

Lecture 36

(36.1)

Typically we apply the thermodynamic formalism to problems where the number of particles N is of order 10^{23} (Avogadro's number) and we can ignore the difference between $\frac{3}{2}N$ and $\frac{3}{2}N - 1$. We therefore simplify our result for the number of microstates of an ideal gas:

$$\Omega(V, E) \propto V^N E^{\frac{3}{2}N}$$

For large N this varies very rapidly with V and E . However, if we force E and V to obey

$$E \propto V^{2/3},$$

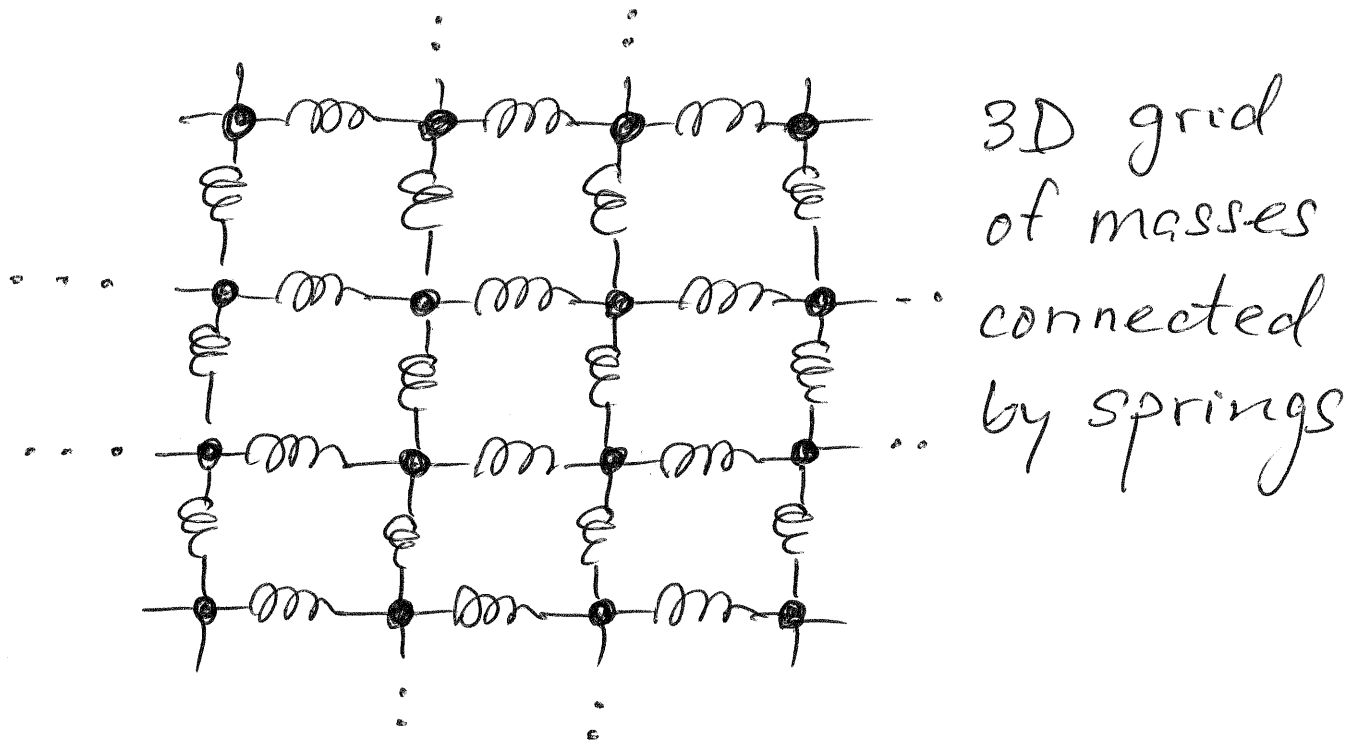
then Ω will stay constant. For

example, if we increase V (36.2) and decrease E according to this rule, then the increase in position states will be compensated by a decrease in momentum states.

Notice this is exactly the law we found earlier in the course, for how the energy in the gas varies when the volume is changed slowly. So we can restate the earlier law by saying that is the relationship needed to keep the number of microstates fixed.

To see how little, in the way of detail, we need when counting microstates, let's consider

a completely different (36.3)
system: a solid of equal-mass
atoms. Here's a cartoon of a
simplified model:



We'll keep the volume fixed (set
by the equilibrium length of the
bonds/springs). The masses have
momentum states and position
states described by vectors \vec{q}

giving their displacements (36.4)

from their equilibrium positions.

