Atomic Clusters and Bulk: Implications of Voids, Especially at High Pressures

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Everybody knows that clusters (except He_n) have either polyhedral or lattice structures in their lowest states, except…

- It’s not necessarily so!
- We shall examine the behavior of simple clusters–and even bulk solids–of rare gas atoms, e.g. Ar_n, at high pressures, and see that there can be other “lowest” forms.

We must first consider glassy and liquid states

- Let’s just use Ar as our model system, but the results are general (no, not *universal*)
- First, consider conventional glassy states, metastable relative to regular, crystalline states, but possibly for *very* long times
- These are typically prepared by some kind of quenching, either vapor deposition on a cold surface or very fast cooling of liquids

What are *structures* of glasses and liquids?

- Both can be considered as mixtures of atoms and *voids.*
- What is a void? Think of it as a relaxed vacancy, originating in a lattice.
- The number of atoms in the system is conserved; the number of voids is not, and in a very disordered system, it may depend on how the counting is done.

How do liquid and glass differ, in terms of voids?

- The voids diffuse easily in a liquid, on a time scale comparable to the slower atomic modes of motion
- The voids diffuse very slowly in a glass, typically on a time scale long relative to our observation time

Voids as configurational excitations

- Warm a perfect, finite lattice and some of the atoms leave their lattice sites and go to the surface--*creating vacancies*!
- These vacancies can both diffuse and relax, so as long as their concentration is low enough that their interactions can be neglected, we can associate relaxed vacancies with configurational excitations

A glass has a higher vapor pressure than a solid, at fixed T

- The “promoted” atoms *on* the surface have fewer contacts (bonds) than those *in* the surface, so can leave with less activation energy.
- This can be demonstrated by making a cold metastable glass and warming it to a temperature at which it can relax to the crystal in an observable time

An experimental demonstration

- From A. Kouchi and T. Kuroda, 1990, Japanese Journal of Applied Physics, Part 2, **29** L807: deposit Ar at 10 K and warm, thus

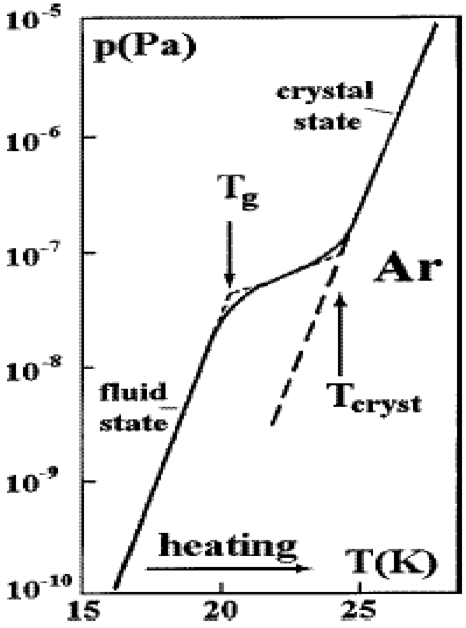
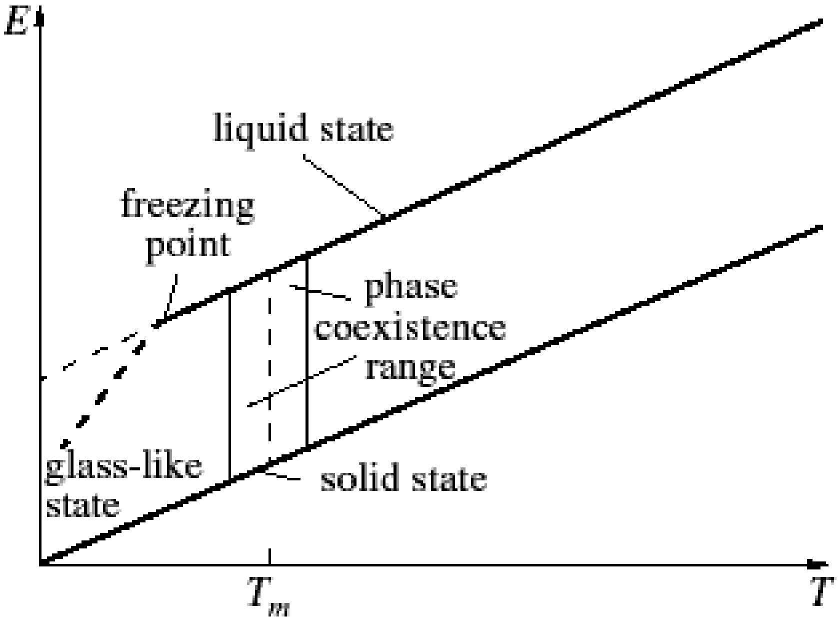


