

# *Entropy and all that*

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- L  
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t  
1
- ◆ The world image of Theoretical Physics
  - ◆ Classical Dynamics
  - ◆ Its computational counterpart: Molecular Dynamics
  - ◆ Classical (Equilibrium) Statistical Mechanics: Ensembles
  - ◆ Derivation of physical properties: what can be done
- L  
e  
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2
- ◆ Thermodynamics  $\longrightarrow$  Thermodynamic potential(s)
  - ◆ Probabilistic interpretation: Entropy
  - ◆ Ensemble Theory: Legendre transforms (characteristic functions)
  - ◆ A misconception: Entropy as a measure of order.
  - ◆ Hard sphere transition

In principle, the behavior of a piece of matter in ordinary conditions comes out of  $t$ -dependent Schroedinger Equation and Q.Stat.Mech. with  
[Relativistic Quantum Field Theory not needed for that!]

$$\mathcal{H}(r, R; p, P) = K_N(P) + K_e(p) + \underbrace{V(r, R)}_{\text{Coulomb}}$$
$$H_e(r, p | R)$$

$$i\hbar \frac{\partial \tilde{\Psi}(r, R, t)}{\partial t} = \mathcal{H} \tilde{\Psi}(r, R, t) \iff \mathcal{H} \tilde{\Phi}_n = \mathcal{H} \tilde{\Phi}_n$$

Not Soluble by Brute Force

### Born-Oppenheimer approximation

since  $m_N \gg m_e$

$$H_e(r, p | R) \Phi_s(r | R) = E_s(R) \Phi_s(r | R)$$

Born-Oppenheimer surface

$$\text{and } \left| \nabla_R \Phi_s \right| \ll \left| \nabla_r \Phi_s \right|$$

$$\Psi(r, R; t) = \sum_s \chi_s(R; t) \Phi_s(r | R) \simeq \chi_0(R; t) \Phi_0(r | R)$$

i.e the (often valid) **adiabatic approximation**  
where

$\chi_0(R; t)$  is given by

$$i\hbar \frac{\partial \chi_0(R; t)}{\partial t} = H_N(R, P) \chi_0(R; t)$$
$$\equiv [K_N(P) + E_0(R)] \chi_0(R; t)$$

the strict **adiabatic approximation** (no electronic jumps allowed)

the dynamics of the nuclei, apparently independent from the electrons, is driven by  $E_0(R)$  as interaction potential (a mean field, modelizable, no more Coulomb!)

when  $\left\{ \begin{array}{l} \text{nuclei are heavy enough} \\ \text{temperature is high enough so that} \end{array} \right.$

$$\Lambda = h / \sqrt{2\pi m_N k_B T} \ll \text{internuclear distance } R$$

Dynamics, no more quantum, is Newton's

$$m_N \ddot{R} = -\nabla E_0(R)$$

### to sum up

- ❖ a classical system of particles interacting via an *effective* interaction potential,  $E_0$
- ❖  $E_0$  can be obtained ab initio (AIMD) or by some suitable fitting procedure  $\longrightarrow$  phenomenological model, e.g. with a Pairwise Additive Potential (PAP) 
$$V(R) = \sum_{i < j} v(R_{ij})$$
- ❖ if PAP, the equations of motion are numerically integrable for a number of particles finite but larger enough to study, by statistical approach, the thermal properties of matter

## (BO originated) Classical Statistical Mechanics Model

*Theoretically:*

- $N(\rightarrow \infty ; N/V = \text{const})$  atoms/molecules  $\iff$  point particles (p.p.),  $(R_1, R_2, \dots, R_N)$  / connected sets of p.p.  $(\{R_1\}, \{R_2\}, \dots, \{R_N\})$
- Interactions between p.p,  $V_N(\{R_1\}, \{R_2\}, \dots, \{R_N\})$
- Boundary Conditions (compulsory: no BC's no equilibrium)
- Initial Conditions (necessary to start although irrelevant for macroscopic behavior. However, they can be a headache!)
- Evolutions laws: Newton equations of motion and Laplace deterministic dream,  $\{R(t; R_0, P_0), P(t; R_0, P_0)\}_{t \in (0, \tau \rightarrow \infty)}$

