DO WE UNDERSTAND HOW THE SOLIDS ARE BUILT;
ORIENTATIONAL VERSUS PERIODIC ORDER IN CONDENSED MATTER**

(INVITED PAPER)

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Recent discovery of quasicrystals have shown that the orientational order is a more fundamental phenomenon in condensed matter than the periodic one. Extensive computer simulations have revealed that the orientational order akin to that observed in quasicrystals exists, on a short length scale, also in supercooled liquids. All that added a new momentum to the development of the orientational order theories of the liquid-solid and liquid-glass phase transformations. In this lecture I shall discuss how much of the interplay between the orientational and periodic order in condensed matter is now understood and how the concept of the orientational order allows us to construct mesoscopic theories which can qualitatively account for most of the liquid-solid and liquid-glass transition properties.

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1. Introduction

How would the solid state physics looks like if the k vector was never invented and there was no Bloch theorem? I know that I am asking strange question particularly here in Jaszowiec. After all we know that solids, more precisely crystals, are periodic structures and recall that almost all textbooks on solid state theory contain the proof that the five fold rotational symmetry is prohibited in crystals because it is incompatible with the spatial periodicity [1].

Is that indeed true that the periodic translational order is the key notion in the theory of crystalline solids? In a recent textbook on crystallography [2, 3] I found the following definition of the crystal: "Crystal is a material body with regular internal structure, physically and chemically homogenous, anisotropic, having all its vectorial physical properties identical in parallel directions as well as in non-parallel directions associated with symmetries". The emphasis on periodicity is evident. Of course crystals possess also the orientional

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symmetries, which are extremely important, but the periodic translational symmetry is the “real thing”; whatever additional symmetry the system has, it must be compatible with the periodicity.

Fortunately for us nature does not depend on the textbooks. About four years ago crystals with five fold symmetry were discovered by Dan Shechtman and collaborators [4], and since then the solid state community is more willing to listen to what statistical mechanics was telling about orientational order emerging in dense and/or supercooled liquids for quite a time (since early thirties for historical record) [5]. Already in the late fifties many researchers, notably Bernal [6], were convinced that this local orientational order contains five fold symmetric structures and the icosaeder becomes a cliche word to describe those structures. Nowadays, non space-filling geometrical symmetries are generally accepted and number of papers about the quasicrystals is growing. The new man-made class of materials, shechtmanites comes to its existence [7] and we have learned a lot about the properties of matter by analyzing them. No doubt sooner or later a “real life” application for them will be found.

The key point in the Shechtman et al. discovery is emphasized in the title of their work: Metallic phase with long-range orientational order and no translational symmetry. Indeed the five fold, and the like, symmetries are incompatible with the long ranged, periodic translational symmetry. They are however fully compatible with the self-similar long range orientational order, and therefore we face the dilemma whether our picture of the crystals as periodically ordered systems is indeed more primitive than that of non-periodic self-similar structures.

In this lecture I would argue that the self-similarity is the fundamental property of the crystals and that the periodical crystals are just one possible realization of that symmetry, perhaps the most common in surrounding nature but by no means the only possible. I shall also argue that when the crystals and glasses are built then the road to that goes via attempt to form the lower energy self-similar structure first and then to go on and form periodic structure. I will also argue that the glass formation, a purely dynamical effect, can also be visualized as the phase transformation in which the formation of the globally self-similar structure is prevented by frustration leading to the system energy hypersurface akin to that known from the spin glass physics.

In order to learn something about the way the solids are built we have to study properties of fluids out of which they are formed in act of freezing. One of the major stumbling block in the development of the freezing theory is the completely different way of thinking about fluids and solids. In the latter case we automatically assume the existence of the lattice, while in the former one the conventional description in terms of distribution functions etc. leaves no space for such a notion as incipient crystalline lattice. Thus, we have to develop a theoretical method, a new language in which the pertinent questions can be asked. I shall outline a particular attempt to do so, developed in collaboration with Sushanta Dattagupta, Reiner Kree and Annette Zippelius [8].

The plan of my lecture is the following: In Section 2, I shall specify what I mean by the concept of self-similar crystal. In Section 3, I will discuss the properties of deeply supercooled liquids and argue that short ranged quasicrystalline order exists in those liquids
close to the both freezing and glassy transitions. Next, in Section 4, I shall outline a mesoscopic model for the freezing and/or glass transition and briefly summarize the results obtained from that model analysis. I shall also compare those results with the known properties of both transitions and try to make honest assessment of our theory stand. The last Section will be devoted to final comments and conclusions.

2. Self-similar versus periodic order

Self-similarity is quite common property of physical systems. By self-similarity I mean here the invariance with respect to the multiplicative changes of scale. The other seemingly more common property of physical systems is the invariance with respect to the additive changes of scale, translations. For quite a long time physicists have ignored the notion of scale invariance. (Who had ever taught physicists the \( \Pi \) theorem, one of the fundamental tools of the pre-supercoumputer hydrodynamics [9]?) All that had changed with the birth of the modern phase transformation physics. The scaling laws have become fashionable also in theoretical physics [10]. One of the most fascinating examples of self-similar structure in physics is that exhibited by chaotic systems. Here with all the regularity gone to bits what remains is the self-similarity.

For solid state physicists the notion of periodicity is connected with the fact that the Bragg spectra of crystals are periodic. But the self-similarity also induces long-range correlations which result in highly structured spectra which looks as if they were periodic. Presumably the simplest example of that is found in the number theory. Consider the set of (Kronecker’s) integers: 0, 1, 2, 3, 4, ..., represent them in binary digits and then take the parity bit of each of those numbers (i.e., the sum of its digits modulo 2). What one gets is the so called Morse–Thue sequence which reads 01101001.... This sequence can be recursively constructed by taking a block of it and appending it with its complemented subsequence.

