0. Introduction

How to treat systems with many degrees of freedom ($N \approx 10^{23}$)
underlying theories: Newtons equation, Schroedinger equation, Maxwell eqs.

Thermodynamics	Statistical Physics
empirical laws	microscopic models
no relationship to microscopics	general machinery
low resolution quantities	few solvable systems
general	quantities of any resolution

I Equilibrium thermodynamics

1. State Variables

extensive variables: proportional to the size of the system
intensive variables: independent of the size of the system

extensive	intensive
volume V	pressure P
magnetization $\vec{M}$	magnetic field strength $\vec{H}$
electric polarization $\vec{P}$	electric field $\vec{E}$
entropy S	temperature T
number of particles N	chemical potential μ
number of mols n	molar chemical potential μ
mass M	specific chemical potential $\tilde{\mu}$
internal energy U	thermal expansivity α_P
free energy F	compressibility κ_T, κ_S
heat capacity $C_{V,\{N\}}$	

10^{23} degrees of freedom $\longrightarrow \mathcal{O}(10^2)$ macroscopic variables further reduction in degrees of freedom:

Thermodynamic equilibrium
The state of a system in thermal equilibrium is characterized by only a few macroscopic variables. The values of all macroscopic variables do not change in time and are independent of the history of the system.

many more variables than degrees of freedom
(will see later how many)
→ they all depend on each other

Types of dependencies:
(i) by definition
(ii) fundamental (following from definitions and laws)
(iii) through equation of state (model dependent, empirical or microscopic)

(i) Dependencies by definition:

- heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

- thermal expansivity $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

- compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

(ii) <u>Fundamental dependencies</u>

Assume: 2 independent degrees of freedom x_1, x_2

every point of the plane (x_1, x_2) corresponds to one equilibrium state of the system

another state variable ϕ is function of x_1, x_2

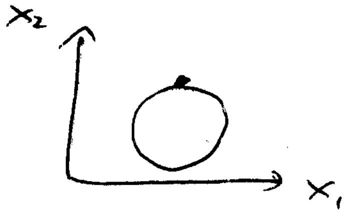
Often only derivatives of Φ with respect to x_i are measurable

$$c_1(x_1,x_2) = \left(\frac{\partial \phi}{\partial x_1}\right)_{x_2} \qquad c_2(x_1,x_2) = \left(\frac{\partial \phi}{\partial x_2}\right)_{x_1}$$

c_1 and x_1 as well as c_2 and x_2 are <u>conjugate</u> variables with respect to ϕ.

Measure $c_1(x_1, x_2)$ and $c_2(x_1, x_2)$.

Total differential of ϕ is $d\phi = \left(\frac{\partial \phi}{\partial x_1}\right)_{x_2} dx_1 + \left(\frac{\partial \phi}{\partial x_2}\right)_{x_1} dx_2 = c_1 dx_1 + c_2 dx_2$



ϕ has to remain unchanged if x_1 and x_2 are varied along any closed curve

$$\oint d\phi = 0$$

$\Rightarrow$ $d\phi$ is an <u>exact</u> differential form

$$\Rightarrow \boxed{\left(\frac{\partial c_1}{\partial x_2}\right)_{x_1} = \left(\frac{\partial c_2}{\partial x_1}\right)_{x_2}}$$

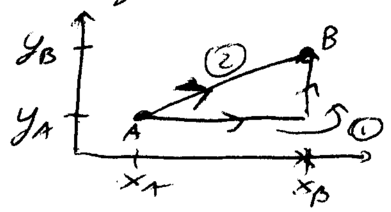
relation between state variables that is true for <u>any</u> system example: $d\phi = (\overset{"c_1"}{x^2+y})\,dx + \overset{"c_2"}{x}\,dy$

is ϕ a state variable?

- differential test

$$\left(\frac{\partial}{\partial y}(x^2+y)\right)_x = 1 \qquad \left(\frac{\partial}{\partial x}\,x\right)_y = 1 \quad \checkmark$$

- integral test



① $$\phi_B - \phi_A = \int_{x_A}^{x_B}(x^2+y_A)\,dx + \int_{y_A}^{y_B} x_B\,dy$$

$$= \tfrac{1}{3}x_B^3 - \tfrac{1}{3}x_A^3 + \cancel{y_A x_B} - y_A x_A + y_B x_B - \cancel{y_A x_B}$$

② $$y = y_A + \frac{y_B-y_A}{x_B-x_A}(x-x_A) \qquad dy = \frac{y_B-y_A}{x_B-x_A}\,dx$$

$$\phi_B - \phi_A = \int_2 (x^2+y)\,dx + x\,dy = \int_{x_A}^{x_B}\left(x^2+y_A + \frac{y_B-y_A}{x_B-x_A}(x-x_A) + x\,\frac{y_B-y_A}{x_B-x_A}\right)dx$$

$$= \tfrac{1}{3}x_B^3 - \tfrac{1}{3}x_A^3 + y_A x_B - y_A x_A + \frac{y_B-y_A}{\cancel{x_B-x_A}}\underbrace{\cancel{(x_B^2-x_A^2)}}_{(x_B+x_A)} - \frac{y_B-y_A}{\cancel{x_B-x_A}}\,x_A\,\cancel{(x_B-x_A)}$$

$$= \tfrac{1}{3}x_B^3 - \tfrac{1}{3}x_A^3 + \cancel{y_A x_B} - \cancel{y_A x_A} + y_B x_B - \cancel{y_A x_B} + \cancel{y_B x_A} - y_A x_A - \cancel{y_B x_A} + \cancel{y_A x_A}$$

Other useful relationships

x, y, z, w four state variables, still two degrees of freedom

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

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

(iii) $\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z$

(iv) $\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z$

~~proof~~:

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

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

combine $\rightarrow$ $\underbrace{\left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z - 1\right]}_{=0 \Rightarrow (i)} dx + \underbrace{\left[\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y\right]}_{=0 \Rightarrow (ii)} dz = 0$

9/30

$x = x(w,y)$: $dx = \left(\frac{\partial x}{\partial w}\right)_y dw + \left(\frac{\partial x}{\partial y}\right)_w dy$

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

$w = w(y,z)$: $dw = \left(\frac{\partial w}{\partial y}\right)_z dy + \left(\frac{\partial w}{\partial z}\right)_y dz$ ← insert into

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

$$\underbrace{\left[\left(\frac{\partial x}{\partial y}\right)_z - \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z - \left(\frac{\partial x}{\partial y}\right)_w\right]}_{=0 \Rightarrow (iv)} dy + \underbrace{\left[\left(\frac{\partial x}{\partial z}\right)_y - \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial z}\right)_y\right]}_{=0 \Rightarrow (iii)} dz = 0$$