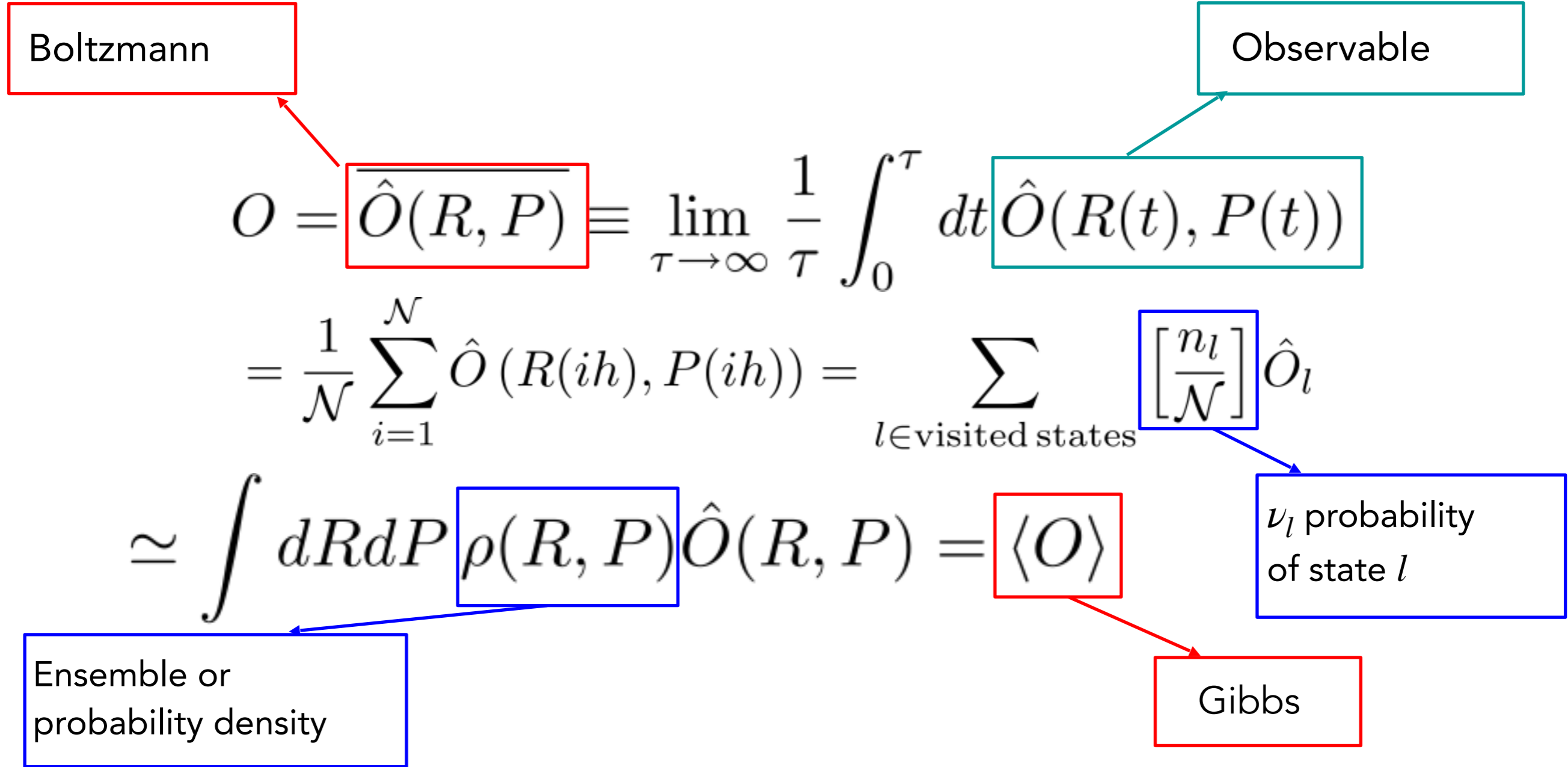


### Computationally:

- $N \sim 32 \div 10^9$ ,  $n = N/V$
- Boundary Conditions: periodic (PBC)
- Initial Conditions: positions, regular lattice; velocities, Maxwellian
- $V_N$ : simple  $\longrightarrow$  pairwise additive  $\left( \sum_{i<j} v_{ij}; \mathcal{O}(N^2) \right)$ ; short range (MIC)
  - extensions*:  $\longrightarrow$  long range (Coulomb) by Ewald Sums
  - $\longrightarrow$   $n$ -body potentials  $\mathcal{O}(N^n)$ , but glue potential  $V_N(\alpha)$  with  $\alpha = \sum_{i<j} \varphi_{ij} \dots$
  - $\longrightarrow$  stiff intramolecular potentials:
    - { Constraints:  $\sigma(r) = 0$ ;  $m\ddot{r} = F - \lambda \nabla \sigma$  : SHAKE
    - { Multiple timestep (Martyna, Tuckerman, Berne): RESPA
- Integration algorithms: robust, time reversible, symplectic: e.g. Verlet
- Various ensembles (thermostats, barostats, ... ):
  - extended variables simulations (Andersen, Nosé, Hoover,...)

- a closed system evolving in time under time-independent forces will reach a **STATIONARY** state
- the microscopic properties are 'irrelevant' while the statistical (or macroscopic) ones are stable and interesting (**THERMODYNAMICS**)
- thermodynamic properties can be computed by **time averages** or, as we will see, by ensemble averages

# Classical Equilibrium Statistical Mechanics (2)



- ◆ properties coming from an observable  $\longrightarrow$  mechanical ( e.g. pressure)
- ◆ properties coming from  $n_\ell$  or  $\rho$ , i.e probability  $\longrightarrow$  thermal ( e.g. free energy)