0
01
0110
01101001
........

The Morse–Thue sequence is manifestly aperiodic, its self-similarity, however, can be easily seen by performing a “decimation” i.e., striking every second of its elements. Very similar but much more interesting from physical point of view is the Fibonacci, or rabbit, sequence. Denoting the mature pair of rabbits by 1 and young pair by 0 one obtains

0
1
10
101
10110
10110101
........

........
In the above the length of consecutive rabbit, or bit, sequences increases with ratio given by consecutive Fibonacci numbers and tends to the Golden Mean \( g = 1.618 \ldots \). Notice that, by construction this sequence is aperiodic. It possesses however a remarkable property, namely that \textit{arbitrary long subsequence} will appear \textit{infinitely often} in the full sequence (in the “thermodynamic limit” when the length of it tends to infinity). The rabbit sequence self-similarity is a bit more complex than those of the Morse-Thué sequences. The self-similar decimation here \textit{depends on} the state of the site from where one starts. If I am on the “empty” site, that is zero, then I strike the next neighbor, when on occupied site, that is 1, I strike the next nearest neighbor.

In Fig. 1 I have shown the Fourier amplitude spectrum for the Morse-Thué sequence — (a), and for the Fibonacci, or rabbit sequence — (b). For contrast with the apparent \textit{Bragg} structure of those spectra I have shown also the spectrum of the Markov (random) process having the same transition probabilities as the rabbit sequence — (c) [11].

The atomic arrangement following the Fibonacci sequence will show similar structure of the scattering function, \( S(q) \sim |n(q)|^2 \) where \( n(q) \) is the Fourier transform of the atomic density. The easiest way of constructing the \( d = 1 \) quasicrystal with the structure related to the Fibonacci sequence is the projection method shown in Fig. 2 [12]. When the channel \( \Omega \) is inclined at the angle \( \alpha \) such that the arc-tan \( \alpha = g \) then the resulting chain is a quasicrystal with the Fibonacci structure. One of the non entirely solved problems is what will be the energy spectrum for an electron moving through such a lattice [13]. That is related to the localization and conductivity in one dimensional quasiperiodic and random systems. It is not clear to me what should be the character of nonohmic behavior of the resistivity of those models. This is not purely academic point for with the MBE [14] one can manufacture layered media with perpendicular to the layer structure which is quasiperiodic [15].

The Al-Mn compounds analyzed by Shechtman et al., Al-Mn-Si or new PDS systems are not one dimensional. Question is, can one construct self-similar quasicrystals in more than one dimension. Indeed that is possible and the projection procedure analogous to those from Fig. 2 exists for constructing three dimensional icosahedral lattices. I will not go into details of that rather complicated \( d = 5, 6 \) crystallography, I will rather concentrate on simple \( d = 2 \) construction which was invented some time ago by the general relativity expert Roger Penrose [16]. In Fig. 3 I have shown one of the Penrose rugs, The Bat [17], obtained by tiling construction described in Gardner’s Scientific American article. Quite similar to the Morse-Thué or Fibonacci sequences the Bat is constructed from two elements \textit{kites and darts} and it exhibits both self-similarity and long range orientational (five-fold symmetry) order. Recall now that one of the nice features of the translational periodic solids is that, when the lattice is perfect, the traveller who goes on it has no means of telling where he is. Each neighborhood looks the same! Now, how is that in the Bat world? It turns out that “almost” as good. Suppose I use my set of darts and kites to construct a rug, and suppose someone else does this as well. How often a given subset of my rug will appear in somebody else one? The answer is: infinitely often! (That holds in the thermodynamic limit only as for the Fibonacci sequence.) The other question is, suppose I take a finite region of the rug, with the size \( R \) and call it my local village. Now I am moved to somebody else rug and put there “somewhere”. Question, how far I have to go to hit a region
like my local village. The answer is: at most $2R$! In this sense traveller moving on the rug finds itself in situation as in the good old lattice. Of course, those quasi-lattices have all sorts of bad properties. For example they have too much of the topological misfits (in the sense of entangled disclination lines) and thus have the mechanical stability impaired.

The Bragg spots on the Shechtman pictures clearly indicate the "forbidden"

Fig. 1. The Fourier amplitude spectra for (a) — the Morse–Thue sequence, (b) — the Fibonacci sequence, and (c) — the random Markov process with transition probabilities given by the rabbit sequence. After Ref. [11]
Fig. 2. Two-dimensional projection method of generating one-dimensional quasicrystal. After Ref. [12].

Fig. 3. The Penrose tile, an example of Penrose tiling. After M. Gardner, Ref. [16].
symmetries. It is then tempting to identify the structure of those crystals with the five-fold symmetric, icosahedral one. But where are the atoms in icosahedral crystals [18]? Usual experimental methods like diffuse X-ray, neutron diffraction or EXAFS give the output encoded in terms of the radial distribution function and therefore do not provide much of the information we need to perform the necessary back transform [19]. Other techniques, like field ion microscopy [20], provide valuable data on two dimensional projection of the icosahedral crystals and they are also not adequate although again they show five-fold symmetries. That question is also pertinent to other problems in solid state physics where there are reasons to suspect that local atomic arrangements are icosahedral, for example in metallic glasses. Radically different approach was recently proposed by Walter [21]. He had suggested that the crystal field splitting of atomic levels in magnetic rare-earth or actinide ions carry the unique imprint of the local icosahedral structure.

The quasicrystals have been discovered. Are they a “freak” atomic arrangements obtained by “accident” or is the nature telling us something more general? I have already mentioned that icosahedral local configurations have been discussed in connection with metallic glasses. Let me now go on and discuss, quite briefly main properties of glasses and supercooled liquids.