FIG. 1. The temperature dependence of the saturated vapor pressure above a heated amorphous argon formed by deposition of the argon flux on a copper substratum at the temperature 10 K (Ref. 13), and its approximation by the limiting cases (Ref. 4) referred to the glassylike and crystal argon states.

We can see this in a phase diagram for clusters

- Their small size makes it possible for two or more phases to be in equilibrium over a *band* of T and p or T and ⟨E⟩. So...



Now let’s go to high pressures!

- Consider a static pressure on a system of Ar atoms, a pressure high enough that the atoms are all pushed to the repulsive region of their pairwise interaction potentials
- But don’t fix the volume.

How do atoms really pack?

- The packing density, φ, is the number density of spheres, N, x the volume/sphere, $(4\pi/3)r^3$.
- For a close-packed system, e.g. fcc lattice, $\varphi=0.74$.
- Experiments with hard balls gives $\varphi=0.64$ and simulations give $\varphi=0.644 \pm 0.005$

How many neighbors?

- In the close-packed lattice, the coordination number *q* (= $12\varphi/\varphi_{crystal}$ = $16.2\ \varphi$) is 12, but in the *dense random packed state, q* = 10.4.
- Liquid rare gases at normal pressures have *q* = 10.1, only slightly smaller.
- Hence we infer that the "natural" packed state of solid rare gases has a structure more like that of the liquid than of the crystal.

But is this the equilibrium state?

- At atmospheric pressure, no, the close-packed crystal is obviously the stable form at temperatures below the melting point.
- But *what happens if the pressure is high, high enough that the interparticle forces are dominated by repulsions?*
- Don't go so high that the solids turn to metals, as with solid Xe above 150 *Gpa*.

We’ll see: under severe pressure,

- You can’t avoid a void!

Let’s find some free energies

- For this problem, $\Delta F = \Delta E - T\Delta S \cong \Delta G$.
- At constant p, $\Delta E = n(\Delta \ddot{U} + p\Delta V)$ where n is the number of particles and $\ddot{U}$ is the average interaction energy/atom.
- How does this change when q changes from 12 to a smaller number, say ~10?

When $pV >> T$, we can find p

- We need to know the atom-atom interaction potential, which we take as $U(R) = A/R^{\gamma}$, with $\gamma >> 1$. (Typically, ~6-8)
- Then if a is the nearest-neighbor distance, $p = 2\sqrt{2}\,\gamma\,(q/12)^2\,U(a)\,/\,a^3$, which means
- $\Delta E/n = (1 + \gamma/3)\,(U_{\mathrm{cryst}} - U_{\mathrm{random}})$ which, at fixed p,
  $= 6U(a_{cryst})(1 + \gamma/3)[1 - (12/q)^{(\gamma-3/\gamma+3)}]$

Let’s look at that:

- $\Delta E/n = 6U(a_{cryst})(1 + \gamma /3)[1 - (12/q)^{(\gamma - 3/\gamma + 3)}]$ in which everything is positive except the last term in brackets.
- Thus, if $q < 12$, the energy of the disordered state is lower than that of the crystal!
- This is a simple consequence of the dominance of the repulsive forces.