## THE NATURE OF THE ENSEMBLE

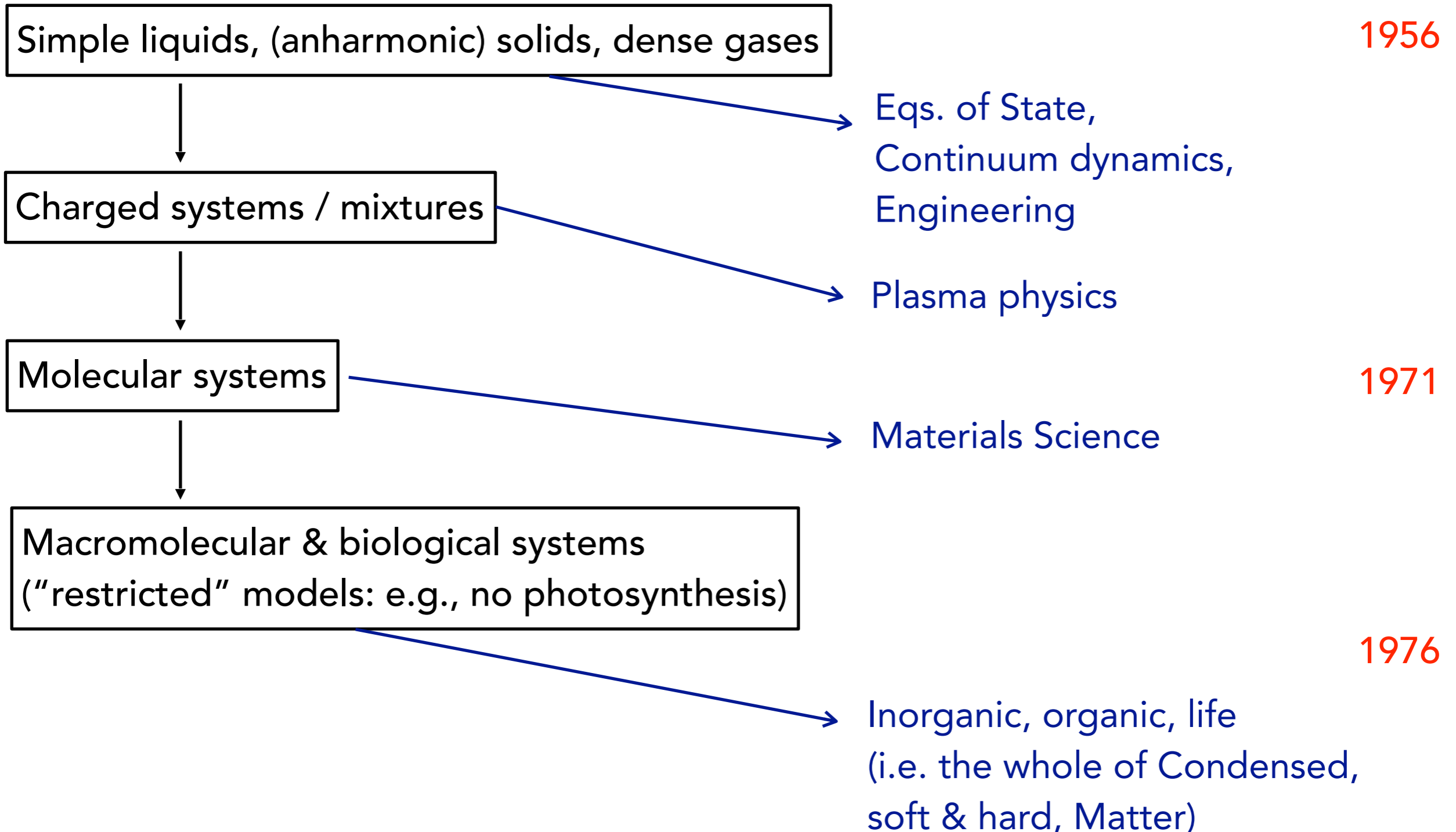
- The Boltzmann hypothesis:

ALL VISITABLE MICROSTATES ARE EQUIPROBABLE

- Since the motion is constrained to be on the hypersurface  $H = E$ , the so-called Microcanonical Ensemble becomes:

- $$\rho = \frac{1}{\mu(\text{surf } H = E)} = \frac{1}{\int d\Gamma \delta(H - E)} = \frac{1}{\Sigma(E)}$$

## What has & can be done?



- For whatever system describable by Classical Dynamics we have achieved our goal: Theoretical Physics (via Statistical Mechanics) can reconstruct and understand the physical world.
- All phenomena requiring a quantum description, i.e. describable by Quantum Dynamics and its statistical treatment, still need a lot of technical work which we will not be pursued here.  
HOWEVER the path to follow has been laid down, completing the program of Theoretical Physics.
- We can now turn to dig on the statistical concepts introduced, to better see their meaning, with particular emphasis on ENTROPY.

## A useful distinction by Einstein for physical theories:

- Theory of principles: main example Thermodynamics
  - Theories which delimit but do not predict or compute
- Constructive theories, e.g. Statistical Mechanics
  - Theories proceeding from the fundamental laws (dynamics) which compute and predict

# Thermodynamics and Thermodynamic Potentials (1)

1<sup>st</sup> and 2<sup>nd</sup> principles can be resumed (for a simple one-component fluid with given  $N$ ) as

$$dS = \frac{1}{T}dE - \frac{p}{T}dV \Rightarrow S = S(E, V)$$

such that  $\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$  and  $\left(\frac{\partial S}{\partial V}\right)_E = -\frac{p}{T}$

NOTHING ELSE HAS TO BE ADDED TO KNOW COMPLETELY  
THE SYSTEM FROM THE THERMODYNAMIC POINT OF VIEW.

Every physical property of the system should be derivable from  $S$  via analytical operations.



$S = S(E, V)$  is the first THERMODYNAMIC POTENTIAL

while, e.g.  $T = T(E, V)$  or  $p = p(E, V)$  are just EQUATIONS OF STATE



## Thermodynamics and Thermodynamic Potentials (2)

1.  $S = S(E, V; N)$

and

$$\Sigma = \Sigma(E, V; N)$$

are two completely independent functions who both generate all thermodynamic properties of any mechanical system (of many particles) by analytical operations

2.  $S(E, V; N)$

is an extensive property of the system homogenous of first degree in  $N$

$$S(E, V; N) = N S(E/N, V/N; 1)$$

$$\Sigma(E, V; N)$$

grows with  $N$  as  $\mathcal{O}(e^N)$

3. They convey on different scales exactly the identical information ( $N$  is the fundamental thermodynamic/statistic parameter since everything said must be true for  $N, V \longrightarrow \infty$  with  $N/V$  constant ).



## STATISTICAL INTERPRETATION OF THERMODYNAMICS

## Probabilistic interpretation of the thermal properties

- Entropy (Boltzmann, the famous  $S = k \ln W$ )

$$S(E, V) = k_B \ln \Sigma(E, V) \equiv -k_B \ln \frac{1}{\Sigma(E, V)} = -k_B \ln \mathcal{P}_E(\Gamma)$$

- Similarly in general ensembles as we will see

$$M(T, V) = -\frac{F(T, V)}{T} = k_B \ln Q(T, V)$$

where  $Q$  generates the probability density function of the given ensemble

## Mechanical vs thermal properties

$$\begin{aligned}
 \mathcal{O} &= \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt \hat{\mathcal{O}}(\Gamma(t)) = \sum_s \mathcal{P}_s \mathcal{O}_s \stackrel{\text{mechanical property}}{=} \\
 &= \int d\Gamma \underbrace{\left( \frac{\exp[-\beta S(E)]}{0} \right)}_{\frac{\delta(H(\Gamma) - E)}{\int d\Gamma \delta(H(\Gamma) - E)}} \hat{\mathcal{O}}(\Gamma) \stackrel{\text{thermal property}}{=} \\
 &= \int d\mathcal{O}^* \mathcal{O}^* \left\{ \int d\Gamma \delta(\hat{\mathcal{O}}(\Gamma) - \mathcal{O}^*) \frac{\delta(H(\Gamma) - E)}{\int d\Gamma \delta(H(\Gamma) - E)} \right\} \stackrel{\text{probability density}}{=} \\
 &= \int d\mathcal{O}^* \mathcal{O}^* \mathcal{P}_{\hat{\mathcal{O}}}(\mathcal{O}^*) \stackrel{\text{marginal of probability density}}{=}
 \end{aligned}$$