3. Glasses, supercooled liquids, and their local structure

It is quite difficult to define what is glass [22]. When one cools a liquid and when that liquid is sufficiently clean and the care is taken to prevent nucleation one finds that there is no problem with reaching temperatures much below the equilibrium freezing point. Clean water does not freeze at 0°C as told in most of the school books. It can be under-cooled by about thirty degrees depending on how the experiments are done [23]. Systems with soft repulsive part of the interparticle potential, for example liquid metals, can be considerably supercooled. Ga with equilibrium freezing point around 300 K can be easily supercooled down to 160 K [24]. So what happens when we are cooling liquid further down from its equilibrium freezing point? Experimental situation is shown in Fig. 4. Before we reach the point at which the liquid entropy will become less than that of solid [25] something has to happen. Either the nucleation will take over and the liquid will undergo first order phase transformation into the crystal or a new phenomenon the glass transformation does occur. But what is meant by that? The difficulty here is that the glass does not exist when one sticks to the rules of equilibrium statistical mechanics. Clearly, we need to use non-equilibrium statistical mechanics to describe glass or to modify somewhat conventional equilibrium description in order to bring in the time scale. In Fig. 5 I have shown the typical behavior of the viscosity and specific heat for a typical glass former. Now, glass is conventionally defined as the state of the system when viscosity becomes enormous \( \eta \propto 10^{12} \). Using the Stokes–Einstein relation one finds that this corresponds to the decrease of the self-diffusion \( D \) below value usually quoted for crystals [26]. When viscosity of a liquid becomes so high one expect that short wavelengths and high frequency properties of it will manifest themselves at effectively low frequencies. What is high and what is low frequency is determined by the value of the Maxwell relaxation time and the proper model
A typical glass-former

\[ \Pi = \frac{\Delta \phi \Delta K_T}{TV(\Delta x_P)^2} ; \quad \Delta \phi = t_f - t_g \]

The Prigogine-Deluy ratio

\[ \Pi > 1 \]

Fig. 4. The rudimentary phase diagram for a typical glass former. For the second order phase transformations the Prigogine-Deluy ratio equals 1, for a typical glass transformation \( \Pi > 1 \).

for a liquid close to glass transition should be the visco-elastic one [27]. On the other hand, glass exhibits truly low frequencies elastic properties and therefore has finite shear modulus even at zero frequency. Note also that the specific heat in the vicinity of the transition has a broad maximum — a bump, rather than singularity with which we are accustomed in phase transformation physics. The other thermal property important for understanding the nature of glass transition is that there is no latent heat associated with it. For this reason glass transition is frequently referred to as "second order" phase transformation.

The very important property of the "phase diagram" close to the glass transition temperature is its time dependence. By that I mean that the actual value of the \( T_g \) depends on the rate of cooling. Actually the faster the liquid is quenched the higher is \( T_g \). I have already mentioned that in order to see supercooled liquid and also glassy transition the care must be taken to prevent nucleation. Indeed the inverse rate of nucleation sets the time scale with respect to which the quench rates are measured. To see a glass we have to cool sufficiently fast to be faster than nucleation! This is extremely difficult task in laboratory, particularly with noble gases, materials close to theoretical tractable models. The situation is quite different in computer experiments. Here quench rates can be very large.
and indeed one can get glassy, or vitreous state of the Lennard Jones liquid (computer liquid Ar) or keep the not nucleated liquid argon at temperature around 15 K [28].

The general consensus between experts is then that the glass transformation is a dynamical effect caused by a dramatic change in the nature of the one-particle motion in the supercooled liquid, that motion get arrested and the self-diffusion changes from the fickean into the hopping like diffusion. This assumption was the key point in the microscopic theory of the supercooled liquids theory, suggested a decade ago by Alf Sjölander and myself [29], which has been recently expanded into a sophisticated atomistic level theory of glass transformation by Sjölander and his collaborators [30].

The main difficulty in learning more about the nature of the glass transition is that it is not clear what should be the proper language for that description. Conventionally liquid state physics is formulated in terms of objects like the pair correlation function. The first systematic theory of crystallization, proposed by John Kirkwood and Mrs Monroe [31], did just that by suitable truncation of the BBGKY hierarchy. This direction of reasoning continues up to now, and several functional density like theories, more or less distant cousins of the Kirkwood and Monroe theory, are now on the market [32]. Those theories propose scenario of freezing in which the first order phase transformation between a liquid and solid leads to emergence of a periodic density pattern. This is happening when solutions of a certain non-linear integro-differential equation bifurcate. The main difficulty
with those theories, leaving aside mathematical ones like poor convergence of functional series etc., is that they try to describe solid-crystal transition using the language proper for liquid state. In other words crystals are being calculated perturbatively out of liquids. Some of those theories are inconsistent [33], some other, notably those developed by Ramakrishnan and collaborators [34] are successful in prediction several properties of solids. The main difficulty with those theories is that the pair correlation function, \( g(r) \sim \langle n(r)n(0) \rangle \), cannot really tell us what we need to know about liquid-solid transition. In Fig. 6 I have shown, quite schematically the behavior of the function \( g(r) \) in various phases of the simple monatomic fluid together with the behavior of its Fourier transform the static structure factor \( S(q) \) [35]. The later quantity is what we can measure in scattering experiments. In Fig. 7 I have shown experimental results on pair correlation function for the Lennard Jones system obtained from computer simulations [36]. One clearly sees that the only change in \( g(r) \) below the glass transition \( T \sim 0.5 \) is the splitting of the second maximum. In Fig. 8 I have shown similar results for pair correlation functions of soft spheres liquid binary mixture [37]. The glass transitions for soft spheres happens at the value of the scaling parameter \( F^* \approx 1.5 \). Soft spheres mixtures are very interesting from the point of view of glass formation since they are not only more realistic models of glass formers but also because it is easier to control their equilibrium properties which in fact depend only on the value of the effective reduced density defined as:

\[
F^* = n^*(T^*)^{1/4}(\sigma_{s0}/\sigma_{s1})^4.
\] (3.1)

---

Fig. 6. Schematic dependence of the pair correlation function \( g(r) \) and its Fourier transform --- static structure factor \( S(q) \), for gases, liquids and solids. After Ref. [35]
Here $\rho^*$ is the reduced number density for the system equals the mean density multiply by the cube of the species interaction radius $\sigma_1^*$, and $\sigma_{eq}$ is the one-fluid van der Waals equivalent diameter [38].