What about entropy?

- Obviously, the entropy of any disordered structure is higher than that of an ordered crystal.
- **Consequently, the free energy of the disordered state is lower than that of the crystal, for solid rare gases under pressure, at a nonzero temperature.**

And phase transitions?

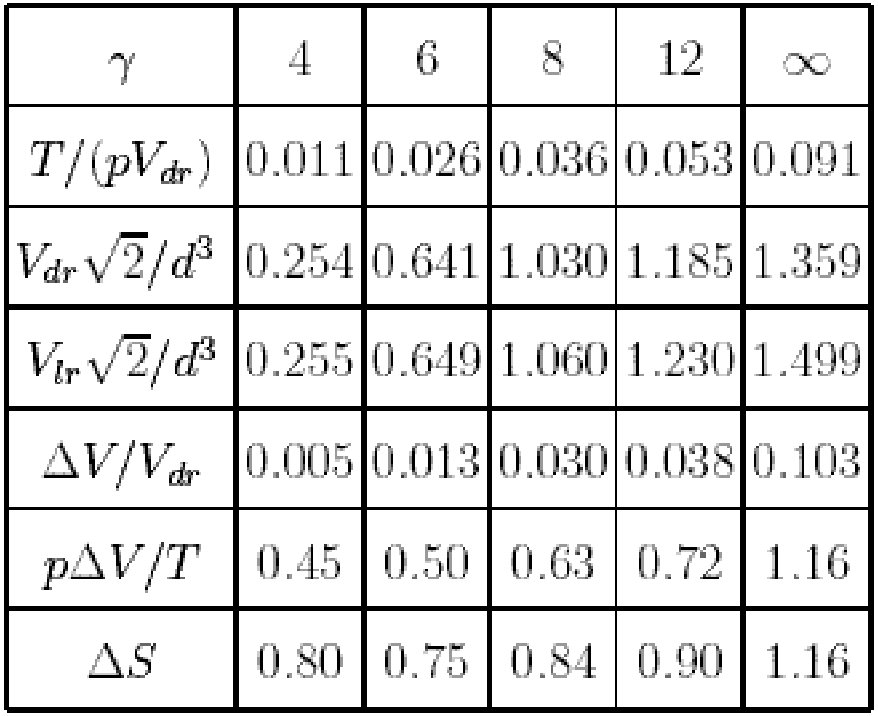
- Two kinds to consider: melting of the disordered state, and transition between a disordered solid and a crystal
- Simulations (Rintoul & Torquato) imply a loose random packed state with φ ~0.494 and a dense random packed state with φ~0.545, corresponding to 8.0 and 8.8 neighbors
- Identify: loose~liquid, dense~glassy

Identify the loose and dense random packed forms

- Suppose these both have *locally* ordered regions, but that the regions are disordered. This can give packing densities very much like those of Rintoul and Torquato
- From these densities, we get conditions for the melting of the glassy form to liquid

