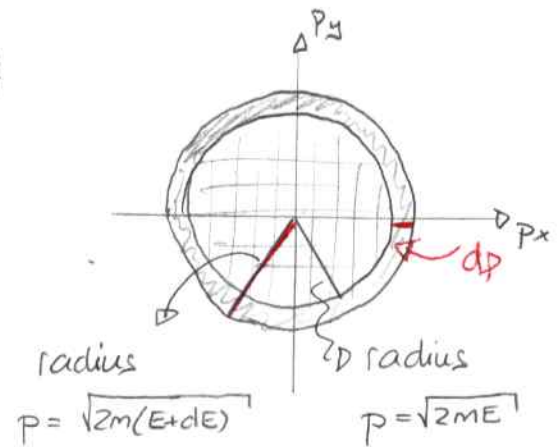
$$\Rightarrow T = \frac{E}{k \alpha N}$$

These are the same.

## Calculating the density of states

Conceptually the scheme for calculating density of states involves volumes and areas.

If we represent the momentum states in  $p_x, p_y, p_z$  space then we would need to compute the area of the inner ring and divided by the area of one grid cell to determine the number of states enclosed.



Although we could do this classically, a more natural approach imagines the gas as consisting of quantum particles in a box.

## Quantum particle gas

We can naturally attain a discrete space of states by assuming that the gas particles are quantum particles in infinite wells. Consider first a single particle of mass  $m$  in a cubic infinite well with sides  $L \times L \times L$ . Then quantum theory predicts:

1) the state of the particle can be represented by three integers

$$\left. \begin{matrix} n_x \\ n_y \\ n_z \end{matrix} \right\} = 1, 2, 3, \dots$$

2) the particle energy is

$$E = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

Examples of particle states and energies are:

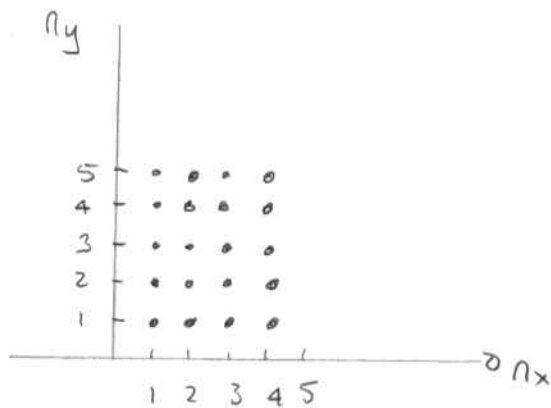
state			energy
$n_x$	$n_y$	$n_z$	$E$
1	1	1	$3 \frac{h^2}{8mL^2}$
1	1	2	$6 \frac{h^2}{8mL^2}$
1	2	1	$6 \frac{h^2}{8mL^2}$
2	1	1	$6 \frac{h^2}{8mL^2}$

*different states* → (1,1,2)  
*same energy* → (1,2,1) and (2,1,1)

They can be represented in a three dimensional  $n_x, n_y, n_z$  space

Each point represents one state.

We can then use geometrical arguments to determine  $\Gamma(E)$  and the density of states





## 2 Density of states: single quantum particle in a box

Consider a single quantum particle with mass  $m$  in a cubic box with sides of length  $L$ .

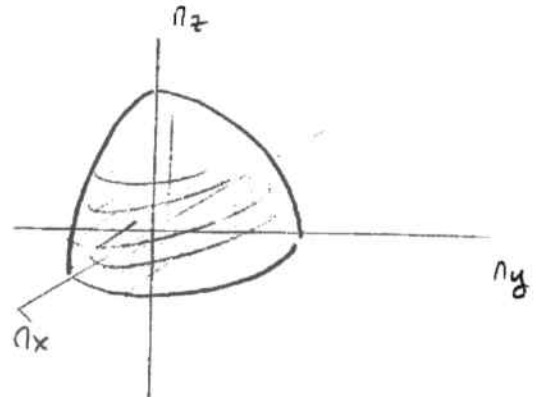
- The states of the particle can be represented on a three dimensional  $n_x, n_y, n_z$  diagram. For a given value of energy  $E$  illustrate geometrically the region that contains all states with energy less than  $E$ .
- Use the geometrical illustration to determine  $\Gamma(E)$  and express this in terms of  $E, m, h$  and the volume of the box.
- Determine the density of states.

Answer a) 
$$E = \frac{h^2}{8mL^2} \underbrace{(n_x^2 + n_y^2 + n_z^2)}_{\text{radius}^2 \text{ in } n_x, n_y, n_z \text{ diagram.}}$$

We need all  $n_x, n_y, n_z$  such that

$$n_x^2 + n_y^2 + n_z^2 \leq \frac{8mL^2 E}{h^2}$$
$$\Rightarrow \sqrt{n_x^2 + n_y^2 + n_z^2} \leq \sqrt{\frac{8mL^2 E}{h^2}}$$

This is the "positive" octant of a sphere of radius  $\sqrt{8mL^2 E/h^2}$



b) Number of states =  $\frac{\text{Volume of octant}}{\text{volume occupied by one state}}$

Each point occupies a region  $1 \times 1 \times 1 = 1$

$$\begin{aligned} \text{Then volume of octant} &= \frac{1}{8} \frac{4\pi}{3} \left[ \sqrt{\frac{8mL^2 E}{h^2}} \right]^3 \\ &= \frac{1}{8} \frac{4\pi}{3} \frac{L^3}{h^3} (8mE)^{3/2} \end{aligned}$$

$$\begin{aligned}\text{So } \Gamma(E) &= \frac{\pi}{6} \frac{L^3}{h^3} (8mE)^{3/2} \\ &= \frac{\pi}{6} \left(\frac{8m}{h^2}\right)^{3/2} V E^{3/2}\end{aligned}$$

$$c) \quad g(E) = \frac{d\Gamma}{dE} = \frac{\pi}{6} \left(\frac{8m}{h^2}\right)^{3/2} \frac{3}{2} V E^{1/2}$$

□