Having concluded that $g(r)$ or $S(q)$ are not really useful for our problems what we can do now? Obviously one needs higher order correlation function but both experiments and theory have little to say about them. For simple cubic lattice the complete information is stored in the four particle correlation function $g_4(r_1, r_2, r_3, r_4)$. To develop a theory in which $g_4(r_1, r_2, r_3, r_4)$ will feature in its full glory is not the easiest task and so far no such a theory has been proposed. Several recent attempts to use the multipole expansion of the free energy [39] or the expansion of two point, local density-density correlation function [40] are just the first step in that direction. In the recent microscopic theory of glasses developed by the Göteborg group [41] it has been claimed that it is the non-ergodic part of the time dependent $g_4$ which contains information about the glassy transition. Again, due to the lack of the theory for $g_4$ authors of those works have to restore to a mode-mode coupling approximation. On experimental side the situation is equally unsatisfactory.

Fig. 7. The temperature dependence of the pair correlation function for the Lennard Jones liquid obtained from computer simulations. After Ref. [36]
Fig. 8. Pair correlation function $g_2(R)$ for equal proportion soft sphere mixture with $a_{22} = 1.1a_{11}$ plotted for various values of the parameter $\Gamma^*$. Solid line $\Gamma^* = 1.7$ — a glass, dashed line $\Gamma^* = 1.37$ and dotted line $\Gamma^* = 1.26$. After Ref. [37].

Pieces of $g_2$ can be estimated from the thermodynamic measurements and for some particular systems like hydrogenated transition metals $g_2$ can be measured by means of the diffuse X-ray scattering [42]. However no experiment we know can map the whole $g_2$. It is precisely at this stage that the computer enters as an invaluable tool in the analysis of the structure of liquids and glasses.

Up to now I have carefully avoided to mention what kind of materials I have in mind when I am talking about liquids and glasses. The reason for that is that theorists like to talk about something very simple, while obviously in experiments we have to do with materials which are far beyond limits of our theories. Indeed, the systems I am having in mind are classical, monotomic liquids like liquid Ar or various liquid metals for which the equilibrium structure can be well approximated either by the hard sphere liquid model (particularly good for liquid metals) or the Lennard Jones liquids. It is only recently that the binary mixtures of the soft sphere liquids have been attacked by Ray Mountain and his coworkers. These later systems are closer to realistic materials out of which the window glass is built, but still these are examples of what I would call the computer liquids and glasses. In what follows my discussion will be restricted to the computer liquids, i.e. monotomic, classical liquids with the Lennard Jones like interactions.

The Monte Carlo and molecular dynamics simulations provide us with a wealth of
data on liquid behavior and structure. As said above I shall discussed here exclusively properties of the Lennard Jones (12-6 potential) systems but similar results can be obtained by conceptually a bit simpler but numerically much more difficult hard sphere systems. Computer simulations can provide us with all the information about the higher order correlations, the limits are set by hardware, software and research budgets, not necessarily in that order of importance. Computer can provide us with all the knowledge about the local geometry of a liquid. They replace the ball bearing balls models used by Bernal [43]. In fact already in the fifties it was known that the atomic clusters (12 atoms and up) have ground state configurations which do not correspond to the crystallographic one. This fact well established for the Lennard Jones clusters is in fact much more universal. Gajda and Mostowski [44] have shown that the same ground state configurations are pertinent for ions inside the ionic trap.

For truly many body systems the local structure is frequently analyzed by means of the so called Voronoi polyhedra (the local Wigner-Seitz cells) or their dual structures the Delaunay tetrahedra [45]. Once the Voronoi polyhedra are constructed one can analyze various topological informations provided by that construction. However just paving the snapshot configurations of a liquid volume with those cells in not enough since liquids tend to flow. The geometrical constructions like the Voronoi cells become useful concepts when the mobility of constituent atoms becomes quite low and that is precisely what happens when one supercool a liquid. When the self-diffusion becomes extremely low \((D_1 \sim 10^{-7} - 10^{-9} \text{ cm}^2/\text{sec})\) liquids look liquid only when probed at sufficiently low frequencies. That implies that local atomic arrangements are very long lived and it is therefore sensible to use them as building blocks for the theoretical description. Actually one does not need to supercool liquid too much to see that the local structures are indeed long lived. Hess [46] has analyzed the local structure of a liquid above the triple point and along the melting line. His results show that the local orientational structures decays on the time scale large compared with the Maxwell relaxation time. The analysis of the local liquid structure, by means of the Voronoi cells or Delaunay tetrahedra, provides also some indirect information about the self diffusion. As argued by Kimura and Yonezawa, the flattening of the distribution function of the Delaunay tetrahedra distortion is related to the change in the free volume. The changes in the free volume are believed to be important for changes in the diffusion (viscosity) of a liquid. In Fig. 9 I have shown the results of the Voronoi cells analysis for the Lennard Jones liquid (liquid Ar) obtained by Skripov [47]. The Voronoi cells were constructed and then the histogram of cells with given number of faces and with given number of edges were assembled. The purely topological information one gets this way depends on how the cells are constructed and whether cells with "too small are of a face" are included into the statistical population or not. The rejection of the cells with "too small faces" is analogous to short-time pre-averaging of the atomic positions used in the molecular dynamics analysis. The results shown in Fig. 9 indicate that the local orientational structure in liquids exists and that it undergoes a change when liquid freezes. Theicosahedron with five fold symmetry axis become very important for analyzing the data. Very similar conclusions were obtained in much more conclusive simulations done by Nose and Yonezawa [48]. Those simulations done by means of the constant pressure algorithm
allow one also for analysis of the distortion of the Delaunay tetrahedra. For each of the tetrahedron one can calculate all the solid angles forming the tetrahedron. Denoting the $m$-th angle by $\Omega_m$, one can calculate the quantity