Some examples of conditions for the transition

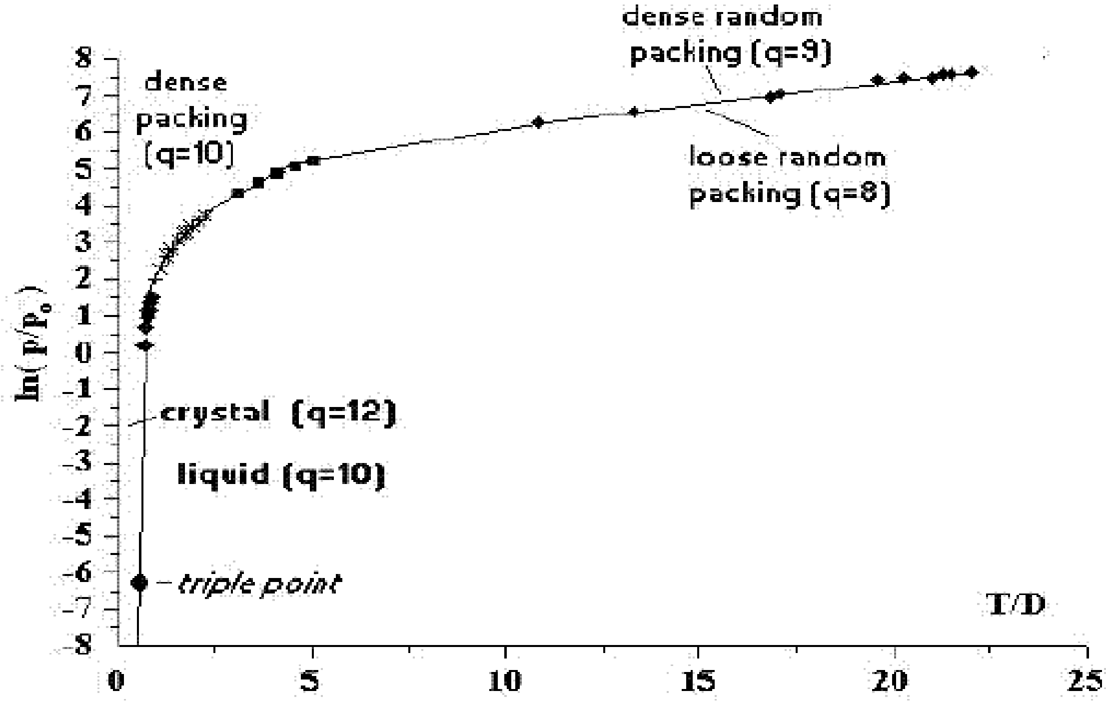
- All in terms of reduced variables, to inhibit clarity,



γ	4	6	8	12	∞
$T/(pV_{dr})$	0.011	0.026	0.036	0.053	0.091
$V_{dr}\sqrt{2}/d^3$	0.254	0.641	1.030	1.185	1.359
$V_{lr}\sqrt{2}/d^3$	0.255	0.649	1.060	1.230	1.499
$\Delta V/V_{dr}$	0.005	0.013	0.030	0.038	0.103
$p\Delta V/T$	0.45	0.50	0.63	0.72	1.16
ΔS	0.80	0.75	0.84	0.90	1.16

Easier to understand, with $dp/dT=4+a[(T/T_{tr})^k - 1]$, a,k empirical

- From experimental data and the relations here,



What is the structure?

- Nobody knows, yet. It could well be a mix of cubic (fcc) and hexagonal close-packed (hcp) clusters or microcrystals, or just disordered microcrystals
- But stacking disorders do appear about 5 *Gpa*. *Local* structure above *ca.* 70 *Gpa* is hcp, from X-ray studies.

Look at overall T-dependence

- At low T, high *p*, dense disordered solid with q~10.4.
- At T~T_{melt}, but at high *p*, q~8.8, still solid.
- At low T, low *p*, face-centered cubic crystalline, $q = 12$.
- Above T_{melt}, $q \cong 7.4$, in the normal liquid at ordinary pressures, but q depends on p in the liquid.

What kinds of phase transitions?

- There seem to be at least three kinds.
- Normal melting: crystal to liquid
- Melting of the disordered solid
- Transition between disordered solid and crystal
- Do we understand these transitions?

There are big, open questions!