## Free energy of collective variables

- Given a collective variable (i.e. a function of the configuration space)  $\hat{\mathcal{O}}(x)$ , the free energy associated with its probability density function is

Free energy or reversible work

$$-\frac{F_{\hat{\mathcal{O}}}(\mathcal{O}^*)}{T} = k_B \ln \mathcal{P}_{\hat{\mathcal{O}}}(\mathcal{O}^*) = \text{marginal probability density}$$

$$= k_B \ln \int d\Gamma f(\Gamma) \delta(\hat{\mathcal{O}}(x) - \mathcal{O}^*)$$

## More equivalent descriptions

$$S = S(E, V) \quad \longleftrightarrow \quad E = E(S, V)$$

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T(E, V)}, \quad \left(\frac{\partial S}{\partial V}\right)_E = -\frac{p(E, V)}{T(E, V)} \quad \left(\frac{\partial E}{\partial S}\right)_V = T(S, V), \quad \left(\frac{\partial E}{\partial V}\right)_S = -p(S, V)$$

New description

$$M(1/T, V) = -\frac{F(T, V)}{T} = S - \frac{1}{T}E \quad \longleftrightarrow \quad F(T, V) = E - TS$$

Massieu function Helmholtz free energy

$$dM = E d\left(\frac{1}{T}\right) - \frac{p}{T} dV \quad dF = -S dT - p dV$$

$$\left(\frac{\partial M}{\partial 1/T}\right)_V = E(1/T, V) \quad \left(\frac{\partial M}{\partial V}\right)_{1/T} = -p\left(\frac{1}{T}, V\right) \left(\frac{1}{T}\right) \quad \left(\frac{\partial F}{\partial T}\right)_V = -S(T, V) \quad \left(\frac{\partial F}{\partial V}\right)_T = -p(T, V)$$

or, e.g.

$$H(S, p) = E + pV \quad dH = T dS + V dp \quad \left(\frac{\partial H}{\partial S}\right)_p = T(S, p) \quad \left(\frac{\partial H}{\partial p}\right)_S = V(S, p)$$

Enthalpy

where from all this multitude ?

## Legendre Transforms (2)

Legendre transform (of a convex function) [from calculus!]:

let  $f(x_1, x_2)$  be such that

$$u_1 = \left( \frac{\partial f}{\partial x_1} \right)_{x_2} = u_1(x_1, x_2), \quad u_2 = \left( \frac{\partial f}{\partial x_2} \right)_{x_1} = u_2(x_1, x_2)$$

$$\implies df = u_1 dx_1 + u_2 dx_2 \quad \text{and} \quad x_1 = x_1(u_1, u_2), \quad x_2 = x_2(u_1, u_2)$$

$$\implies g_1(x_1, u_2) = f(x_1, x_2(x_1, u_2)) - u_2 x_2(x_1, u_2) \quad \text{since}$$

$$dg_1 = (df) - d(u_2 x_2) = (u_1 dx_1 + u_2 dx_2) - (u_2 dx_2 + x_2 du_2) = u_1 dx_1 - x_2 du_2$$

Or also:  $g_{tot}(u_1, u_2) = f - (u_1 x_1 + u_2 x_2)$

in fact,  $dg_{tot} = x_1 du_1 + x_2 du_2$

Remember not only the various thermodynamic potentials but also the correspondence Lagrangian  $\leftrightarrow$  Hamiltonian

**FUNCTIONS ASSOCIATED BY A LEGENDRE TRANSFORM REPRESENT THE SAME INFORMATION IN A DIFFERENT REPRESENTATION.**

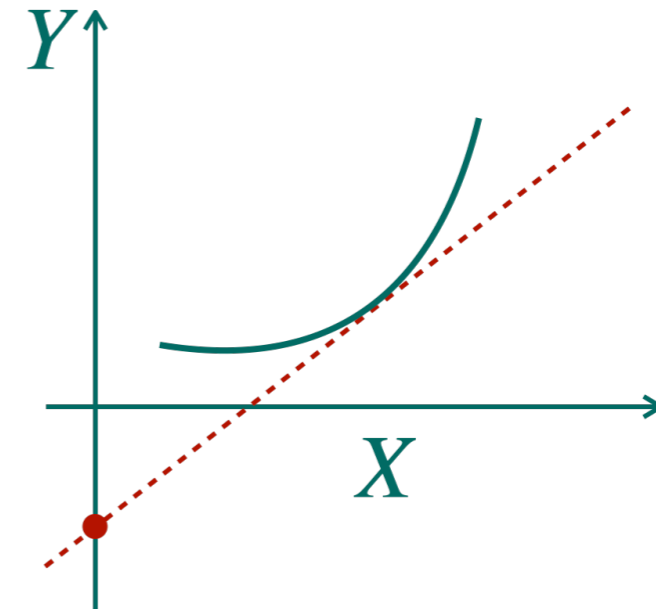
see that geometrically  $\longrightarrow$

## Legendre Transforms (3)

Legendre transform (one variable) GEOMETRICALLY

$$Y = f(X)$$

$$U = \frac{dY}{dX} = u(X)$$



Obs 1  $X = x(U) \Rightarrow Y = Y(x(U))$

with a NON-EQUIVALENT MATHEMATICAL CONTENT since to know for any  $U$ ,  $Y$  will not tell us anything on the corresponding  $X$