$$ (\Delta \Omega)^2 = \sum_{n=1}^{4} \frac{1}{8} (\Omega_m - \Omega_n)^2. $$

In Fig. 10 I have shown the plot of the average values of that quantity versus temperature for both liquid and typical glass, recall that for the Lennard Jones system the reduced temperature $T_r = k_B T/c$ where $c$ is the depth of the potential, and that the melting temperature corresponds to $T_r = 0.7$. 

Fig. 9. The histogram for the Voronoi cell analysis of the liquid Ar simulations. After Ref. [47]
The other way of analyzing the local liquid structure was proposed by Steinhardt, Nelson and Ronchetti [49]. Their method is visualized in Fig. 11. The angles defining the unit vector $\Omega$ are measured with respect to the external, laboratory coordinate frame. Having those vectors one can calculate the second and third order invariants $Q_2$ and $W_3$. (Sum over $m$ is performed in order to get rid of the reducible character of spherical harmonics). The invariants with $l = 6$ play important role since they pick up the icosahedral symmetry. The simulations for L-J liquid by Steinhardt, Nelson and Ronchetti indicated that the correlation function $\langle Q_6(r)Q_6(0)\rangle$ becomes long ranged when one cools the liquid below the triple point. Nose and Yonezawa in an extremely interesting paper [50], have combined the Voronoi cells method with that of bond structure analysis. In Fig. 12 I have shown their results obtained via the constant pressure simulation algorithm. The second and third order invariants $Q_6$ and $W_6$ have been averaged over either the bonds within a given Voronoi polyhedron (local quantities-open face dots) or over all the bonds in the sample (global quantities-full circles). Now, if the appreciable long range five-fold, icosahedral, symmetry would exists in the sample $W_6$ should be of the order $-0.17$. Locally averaged $W_6$ should be of the order $-0.04$ when there is local icosahedral structure. Results in Fig. 12 show that indeed there exists a local icosahedral structure but there is no long range icosahedral correlation. Analysis of the second order invariants $Q_6$ is also quite

\[ \langle (\Delta \Omega)^2 \rangle \sim \langle \Pi \rangle^2 \]

![Graph](image)

Fig. 10. The temperature dependence of the Delaunay tetrahedra distortion obtained from constant pressure molecular dynamics simulation of the Lennard Jones liquid. After Ref. [45]
interesting. It shows that there is a high symmetry local order in a liquid and that this order changes slightly when the liquid freezes into a fcc crystal. The range of that local order correlation increases on freezing in a manner characteristic of the the first order phase transformation. Another method of looking at the local orientational correlations in a liquid was used by Mountain and Thirumalai [51]. Those authors use the time dependent probe, the function $\phi(t)$ which describes the possibility of a bond joining two atoms undergoing local rotation. Specifically that function is given by:

$$
\phi(t) = \frac{1}{N} \sum_{i,j} \langle \cos \theta_{ij}(t) \rangle,
$$

where the average is over all central atoms, $i$ and all near neighbor atoms, $j$, as in Fig. 11, and $\theta_{ij}$ is the angle between bond $ij$ at time $t$ and the same bond at time zero. At high
Fig. 12. The temperature dependence of the averaged values of the third order ($W$) and second order ($Q$) bond orientational parameters. Local averages — open face circles, global — full dots. After Ref. [48]

Fig. 13. The time dependence of $\phi(t)$ for equal portion mixture of the soft spheres plotted for various values of the parameter $T^*$. Dash-dotted line $T^* = 0.95$, dotted line $T^* = 1.26$, dashed line $T^* = 1.37$, and solid line $T^* = 1.7$. Notice the sensitive dependence of $\phi(t)$ on supercooling. After Ref. [37]
different rules for that. One, purely metric, says: take $M_\alpha$ and try to match it to the liquid volume by deforming lattice in such a way as to minimize the function $d(\bar{x})$:

$$d(\bar{x}) = \sum_{\mathbf{r}_\alpha} \sum_{\mathbf{R}_\beta} \text{distance} \{\mathbf{r}_\alpha, R_\beta\}. \quad (4.1)$$

Here $\mathbf{r}_\alpha$ are the positions of atoms and $\mathbf{R}_\beta$ are the lattice points. The function distance might be the Euclidean distance but weighted norms rejecting some "improbable" configurations should also be tested.

Slightly more physical is the matching rule which compares the potential energies of the liquid volume with its lattice counterpart. Denote by $E_{\text{pot}}(\{\mathbf{r}_\alpha\})$ the potential energy of the liquid volume $V_\alpha$ and $E_{\text{pot}}(\{\mathbf{R}_\beta\})$ the same energy of the lattice chunk $M_\alpha$. Request now that

$$\langle [E_{\text{pot}}(\{\mathbf{r}\}) - E_{\text{pot}}(\{\mathbf{R}\})]^2 \rangle = \min, \quad (4.2)$$

where the average is now over the liquid $N$-particle distribution function. If one tries to match the whole liquid volume with the perfect lattice, then the rule, Eq. (4.2), leads to the Percus–Yevick integral equation for the pair correlation function.

