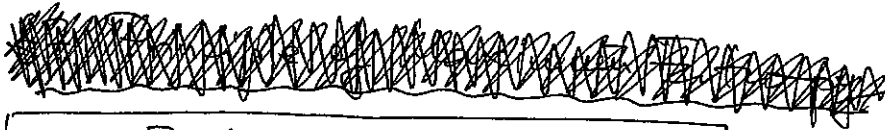


# Lectures on Statistical Physics (A1)

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## PART III. FOUNDATIONS OF STATISTICAL MECHANICS



S7. From microphysics to macrophysics

### 2.1 What are we trying to do?

Thermodynamics was all about flows of energy, in two basic forms:

$$\delta U = \delta Q + \delta W = \underbrace{T \delta S}_{\substack{\text{"} \\ \delta Q_{\text{rev}}}} - \underbrace{P \delta V}_{\substack{\text{"} \\ \delta W_{\text{rev}}}} \quad \leftarrow \begin{array}{l} \text{T \& S introduced via} \\ \text{this relation!} \end{array} \quad (1)$$

This was completely general.

But to calculate anything specific, we needed two further pieces of information:

- 1) Equation of state  
 $P = P(V, T)$

Ideal gas  
(a specific model of substance):  
 $PV = RT$  (or  $p = nk_B T$ )

- 2) Energy  
 $U = U(V, T)$

$$U = \frac{3}{2} k_B T N$$

These required some microphysical model of the substance our system was made of.

Similarly, for non-PV systems, we required some model of the stuff in order to determine, e.g. tension  $f(L, T)$ , magnetisation  $\vec{M}(\vec{B}, T)$  etc.

So, the goal is, given a system with certain known microphysical properties, to learn how to construct the eqn of state for it and the relationship between energy and temperature (and other parameters, e.g.  $V$ ). Note that the latter often takes the form of calculating heat capacity, e.g.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

So it is also useful to be able to calculate  $S(V, T)$ . To be even more systematic, recall that free energy satisfies  $F = U - TS$  and

$$dF = -SdT - PdV$$

and so  $P = -\left(\frac{\partial F}{\partial V}\right)_T$  equation of state (2)

$S = -\left(\frac{\partial F}{\partial T}\right)_V$  entropy (3)

$U = F + TS$  energy (4)

Since  $-pdV = \left(\frac{\partial F}{\partial V}\right)_T dV$   
 $F$  is sometimes called "work content"

! So if we learn how to calculate  $F = F(T, V)$  for a given system, we will know everything we wish to know (thermodynamically) about this system.

NB: We are talking about systems in equilibrium.

If we want also to know how they get there, we need a lot more than just  $F(T, V)$ ! Kinetic theory dealt with such questions (transport eqns etc), but Statistical Mechanics will not.

7.2 System and its states.

What does it mean to have a microphysical model (description) of a physical system?

Well, any physical system is a quantum mechanical system and a quantum mechanical system is basically something that can be in a number of quantum states - call them microstates, they are defined by a set of quantum numbers (eigenvalues of a complete set of commuting variables) and each such set has a certain probability

NB: For systems with many degrees of freedom (e.g. many particles), we are talking about collective states of the system, not of the states of any individual particles (e.g., to anticipate, a simple state of a box with ideal gas in it will be a state with a certain # of particles having each of a discrete set of values of momentum and spin available in the box)

~~.....~~

Let us enumerate these states:

$\alpha = 1, 2, 3, \dots, \Omega \gggg 1$  (total # of microstates huge for a large system)

$P_1, P_2, P_3, \dots, P_\Omega$  their probabilities  $\sum_{\alpha=1}^{\Omega} p_{\alpha} = 1$

$E_1, E_2, E_3, \dots, E_{\Omega}$  their energies

... other things: momenta, angular momenta, spins, ...

If we ~~could know all these things~~ knew all these things,

We could then calculate various macrophysical quantities as averages: e.g.,

Energy:  $U = \sum_{\alpha} P_{\alpha} E_{\alpha} (= \langle E_{\alpha} \rangle)$  (5)

although it is at this stage not really clear what such things as  $S, T, P$  are.

In fact, I can clear up the question of what is  $P$  right away: 7.3 Pressure

The concept of pressure arises in connection with changing the volume of the system.

Let us consider deformations that occur very very slowly. We know from QM (Binney §11.1)

that if an external parameter (here volume) is changed slowly in an otherwise isolated system, the system will stay in the same eigenstate (say,  $\alpha$ ) and only its energy  $E_{\alpha}$  will change slowly.

Thus, the microstates will stay the same and their probabilities  $\{p_\alpha\}$  will not change in this process, called adiabatic (we will learn soon that this meaning of "adiabatic" is equivalent to the thermodynamic one). [See Binney's QM §11.1-3]

The corresponding change in mean energy is then

$$dU_{ad} = \left( \frac{\partial U}{\partial V} \right)_{p_1 \dots p_{\Omega}} dV = \sum_{\alpha} p_{\alpha} \left( \frac{\partial E_{\alpha}}{\partial V} \right)_{p_1 \dots p_{\Omega}} dV \quad (6)$$

But <sup>the</sup> slow change of energy in an isolated system, due exclusively to change in its volume can be related to the work done on the system by whatever force is applied to effect the change = minus work done by the system against that force.

$$\text{So } dU_{ad} = dW_{ad} = -P dV \quad (7)$$

and we may therefore define pressure as

$$\boxed{P = - \left( \frac{\partial U}{\partial V} \right)_{p_1 \dots p_{\Omega}} = - \sum_{\alpha} p_{\alpha} \left( \frac{\partial E_{\alpha}}{\partial V} \right)_{p_1 \dots p_{\Omega}}} \quad (8)$$

~~Similarly~~ Similarly,

$$\text{tension } f = \sum_{\alpha} p_{\alpha} \left( \frac{\partial E_{\alpha}}{\partial L} \right)_{p_1 \dots p_{\Omega}} \quad (9)$$

$$\text{magnetization } \vec{M} = - \sum_{\alpha} p_{\alpha} \left( \frac{\partial E_{\alpha}}{\partial \vec{B}} \right)_{p_1 \dots p_{\Omega}} \quad (10)$$

etc.

Thus, if we know  $\{p_\alpha\}$  and  $\{E_\alpha\}$  (the latter as functions of  $V$  or other parameters), we can calculate pressure and similar quantities.

It is clear that I can't make any progress on calculating  $\{E_\alpha\}$  w/o specifying what my system is made of and how it is constituted.

So this is a job for microphysical (in general, quantum) theory. Usually, we will only be able to solve for simple models (like the ideal gas).

The amazing thing is that in equilibrium, we will be able to determine  $\{p_\alpha\}$  as functions of  $\{E_\alpha\}$

in a completely general way - w/o having to solve the  $\Omega$ -dimensional Schrödinger equation for our system (clearly hopeless!)

To do this, we will make a philosophical leap and learn to calculate things not on the basis of what we know but on the basis of what we don't know!

When I say "determine" what I really mean is find a set of  $\{p_\alpha\}$  s.t. upon insertion into averages ~~etc.~~ such as (5) or (8), correct (explicitly verifiable) macroscopic quantities will be obtained (so I do not mean that those  $\{p_\alpha\}$  will literally be solutions of the Sch. equ.