Obs 2 Knowing the tangent in  $X, Y$ , i.e.  $U$ , and constructing the intercept at  $X = 0$ , gives  $U = \frac{Y - G}{X - 0}$ , i.e

$$G(U) = Y - UX \equiv Y(U) - UX(U)$$

Now  $dG = -XdU$  i.e.  $\frac{dG}{dU} = -X$

The curves  $(X, Y)$  and  $(G, U)$  contain exactly the same information

## Ensembles

$$\Sigma(E) \equiv \int_V d\Gamma \delta(H - E) = \int_{H=E, V} d\Sigma(E, V)$$

geometric measure of the hypersurface  $H = E$

Hypothesis of equiprobability of the mechanical states  $(r^N, p^N)$ , i.e. points  $\Gamma$  in phase space  $\Rightarrow$  for the probability to be around  $\Gamma$  by  $d\Gamma$

$$\mathcal{P}(\Gamma, d\Gamma) = \frac{d\Sigma(E, V)}{\Sigma(E, V)} \text{ with the probability density } f(\Gamma) = \frac{1}{\Sigma(E, V)}$$

as said, THEN,  $S(E, V) = k_B \ln \Sigma(E, V)$

Ensemble

### Question:

Given the Massieu function  $M\left(\frac{1}{T}, V\right)$  and its corresponding

Canonical Ensemble  $f_c(\Gamma) \propto \exp\left\{-\frac{H}{k_B T}\right\}$

normalized by  $Q = \int d\Gamma e^{-\mathcal{H}/k_B T}$ , such that  $M\left(\frac{1}{T}, V\right) = k_B \ln Q$

WHAT IS THE RELATION BETWEEN  $Q$  and  $\Sigma$  ?



$Q$  vs  $\Sigma$  !

$$Q = \int d\Gamma e^{-\beta H} = \int_0^\infty dE e^{-\beta E} \int_{\Sigma(E,V)} d\Gamma \delta(H - E) = \int_0^\infty dE \Sigma(E, V) e^{-\beta E}$$

$\beta = \frac{1}{k_B T}$

Laplace transform of  $\Sigma$

$$Q = \text{LT}(\Sigma)$$

$S$  and  $M$ , as much as  $Q$  and  $\Sigma$ , ONE TO ONE

NB In probability  $\Sigma$  is the inverse of a probability density,  $Q$  is its CHARACTERISTIC FUNCTION, then it has the same probabilistic content than  $\Sigma$  in a possibly more suitable representation (here  $(T, V)$  against  $(S, V)$ ,  $S$  much more difficult to measure than  $T$ )

There is more: Equivalence of Ensembles ( $N$  large)  $\longrightarrow$

## Equivalence of Ensembles

$$Q = e^{M_{can}/k_B} = \int d\Gamma e^{-\beta H} = \int dE e^{-\beta E} \int d\Gamma \delta(H - E) = \int dE e^{-\beta E} \Sigma(E)$$

$$= \int dE e^{-\beta(E - TS)}$$

↗  
fixed

with  $E - TS(E, V) \sim \mathcal{O}(N)$   
⇓  
Its max dominates the integral

$$\bullet \frac{\partial}{\partial E}(E - TS) = 0 \quad \Rightarrow \quad \left( \frac{\partial S}{\partial E} \right)_V = \frac{1}{T(E, V)} = \frac{1}{T}$$

↖ fixed, canonical temperature

$$\bullet \bullet E - TS \simeq E_{mc} - TS_{mc} + \frac{1}{2} \frac{(E - E_{mc})^2}{T C_V} \quad Q = e^{-\beta(E_{mc} - TS_{mc})} \int dE e^{-\frac{1}{2} \frac{(E - E_{mc})^2}{k_B T^2 C_V}}$$

$$\Rightarrow M_{can} = M_{mc} + \frac{1}{2} k_B \ln C_V$$

$$\Downarrow$$

$$\mathcal{O}(\ln N)$$

NB:  $N \sim 10^{23}$      $\ln N \sim 23$

# A paralogism: Entropy as a measure of disorder.

From Wikipedia (En)

In thermodynamics **Entropy** is often **incorrectly** associated with the amount of order or disorder in a **thermodynamic system**.

To highlight the fact that order and disorder are commonly understood to be measured in term of entropy, below are current science encyclopedia and science definitions of entropy:

- A measure of the unavailability of a system's energy to do work; also a measure of disorder; the higher the entropy the greater the disorder. [4]
- A measure of disorder; the higher the entropy the greater the disorder. [5]
- In thermodynamics, a parameter representing the state of disorder of a system at the atomic, ionic, or molecular level; the greater the disorder the higher the entropy. [6]
- A measure of disorder in the universe or of the unavailability of the energy in a system to do work. [7]