The potential energy of atom i is

$$U = \frac{k}{2} (q_{ix}^2 + q_{iy}^2 + q_{iz}^2)$$

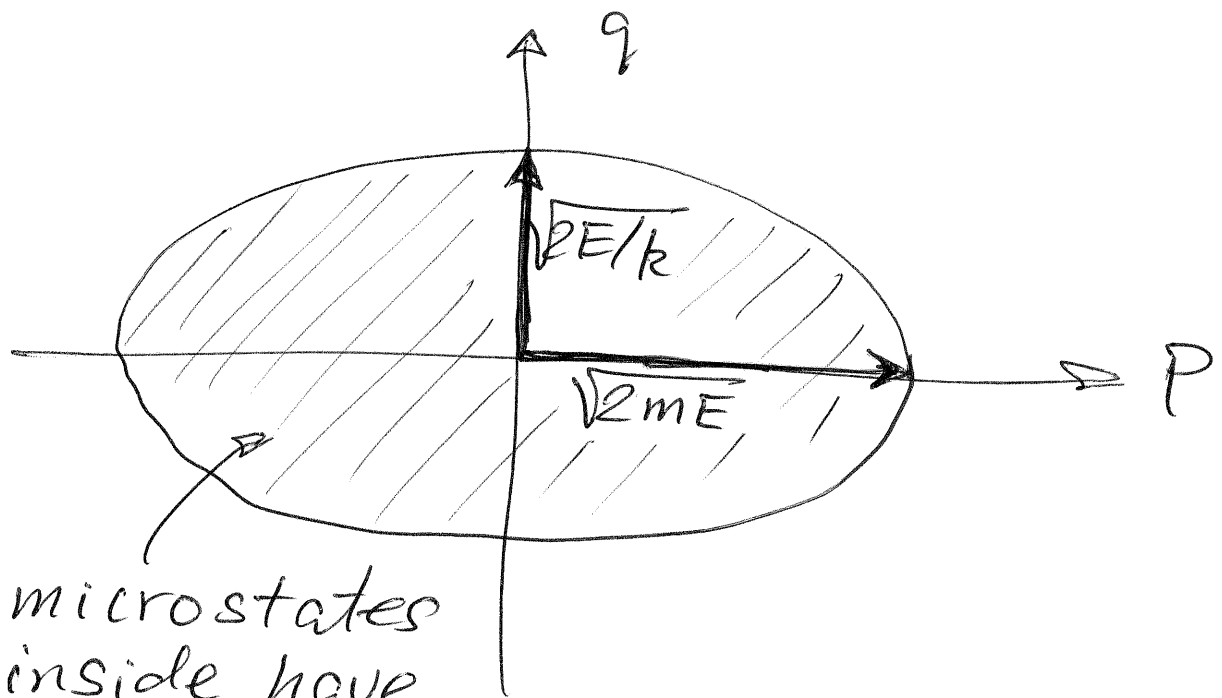
with minimum at $q_{ix} = q_{iy} = q_{iz} = 0$

and linear restoring force with Hooke's constant k in all three directions. The total energy of our model solid is the energy of $3N$ harmonic oscillators:

$$E = \frac{1}{2m} (P_{ix}^2 + P_{iy}^2 + P_{iz}^2 + \dots + P_{Nx}^2 + P_{Ny}^2 + P_{Nz}^2)$$

$$+ \frac{k}{2} (q_{ix}^2 + q_{iy}^2 + q_{iz}^2 + \dots + q_{Nx}^2 + q_{Ny}^2 + q_{Nz}^2)$$

This equation describes (36.5)
a hyper-ellipse in $6N$ dimensions.
The radius in the p -dimensions
is $\sqrt{2mE}$ and in the q -dim-
ensions $\sqrt{2E/k}$:



microstates
inside have
energy less than E

The behavior of the volume with
 E is the same as for a hyper-
sphere : the size scale in all
dimensions goes as \sqrt{E} , with

the "shape" only affecting (36.6)
the proportionality constant we
don't care about.