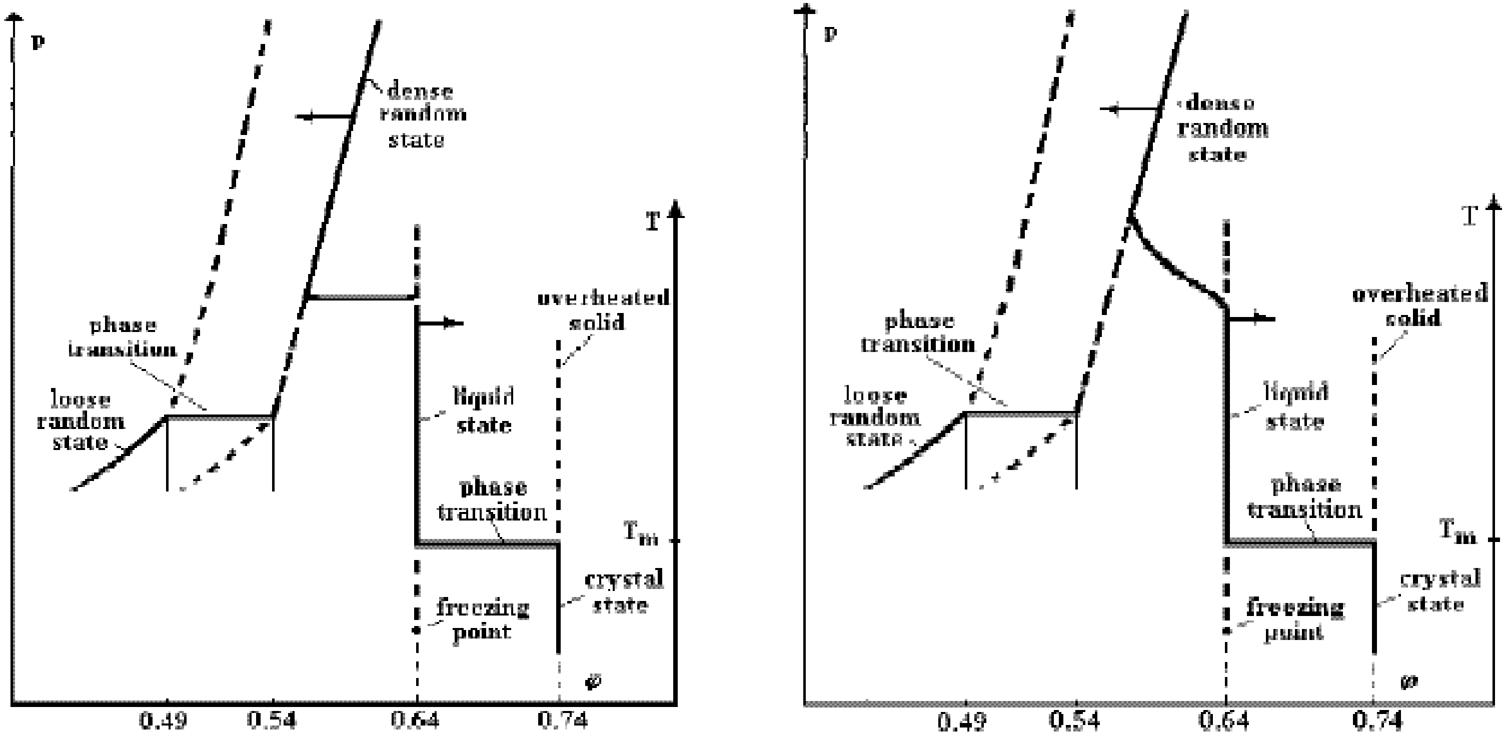
- While the crystal-to-liquid transition is a reasonably understood first-order transition,
- Neither the liquid-to-disordered solid nor the crystal- to-disordered solid is understood at present. There are several possibilities, all of which might happen.

Possible phase diagrams

- Unconventional but useful: coexistence curves as functions not of *p* and T but of *p* and φ
- The dense-to-loose transition might be first-order, or it might be second-order. Either is physically plausible, and therefore probably both cases occur.

Here are schematic examples;

(a) first-order; (b) second-order



(a)

(b)

So we conclude that…

- Crystals aren’t necessarily the thermodynamic equilibrium states of solids; somewhat or very random states can, under some conditions, be the most stable forms.
- One place we might look for these in nature is deep underground, maybe in the earth’s mantle or below.

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