[4] Oxford Dictionary of Science, 2005

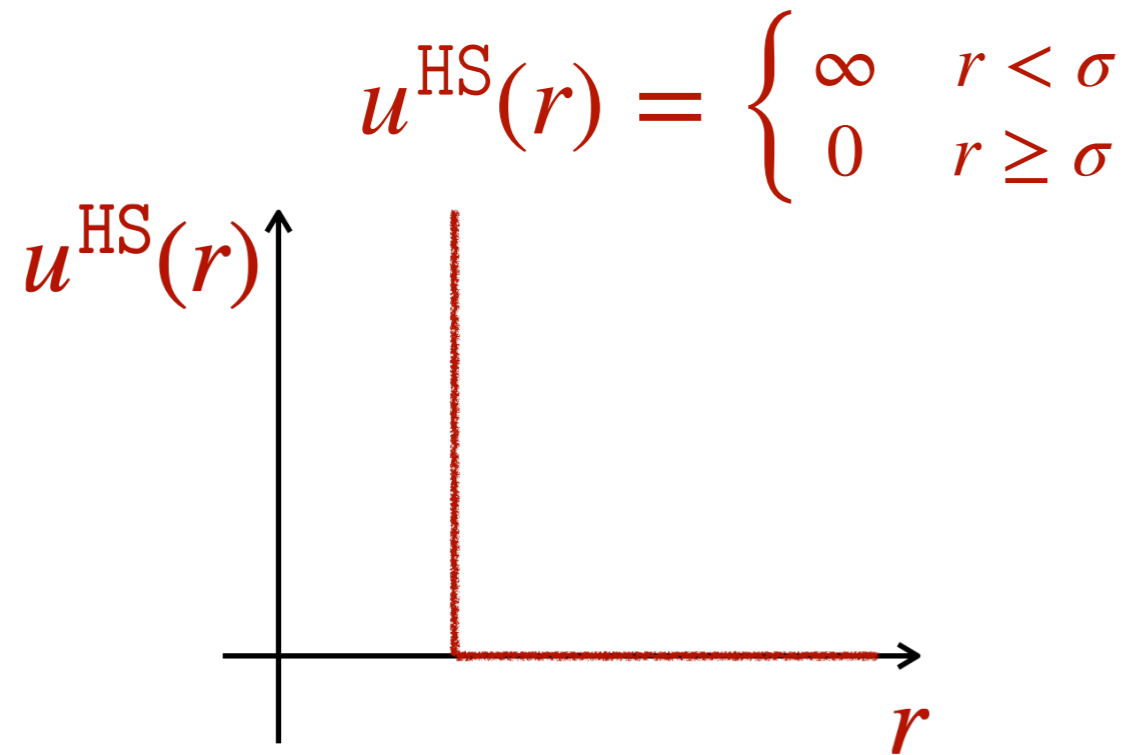
[5] Oxford Dictionary of Chemistry, 2004

[6] Barnes & Noble's *Essential Dictionary of Science*, 2004

[7] Gribbin's *Encyclopedia of Particle Physics*, 2000

Let's clarify the misconception by one (of a family of) counterexample(s):  
The spontaneous crystallization on decreasing density of hard spheres.

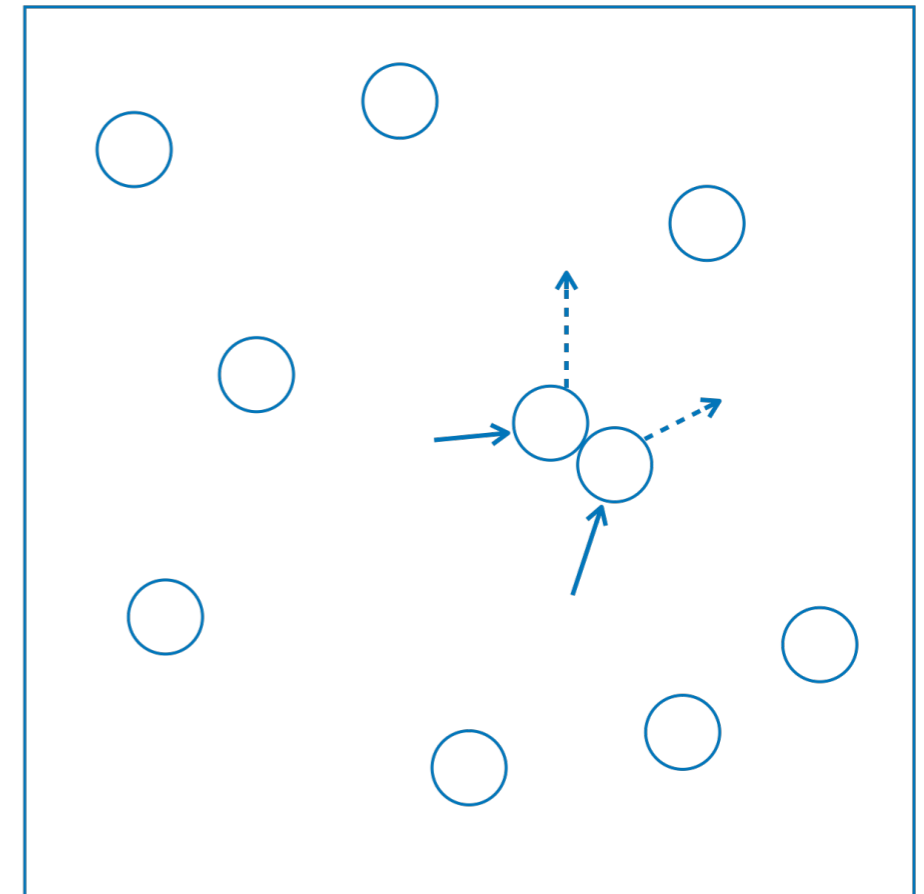
## The model



Dynamics: only binary  
elastic collision  
conserving kinetic energy

Temperature not a thermodynamic variable  
only parameter  $\rho = N / V$  better measured  
as  $\eta = \text{packing fraction}$

PBC



Event driven dynamics:  
(1) Collision times (CT)  
(2) Solution of collision  
(3) updating of CT

