

Lecture 1

Thermodynamics

Macroscopic bodies like rocks or water
contain many atoms.

To many to track in detail

Don't usually went to track in detail

Empirically, just a few "macroscopic" variables
are interest.

Example: Pressure of gas
Magnetization of magnet
Number of particles in reaction

Thermodynamics: theory for how macro variables
evolve & interact

• Based on empirical laws, just like Newtonian mechanics

Statistical Mechanics: methods for deriving thermodynamic
behavior from microscopic model

⇒ good for understanding thermo

But often stat mech doesn't work:

microscopic model too complex (glass, water,
quark-gluon plasma, ...)

Can still get useful results from thermo by itself

So start with study of thermo as independent theory

Describe system by state variables
→ think of like generalized coordinates

Basic variables come in pairs:
Generalized force + generalized displacement

See chart - assume you know all but T, S, μ

Note displacements extensive: scale with size
forces intensive: indep size

Other main state variables are potentials

Energy = total energy in system

others = free energies = Legendre transforms
will discuss

Response functions are derivatives of others
Many other combinations w/o special names

Lots of variables to track: one of main difficulties

Remember how math works:

$$\text{Say } F = F(x_1, x_2)$$

if x_1 + x_2 change by small amount dx_1, dx_2

then F changes by

$$dF = \left(\frac{\partial F}{\partial x_1} \right)_{x_2} dx_1 + \left(\frac{\partial F}{\partial x_2} \right)_{x_1} dx_2$$

↑ fixed ↗

If given $dF = C_1(x, y)dx + C_2(x, y)dy$

then function F exists if $\left(\frac{\partial C_1}{\partial y}\right)_x = \left(\frac{\partial C_2}{\partial x}\right)_y$

$$\text{i.e., } \frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x}$$

Then say dF is exact

Since state variables exist, all differentials of state variables are exact

Some other differentials are not exact:

$dQ =$ increment of heat transfer

$dW =$ increment of work done

"heat" & "work" not state variables

\rightarrow describe a process, not a state

Given exact dF , construct F by

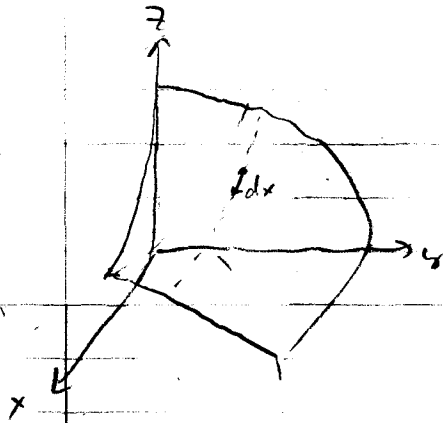
$$\begin{aligned} F &= \int C_1 dx + K_1(y) \\ &= \int C_2 dy + K_2(x) \end{aligned} \quad \left. \begin{array}{l} \leftarrow \\ \leftarrow \end{array} \right\} \text{arb fns}$$

Compare forms to identify K 's (up to a constant)

Now, suppose three variables x, y, z

that satisfy relation $f(x, y, z) = \text{const}$

Defines 2D surface: $\left(\frac{\partial z}{\partial x}\right)_y$ is how z changes as x varies, in order to stay on surface



Can take any two of x, y, z as independent variables.

Write

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

→ how x changes as y & z vary

$$\text{or } dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

Can combine these:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \right] + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$0 = dx \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z - 1 \right] + dz \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y \right]$$

Since dx & dz arbitrary, need

$$(a) \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

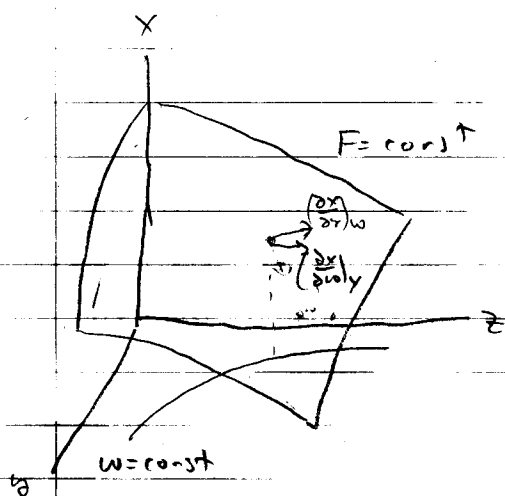
$$(b) \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Now let's introduce another function $w = w(y, z)$

Could equally well express as $w(x, y)$ or $w(x, z)$
(using F)

So $\left(\frac{\partial x}{\partial y}\right)_w$: how x changes with y , to stay on surface $F = \text{const}$, when we vary y but simultaneously change z to keep $w = \text{const}$

Compare $\left(\frac{\partial x}{\partial w}\right)_y$: how x changes with w along
lines $y = \text{const}$



Consider $x = x(y, z(w, y))$

$$\text{Then (c) } \left(\frac{\partial x}{\partial w}\right)_y = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial w}\right)_y$$

$$\text{(d) } \left(\frac{\partial x}{\partial y}\right)_w = \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_w$$

Four useful relations.

In thermo; role of $F = \text{const}$ played by eqn of state

= relation between primary state variables

Get from stat mech or experiment

Examples:

• Ideal gas $PV = Nk_B T$

$$k_B = \text{Boltzmann's constant} \\ = 1.38 \times 10^{-23} \text{ J/K}$$

- Van der Waals gas

$$\left(P + a \frac{N^2}{V^2}\right) (V - bN) = Nk_B T$$

↑
attractive
long range
interaction

↑
excluded
volume from
particle core

- Virial gas $PV = Nk_B T \left[a_1 + a_2 \frac{N}{V} + a_3 \left(\frac{N}{V}\right)^2 + \dots \right]$
 $a_2 =$ virial coefficients

- Stretched wire

$$J = K(T) (L - L_0)$$

↓
T-dep
spring constant

↓
unstretched
length

- Curie's Law

Recall $\vec{B} = \mu_0 (\vec{H} + \vec{M})$

$\vec{H} =$ applied field

Eqn of state: $\vec{M} = D \frac{N}{VT} \vec{H} = \frac{C}{T} \vec{H}$

$D =$ constant

$C = \frac{N}{V} D \approx$ constant for solids

Note, eqns of state hold only for systems in thermal equilibrium

- Thermal variables constant in time
- No macroscopic flow

For very slow changes, stay arbitrarily close
to equilibrium

time scale \gg equilibration time

experimentally determined

Call slow changes reversible

arb close to equilibrium, process can go either direction

Non-equilibrium behavior much more complicated

State variables not well-defined

\Rightarrow irreversible

But non-equilibrium process still connects
well-defined equilibrium states