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SMR/94- 2

SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

MODELLING OF LIQUIDS AND AMORPHOUS SOLIDS

(Lecture I)

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MODELLING OF LIQUIDS & AMORPHOUS SOLIDS

GENERAL SCOPE OF COURSE.

The development & use of techniques to model the structures of non-crystalline dense assemblies in the laboratory & on the computer. Stress will be given to amorphous solids & glasses where the technical problems are greatest, & examples drawn from current work on binary amorphous alloys and - if time permits - liquid water.

LECTURE 1. INTRODUCTION; IDEAL SINGLE COMPONENT ASSEMBLIES. LABORATORY MODELS.

1. CRYSTALS, GASES, & LIQUIDS: THE NATURE OF MODELS.

The nature of ideal crystal & ideal gas models; time scales & the meaning of structure.

Imperfect (real) crystals & gases as perturbations from ideality

Thermodynamics & the equation of state: to derive from a theory or a model requires evaluation of the partition function

$$Z = \sum_{\substack{\text{all}\\ \text{configurations}}} e^{-\mathcal{H}/kT}$$

where $\mathcal{H}$ the Hamiltonian. The kinetic energy terms in the Hamiltonian are independent & may be integrated out giving

$$Z = Z_K . Q$$

where Q, the configurational integral contains structural input through the potential energy $U(q_1 \to q_N)$

$$Q = \frac{1}{V^N N!} \int \cdots \int e^{-U(q_1 \to q_N)/kT} \, dq_1 \to dq_N$$

In general, a model is required to evaluate $U(q_1 \to q_N)$, be it a theoretical statement/approximation, or a set of sample coordinates which could be termed a structural model. The problems of liquids & non-crystalline solids means we normally appeal to models such as these.

2. MODELS OF GASES & CRYSTALS: APPLICABILITY TO LIQUIDS?

$Q \equiv 0$ i.e. there is no structure [illegible] REF [illegible] features

Ideal gas: instantaneous positions determined solely by statistics (no intermolecular potential & no molecular size).

→ Imperfect gas: few, weak interactions, which can be considered in terms of pairs (→ triplets & higher as density increases).

"Cluster expansion" (standard statistical mechanics & liquid texts) fails to converge as density increases. Hence not easily applicable to liquids.

Ideal crystal: unlike gas (small no weak interactions) we have large no. of strong interactions, ...

BUT we effectively know the location of every atom: described on a lattice. Hence from structure can write down $U(q_1 \to q_N)$.

→ Real (imperfect) crystal: perturbation from ideal: we know the mean position of each atom, & the problem is now of characterising the lattice vibrations.

Liquids: The problem is intermediate: | large number of strong interactions

!! Gas approximation: fails to converge for large no. of interactions (cf more sophisticated liquid state theories)

!! Crystal approximation: we cannot make because we have no crystal lattice.

SO WE LOOK TO OTHER POSSIBLE APPROACHES.

3. MODELS OF IDEAL SINGLE COMPONENT LIQUIDS.

By analogy with the *ideal crystal*, we try to construct a *model* – initially in the laboratory – of an *ideal liquid*. Real liquids may then be referred to the ideal in a similar way that real crystals relate to ~~real~~ ~~liqu~~ ideal crystals.

An *acceptable model* must be consistent with
- density
- RDF

} both available experimentally.

Early attempts.

JCP 1 (1933) (1) Bernal & Fowler: water: 1933. Relate to variable topology in silicates & ices. Too difficult at the time → simple liquids.

JCP 12, 1-18 (1944) (2) O.K. Rice 1944: suspended gelatin spheres → light scattering measurements & comparisons with liquid x-ray scattering.

(3) Bernal late 1950's work from RDF to see what looks like.

* (4) Look more at geometrical consequences of interatomic interactions

Crystal: a structure consistent with *density*, *potential function*, & *lattice*
Liquid " " *density*, *potential function*, & *no lattice*.

Ideal crystal: based on *hard spheres*: no overlap. consequences of volume exclusion. Accepted models of *close packed crystals*

TRY: Ideal liquid: based on *hard spheres*: no overlap; consequences of volume exclusion. → model of *ideal liquid*.

JDB. PRS A280, 299 (1964)

MODEL CONSTRUCTION.
(1) Pack together hard spheres.
(2) *Prevent crystallisation*
(3) Knead/vibrate to maximum density
(4) Fix
(5) Strip
(6) Measure coordinates. (7) Reconstruct ball & stick.

MAJOR RESULTS

(1) *Density* $\rho \sim 0.637$. cf $\rho_{\text{crystal close packing}} = 0.7405$.

NOTE $0.637 < \rho < 0.7405$ a prohibited region for a homogeneous assembly (except b.c.c. ~ 0.68)

cf $\Delta V_{\text{melting}} \sim 0.15$

Ⓣ (2). RDF: cf liquid looks ~ OK (but note first peak?).

Thus, this "homogeneous, coherent, & essentially irregular assemblage of molecules containing no crystalline regions" is taken as our *ideal liquid model*. This essentially simple idea is seen by Ziman (Models of Disorder, § 2.11) as "the key to any qualitative or quantitative understanding of the physics of liquids," & "supersedes various other theoretical approaches based on phenomenological constructs such as 'holes in lattice,' 'paracrystals,' 'significant structures,' 'dislocations,' ... etc"

It is a model that is "homologous to that of the crystalline solid, as well as radically different in kind, and [has] a general quality of homogeneity" (Bernal). Qualitatively, it accounts for the essential *fluidity* and *high entropy* of the liquid, & explains qualitatively the *discontinuity of state* at the melting point, together with the contrasted *continuity* with the vapour phase & the existence of a critical point.

It can be demonstrated (see later) that the simple model & a simulated liquid can be referred to each other in a simple way, effectively validating the ideal model (cf real & ideal *crystals*).

4. APPLICATIONS TO AMORPHOUS SOLIDS.

More accurate model characterisation (i.e. better measurements) reveal additional structure in RDF second peak – this will be important later. Compare what is known ~~of~~ when freeze out atomic motions from simple liquid → "glass": perhaps consider ideal RCP (random close-packed model) as an ideal zero temperature glass rather than a liquid. Note continuity of state between liquid + glass is consistent with this (though remember possible relaxations may occur → differences in detailed local structures between "glass" + "instantaneous liquid").

Experimental data on amorphous metals (?) + metal alloys: shows general agreement, but note differences in detail

SUMMARY:

CRYSTAL STRUCTURE: Consistent with density, potential function, lattice.
LIQUID/AMORPHOUS STRUCTURE: —— " —— density, potential function, no lattice.

All modelling studies concerned with realising structures consistent with these constraints, either on the computer or in the laboratory.
Note the constraints may be different quantitatively (eg. silicates where hard spheres are just not a correct approximation), but the general philosophy is still the same.