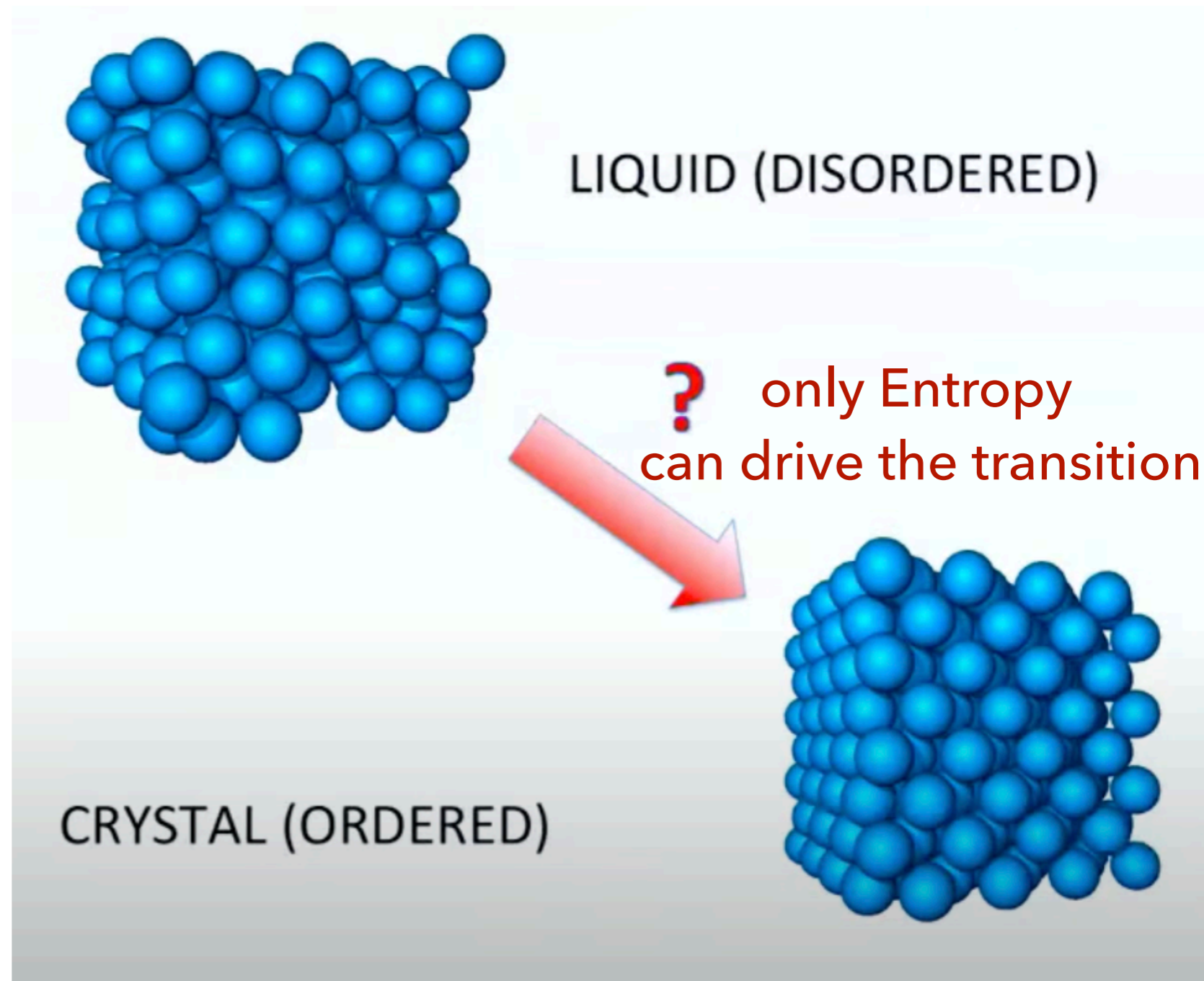
## The counterexample of hard spheres (2)

Alder & Wainwright 1957 MD  
+  
Wood & Jacobson 1957 MC

found a spontaneous crystallization  
with increasing density for a  
packing fraction  $\eta = 0.49$

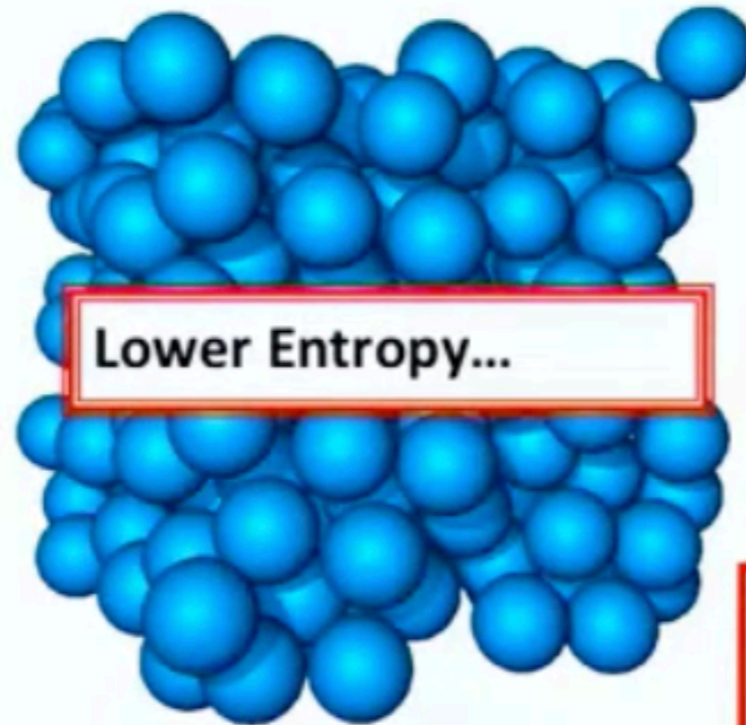
For a disordered system  
free volume = 0  $\Rightarrow \eta_{cp} = 0.64$

For an FCC crystal  $\eta_{cp} = 0.74$





# The counterexample of hard spheres (3)



Hard-sphere liquid

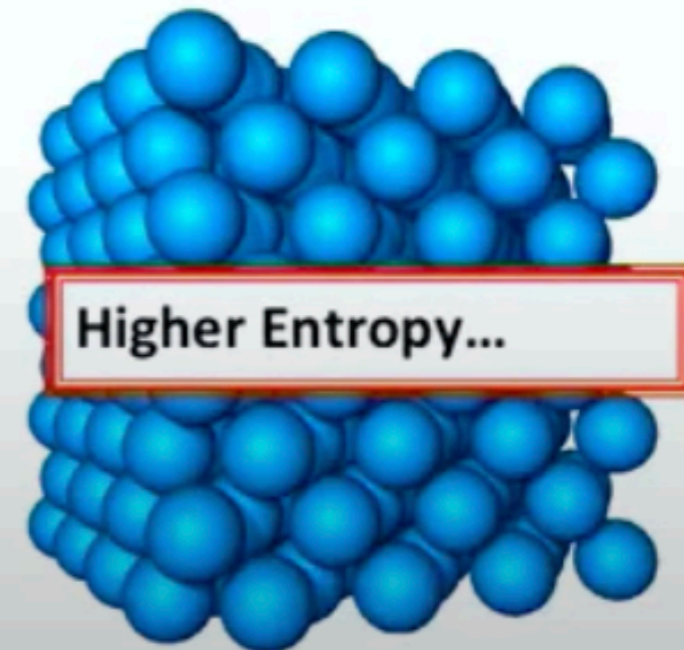
Cannot pay energy

$$M = S - \cancel{\frac{1}{T}E}$$

Experimentally

Freezing in a suspension of hard colloids is driven by entropy !