Suppose now that the matching of sub-volumes have been successfully performed for all cells. We are now left with a collection of lattice “patches” $M_\alpha$ which we can “glue” together into one manifold $M$. $M$ is now locally invariant with respect to the reference lattice symmetry group $G$ but is not globally invariant with respect to the same group. In the limiting case we may visualize those local patches $M_\alpha$ as being described by our local tripods — the basis vectors for icosahedron or local Bravis lattice base.

In Fig. 15 I have sketched the above construction which is just the well known in modern differential geometry construction of a fiber bundle. Just outlined procedure is an introductory step in developing statistical differential geometry of liquids, and perhaps more generally condensed matter state. Early attempts to use similar constructions for crystals with continuous distribution of dislocation lines [54] should now be reformulated along the line of analysis proposed by Kerner for silica glasses [55]. Different approaches to the structure of glasses based on dislocation theory were suggested by Kleinert [56], Patashinskii and collaborators have also tried to develop a dislocational scenario of liquid-solid transformations [57]. In practice their theory reduces to the pure orientational order theory proposed by Patashinskii and Mitsu [58] and earlier by Hess [59].

Sushanta Dattagupta and I [60] we have proposed a variant theory of liquid-solid transition which is based on the concept of local orientational order in liquid. The basic idea in this approach is that the analysis of only orientational degrees of freedom (tripods, bond orientation coefficients etc.) is not sufficient. The local orientational degrees of freedom are in fact coupled to the remaining degrees of freedom of a liquid and that coupling is responsible for the wealth of observable phenomena. Thus the basic ingredient of our theory is the local orientational order field denoted as $A(r)$. We may think about the $A$ as being represented by our icosahedron basis vectors or as local bond orientation coefficient or Wigner rotation matrices [61]. For the sake of computational simplicity we will assume that those vectors are rigidly welded together and that the only fluctuation allowed for
them are discrete rotations and continuous displacement of their "centers". Frequently we found it convenient to think about our $A$ as being modeled by Potts variables. This, we believe captures all the essential physics.

As in all mesoscopic theories we begin with the construction of a free energy functional which in our case will be a functional of orientational fields and the rest of the degrees of freedom. Due to the assumed time scale change in the supercooled liquids we may describe those remaining degrees of freedom via the elastic displacement, or distortion, field. More correctly we should use the whole visco-elastic description for those degrees of freedom [62] but for the present purposes we will use the simpler approach. We postulate that the free energy functional for the orientational field is of the form:

$$F_A[A] = \int d\vec{R}_1 d\vec{R}_2 E(\vec{R}_1, \vec{R}_2) A(\vec{R}_1) A(\vec{R}_2),$$

(4.3)

where the coupling coefficients $E(\vec{R}_1, \vec{R}_2)$ depend on actual positions of the tripod centers.

The crucial point now is that the $A$'s are coupled to the elastic degrees of freedom. It implies that the free energy functional should contain two additional terms. One describing the pure elastic field and the second describing the coupling. There is no problem with
writing down both of them. Indeed the free elastic field free energy reads:

$$F_{\text{elastic}}[\varepsilon] = \frac{1}{2} \mathcal{C}_{ijkl} \int d\mathbf{R} e^{ij}(\mathbf{R}) e^{kl}(\mathbf{R}).$$  \hspace{1cm} (4.4)

Here $e$ denotes the deformation tensor and $\mathcal{C}$ stands for bare elastic moduli for the liquid. Strictly speaking, these are the high frequency moduli, but again due to the time scale shift in supercooled liquid they are pretty much "low" frequency moduli.

The coupling term in the free energy can also be easily written down. Indeed the presence of orientational order field induces a local stress in the liquid and that couples to the deformation field according to:

$$F_\kappa[\varepsilon, \Lambda] = \int d\mathbf{R} e^{ij}(\mathbf{R}) \sigma_{ij}^\kappa(\mathbf{R}).$$  \hspace{1cm} (4.5)

In the above the local stress field tensor is defined as [63]:

$$\sigma_{ij}^\kappa(\mathbf{R}) = \int d\mathbf{R}_1 \tilde{G}_{ij}(\mathbf{R}, \mathbf{R}_1) \Lambda(\mathbf{R}) \Lambda(\mathbf{R}_1).$$  \hspace{1cm} (4.6)

There are several ways how the above form of the local stress tensor can be derived. The crucial point is, however, that it contains coupling between neighboring cages and/or cells of the liquid and, therefore, is bilinear in $\Lambda$'s. It very well might be that the local stress tensor in the liquid should be used as a building block for constructing mesoscopic model like ours. Local stress acting on the atom $i$, can be defined as:

$$\sigma_{\text{local}}(\mathbf{r}_i) = \sum_{j \neq i} F_{ij} R_{ij} + \text{irrelevant kinetic part.}$$  \hspace{1cm} (4.7)

Notice that both distances $R_{ij}$ and forces $F_{ij}$ between $i$ and $j$ atoms are evaluated in each integration step anyway, thus the evaluation of local stress involves no additional computational hardship. The local stress tensor can now be diagonalized and the corresponding eigenvalues and eigenvectors may serve in construction of $\Lambda$'s.

The total free energy functional is now the sum of three terms given by Eq. (4.3–5). Its analysis is a rather formidable task. I shall now outline two applications referring the readers to the original papers for more details [64].

Consider first the free energy Eq. (4.3). One expects that the "pure" $\Lambda$ system should undergo first order phase transformation. From the disordered phase, where there is no preferential orientational order into a orientational order, crystalline state. Indeed this is what one can check for variety of various models of $\Lambda$'s. We may use three [65] and four state Potts model [66] or full rotation matrices [67] with essentially the same result. In Fig. 16 I have sketched the behavior of the order parameter for orientational phase transition calculated by Remler and Haymet [68]. Including the coupling to the elastic field enhanced that transition. This is analogous to the compressible Ising model situation.