$$W(E) \propto \sqrt{E}^{6N} = E^{3N}$$

$$\Omega(V, E) = W(E + \delta E) - W(E)$$

$$\propto E^{3N-1} \delta E \simeq E^{3N}$$

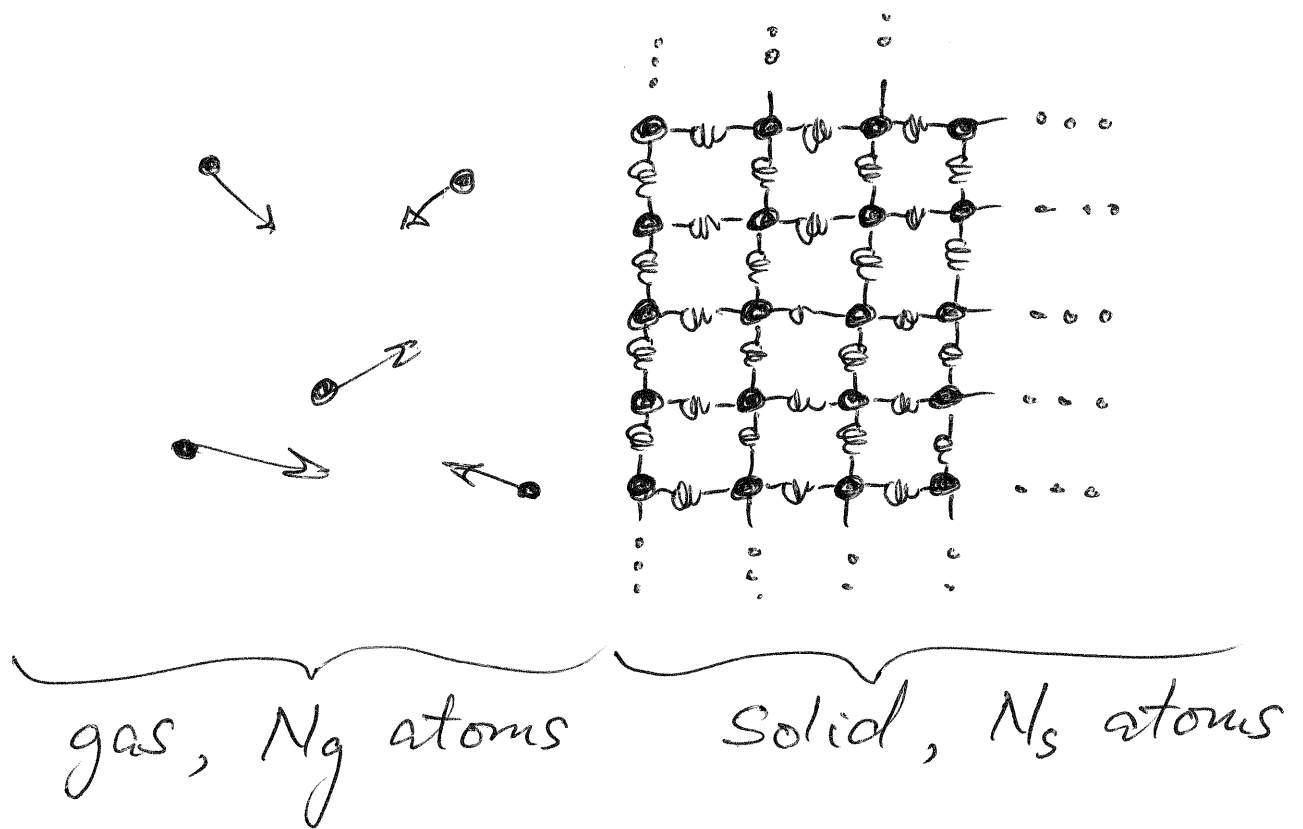
(since $\delta E = \text{constant}$ and N is
enormous)



The usefulness of the micro-
state counts — the function
 $\Omega(V, E)$ — becomes clear when
we look at thermodynamic

equilibrium when there are two systems that can exchange energy with each other. The mechanisms of exchanging energy should be microscopic in the sense that one system is not allowed to change any macroscopic property, such as volume, of the other. Energy exchanged in this sense is called "heat". When energy exchange by heat is possible we say the systems are in "thermal contact". The mechanism of heat is no different than the

mechanism of energy transport within a gas by random collisions. As an example, consider a gas in thermal contact with a solid: (36.8)



Whenever a gas particle collides with an atom in the solid there is an exchange of energy that can go either way, in principle.

Our central hypothesis (36.9) still applies to this compound system. For a complete specification of the microstate we need to specify the microstate of the gas and the microstate of the solid.

For the sake of argument, suppose the energy of the gas is E_g and that of the solid is E_s . These numbers can fluctuate, by the mechanism of heat, but their sum is conserved:

$$E_g + E_s = E.$$

What can we say about (36.10) the most likely values of these energies? The total number of microstates, in the compound system, when the gas has energy E_g is

$$\Omega_{\text{comp}}(E_g) = \Omega_{\text{gas}}(E_g) \Omega_{\text{solid}}(E - E_g) \\ \propto E_g^{\frac{3}{2} N_g} (E - E_g)^{3 N_s}$$

We have left out the factor V^{N_g} in Ω_{gas} because the volume is being held fixed (no macroscopic changes!). Also, Ω_{comp} is just a function of one variable, E_g , since energy conservation determines E_s .