Computer simulation of hard-sphere freezing  
(Alder & Wood 1957)



Hard-sphere crystal

# The counterexample of hard spheres (3)

$$\frac{\beta p}{\rho} = 1 + \frac{2}{3} \pi \rho \sigma^3 g(\sigma)$$

$$\frac{F(\rho)}{Nk_B T} = \frac{F^{id}(\rho)}{Nk_B T} + \frac{1}{k_B T} \int_0^\rho d\rho' p(\rho')$$

$$\beta \mu(\rho) = \frac{\beta G}{N} = \frac{\beta F}{N} + \frac{\beta p}{\rho}$$

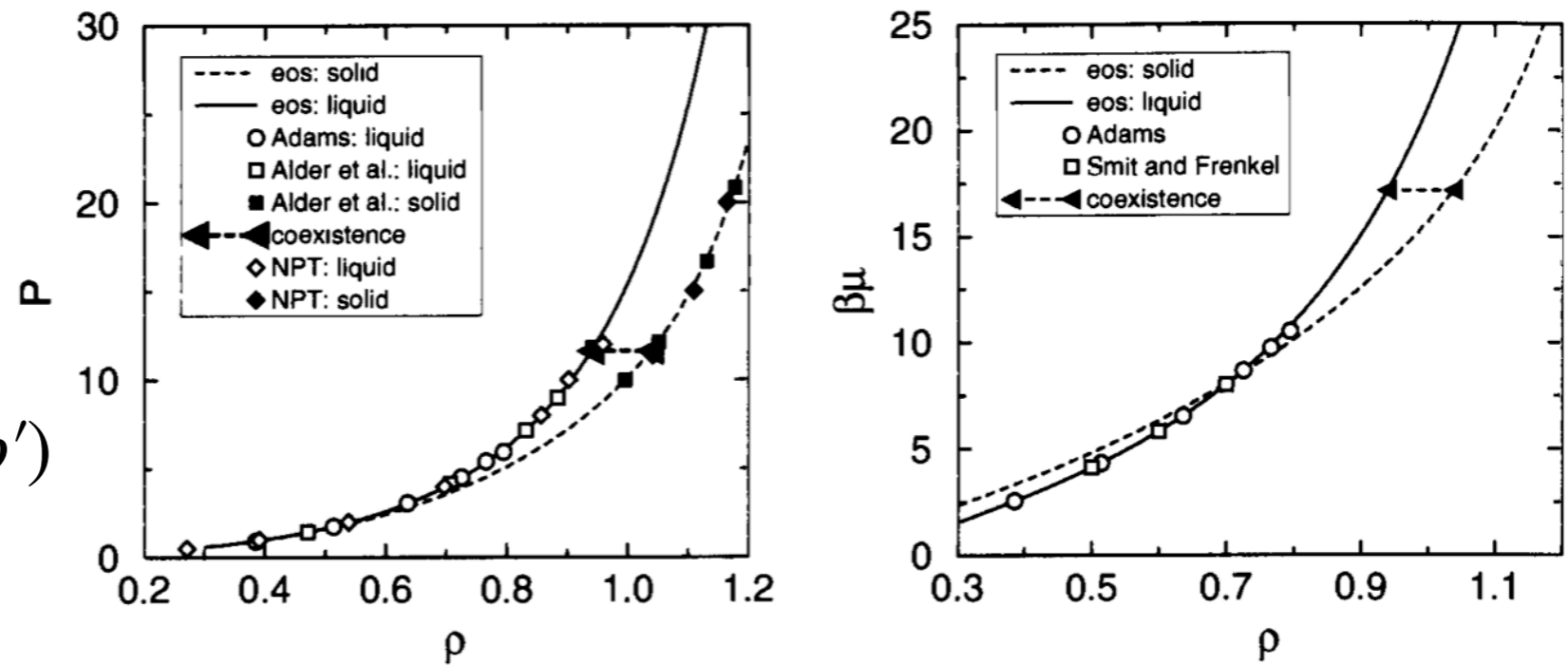
interpolation formulas  
by Speedy for

$$\left(\frac{\beta p}{\rho}\right)_{liq} \quad \& \quad \left(\frac{\beta p}{\rho}\right)_{sol}$$

J. Phys. Cond. Matt.

(a) 9, 8591 (1997)

(b) 10, 4387 (1998)



**Figure 10.2:** Pressure  $P$  (left) and chemical potential  $\mu$  (right) as a function of the density  $\rho$ . The solid curves, showing the pressure and chemical potential of the liquid phase, are obtained from the equation of state of Speedy (a). The dashed curve gives the pressure of the solid phase as calculated from the equation of state of Speedy (b). The open and filled symbols are the results of computer simulations for the liquid and solid phases, respectively. The coexistence densities are indicated with horizontal lines.

From Frenkel and Smit  
Understanding Mol. Sim. p. 256-7

- Our attempt to define aim and method of theoretical physics has been clarified
- **Specific relevant concepts such as Entropy can be clearly defined and well circumscribed**
- Possible pitfalls following abusive definitions can be avoided. A discovery that can help to appreciate what to do to proceed scientifically with confidence