The explicit form of the coupling $F_{\text{int}}$ allows to calculate various important quantities at the transition. For example we can evaluate the volume change at freezing. This turns out to be given in terms of the orientational field correlation function $C(R_1, R_2)$ jump, $C_+ - C_-$, where $+$, $-$ denotes temperatures above and below the transition.

$$\frac{\Delta V}{V} = \text{tr} \int d\mathbf{R}_1 d\mathbf{R}_2 \mathcal{S}_{ij} \tilde{G}^{ij}[C(\mathbf{R}_1, \mathbf{R}_2)_+ - C(\mathbf{R}_1, \mathbf{R}_2)_-].$$  \hspace{1cm} (4.8)
Here $S$ is the bare elastic compliance tensor (inverse of $C$) and as elsewhere the integration over $R$ involves normalizing volume factor.

Eq. (4.8) is very interesting. It shows that the volume change at freezing, one of the best known properties of the freezing is actually related to the ordering of orientational degrees of freedom. It is not the emergence of the periodic translational order, which may or may not accompany freezing which is necessary for the volume change. The ordering transition we describe here is therefore the transition from supercooled liquid into the sheetmanit rather than into the perfect, translational ordered solid.

Within the mean field theory one can evaluate the right hand side of Eq. (4.8) with the result that the volume change becomes proportional (with either sign) to the square of the order parameter jump at the transition. Similarly one can calculate the change in the specific heat [69]. Quite unexpected is the result for the change of the elastic constants at the transition. Recalling that the elastic compliance tensor $S$ is given in terms of the deformation tensor correlation function:

$$S_{\text{phys}} = \int d\vec{R}_1 d\vec{R}_2 \{\langle \epsilon_{ap}(\vec{R}_1) \epsilon_{p}(\vec{R}_2) \rangle - \langle \epsilon_{ap}(\vec{R}_1) \rangle \langle \epsilon_p(\vec{R}_2) \rangle \}$$

we conclude that $AS \sim \tilde{C}(q=0)$ and is positive. That leads to slightly counterintuitive result that elastic coefficient decreases at freezing. That however can be reconcile with intuition by recalling that $\tilde{C}$ in Eq. (4.4) are in fact the high frequency moduli of the supercooled liquid. Skripov (op. cit.) has reported computer simulations results for the elastic coefficients for supercooled Lennard Jones liquid and corresponding solid. His results are in agreement with predictions of our model. Clearly more simulations are needed to clarify that point.
The analysis so far was purely static. But obviously we should be able to treat the problem dynamically. The difficulty here is how the dynamics of orientational degrees should be handled. One possibility is to use the Glauber-like kinetic for our \( A \) using Eq. (4.3) as the Hamiltonian for the system. Here immediately difficulties arise. We have developed an approximate method of analyzing kinetics of the Potts model and have tried to see how it works in simple one-dimensional example [70]. Already here one finds important differences form the kinetics of the Ising model. Again more work is needed to develop kinetic theory of freezing via the orientational order approach and we are currently working on that.

Now what about the glass transition. As discussed in Section 3 when a supercooled liquid is cooled further down at a finite rate it will undergo a transition - a glass transition. This new — glass phase for most of the practical purposes can be viewed as an elastic solid [71]. The analysis of the glass transition within the framework of our model follows the same line of reasoning as for liquid-solid one. While in liquid orientational degrees of freedom \( A \) are uncorrelated and in solid they exhibit long range correlation, in glass we expect them to be *frozen in random orientations*. As discussed in Section 3 the stochastic freezing of the cages manifests itself in the measurable elastic properties of the glassy phase. In particular the glass should exhibit a finite zero frequency shear modulus. To describe that we have to be more specific in our choice of the \( A \)'s than previously. Here we shall represent preferred orientations of cages by \( \rho \) state Potts variables. That allows us to draw information from recent analysis of the Potts glasses [72]. The free energy functional I shall use is identical to that given by Eq. (4.3)-(4.5). Specifically, in our work [73], we use the elastic coefficients corresponding to the homogeneous, isotropic body:

\[
\bar{C}_{\mu\nu\rho} = \lambda \delta_{\mu\rho} \delta_{\nu\lambda} + \mu (\delta_{\mu\rho} \delta_{\nu\lambda} + \delta_{\mu\lambda} \delta_{\nu\rho}), \tag{4.10}
\]

where the bare Lamé coefficients are in general different from the measurable one. In particular we may assume that the bare shear modulus \( \mu \) vanishes.

If a liquid is cooled adiabatically, such that at every instant all degrees of freedom have time to equilibrate, and if we prevent nucleation into solid phase, no glass will be formed. To form a glass we have to cool at a finite rate, such that some fluctuations in the system cannot relax to equilibrium, but are *quenched* in a high temperature configuration. That calls for full non-equilibrium description. In practice, however, the cooling rates can be very small (of the order of 10^{-2}/sec) for good glass formers. We may, therefore, assume that on time scales shorter than the inverse cooling rate the equilibrium statistical mechanics description may be adequate, provided the existence of *quenched fluctuations* is taken into account. This is one of the basic ideas in the theory of spin glasses and following that philosophy I will introduce quenched fluctuations into our model. This is done assuming that direct interaction between the tripod, or cages, that is \( E \) in Eq. (4.3) as well as the local stress tensor, Eq. (4.6), have fluctuating contributions. For mathematical simplicity in explicit calculations we have chosen:

\[
E_{\mu} = \delta_{\mu}(E + \delta E),
\]

\[
G_{\mu\nu} = \delta_{\mu}(G_{\mu\nu} + \delta G_{\mu\nu}), \tag{4.11}
\]

\[
G_{\mu\nu} = \delta_{\mu}(G_{\mu\nu} + \delta G_{\mu\nu}), \tag{4.11}
\]
and consider Gaussian fluctuations only:

\[
[\delta G_{ij}(l)\delta G_{ij}(l)] = K_{ij}G_{ijkl},
\]

\[
[\delta E(i)\delta E(i)] = K_{ij}E.
\] (4.12)

In the above [...] denotes the configurational average and \( i, j \) labels the cage locations. \( K_{ij} \) is a nonrandom function of the cage separation \( [ij] \).

The variance of the quenched variable is a measure of the amount of disorder in the system and increases with cooling rate. We concentrate here on that part of the liquid phase diagram where the systematic (quenched) part of the direct tripod interaction and of the fluctuating stress tensor are small. In that region it does not matter whether the fluctuations of the Potts coupling are chosen isotropic, as in Eq. (4.12), or anisotropic. (The anisotropic part leads to different freezing temperatures for longitudinal and transverse Potts components.)

The random Potts model, without coupling to the elastic degrees of freedom, was analyzed by Gross et al. They find the transition form disordered Potts (paramagnetic) to a Potts glass phase at the temperature \( T_g = E \). As expected the averaged value of the \( \langle A \rangle \) vanishes while the glass is characterized by nonzero value of the Edwards–Anderson order parameter. Here \( \langle \ldots \rangle \) denotes the thermal average. Very interesting result is that the order of the glass transition depends on the Potts dimensionality \( p \). For \( p < 4 \) the transition is continuous, whereas for \( p > 4 \) it is a first order transition. In either case though, there is no latent heat. The specific heat is discontinuous for \( p > 4 \) at \( T_g \) and has a cusp for \( p < 4 \).

Using the replica technique we were able to show that when the random Potts model is coupled with elastic degrees of freedom the following facts hold [74]:

1. The coupling to elastic degrees does not destroy the transition. This is similar to the liquid-solid case discussed previously.

2. The glass transition temperature \( T_g = (E + 1/4 \text{tr}(GC^{ij})^2)^{1/2} \). Thus \( T_g \) depends on the variance of the quenched disorder and therefore on the quench rate. This is in agreement with experiments and computer simulations.

3. There is no latent heat for the transition and that holds for any value of \( p \).

4. The liquid state does not exists as a metastable phase in the glassy state. That means one cannot supercool a liquid below the glass transition even though by adjusting the cooling rate one can obtain the glassy phase at various temperatures. There is no Kauzmann paradox.

5. There is no macroscopic volume change at the glass transition. There are local density fluctuations but on average they vanish.

6. The elastic coefficients are enhanced at the transition. In the weak coupling limit one obtains:

\[
AC_{ij} = \frac{(p-1)G_{ij}\sigma}{k_BT} \int \frac{1}{\delta} q^2(x)dx.
\] (4.13)
where $g(\chi)$ is the Parisi function measuring the mutual overlap of many ergodic components of our glass.

If we assume that the bare elastic coefficients of our liquid, Eq. (4.10), are characterized by a vanishing shear modulus but a finite bulk modulus $B$, then the freezing of orientational degrees of freedom generates a finite shear modulus given by Eq. (4.13) with tensorial components equal to 1212. The change of the elastic constants is continuous and independent of the order of the transition. Comparing this with the experiments which show a sharp increase in values of those constants one should keep in mind that in real systems the bare shear modulus is not strictly equal to zero and that the cooling rates are finite. In any case, however, our model is the only one I am aware of, which predicts the increase in shear modulus.

5. Conclusions

Our model is certainly oversimplified. It already accounts, however, for some of the salient features of the glass transition. Its main drawback, particularly in application to liquid-solid transition is its static character. I believe that our recent heuristic analysis of the dynamics, within the combined mean field Glauber kinetics with visco-elastic theory, as well as recent results on pure Potts model dynamics allow for a real degree of optimism. We should attempt to bridge the gap with microscopic theories following analysis of the local stress correlation and try to disengage ourselves from the Potts variables model perhaps by using Haynet's expansion approach. This later point is of particular importance in analysis of the binary mixtures where the icosahedra are not the structural units one should use.

In the work we have done so far we have concentrated on properties of liquids close to the liquid-solid or liquid-glass transition points. Our model can however be used also to describe the low temperature properties of glasses. In particular the linear heat capacity behavior at low temperatures and the tunneling models can be described in terms of our orientational degrees of freedom theory. Another possible application of our model is in the field of plastic solids and orientational glasses [75]. In these substances local orientational degrees of freedom correspond to actual microscopic degrees of freedom, for example elastic dipoles associated with Br atoms substituted into the KCn matrix. The elastic interaction term, Eq. (4.4), comes from the direct interaction with the host lattice. In those materials, however, the random field effects should also be carefully examined. The other class of problems where our model may be of some use is related to the defects ordering in crystalline bodies [76]. Finally there is wealth of formal problems associated with our model. Just to mention one: how one develops the gauge field theory of glasses. Clearly there is a lot of work to be done before our mesoscopic theory will become a full fledged theory of supercooled liquid and glasses.

XVII century philosopher Pierre Gassendi said in his Sintagma Philosophicum:

"Cold produces a specific and very familiar effect on our senses; and since cold is antagonistic to heat, the atoms corresponding to it must be of a nature opposite to that of the atoms generating the feeling of warmth... Cold atoms have to be sharp angled shaped as tetrahedra and to solidify a liquid when penetrating it".
If I was following Gassendi ideas, in their slightly modernized guise, it was because I believe that this has brought us a bit closer to the main goal of solid state physics, the understanding how the solids are built.

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