

PRIMITIVE MODELS OF PATCHY COLLOIDAL PARTICLES. A REVIEW

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Received August 30, 2009

Accepted December 21, 2009

Published online March 22, 2010

It is a pleasure for me to contribute to this collection of articles in honor of Professor Ivo Nezbeda on the occasion of his 65th birthday, whose work has been seminal.

In this article I will review some recent studies of the phase behavior and of the self-assembly of patchy colloidal particles. These studies have been based on simple primitive models for colloid–colloid interactions, effectively extending to soft matter the seminal work of I. Nezbeda on associated fluids. I will discuss the possibilities offered by the study of the self-assembly of particles with limited valence in deepening our understanding of the onset of the liquid state, of the differences between gels and glasses and of the possible connection between physical and chemical gels. A review with 55 references.

Keywords: Colloids; Self-assembly; Gelation; Aggregation; Empty liquids; Wertheim theory; Flory–Stockmayer theory.

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1. INTRODUCTION

Most primitive models for atomic and molecular liquids condensate the inter-particle repulsion in a hard-core potential and the attractive interactions in an electrostatic or a square-well potential. Such models have been, and currently are, very valuable in the study of the structure and of the thermodynamic properties of several compounds^{1–4}. An ingenious choice of

the hard-core diameters and of the location and number of the “attractive sites” generates models which are able to reproduce many of the essential features of the liquid (and sometime of the crystal^{5,6}) state, despite their intrinsic simplicity. Primitive models are particularly useful, since they allow for a close comparison between theoretical predictions and numeric “exact” results. It is not a coincidence that several novel approaches to the physics of liquids (including critical phenomena and liquid–solid first-order phase transitions) are first tested against these models before being extended to more realistic continuous potentials. In several cases, accurate analytical expressions for the system free energy can be derived by first principle theories^{7,8} and can be used as bases of perturbation theories even in complicated associated liquids as water⁹. For example, one of the first model of water able to capture the tetrahedral coordination and the relevance of the directionality of the interaction has been introduced by Kolafa and Nezbeda¹⁰. The model, which builds on previous simple models mimicking the H-bond interaction^{11–13}, envisions a water molecule as a hard sphere (HS) whose surface is decorated by four short ranged “sticky” spots, arranged according to a tetrahedral geometry, two of which mimic the protons and two the lone-pairs. Following the seminal work of Nezbeda, primitive models have been proposed for several other associated liquids as well as network forming ones. Thermodynamic and structural properties of several primitive models have been studied in detail during the last 30 years^{5,10,14–16}, and these studies have become the landmarks for testing theories of association^{17–23}. Also silica, one of the most important network forming material characterized by low coordination and strong association, has been recently modeled⁶ with a primitive model which envisions a silicon atom as a hard sphere, whose surface is decorated by four sites, arranged according to a tetrahedral geometry. The oxygen atom is also modeled as a hard sphere, but with only two additional sites. Despite the crude modeling, the resulting phase diagram – which includes three solid phases, corresponding to cristobalite, quartz and coesite, a gas, a liquid and a fluid phase – compares very favorably with the experimental one^{6,24}.

Implementing event-driven molecular dynamics simulations²⁵, the dynamics of a few primitive models has also been recently investigated^{26,27}, providing new insight in the microscopic mechanism for molecular diffusion and in the long-standing issue of interplay between packing driven arrest (glass transition) and bond-driven arrest (gelation)²⁸. In this respect, the dynamic properties of simple models of patchy interactions have the potentiality to provide us with an important reference frame and may play a relevant role in deepening our understanding of the dynamic arrest in

network forming liquids. Questions concerning arrest phenomena associated to the establishment of an extensive network of long-lived bonds^{29,30} and arrest related to excluded volume effects and the dependence of the dynamic and thermodynamic features on the number and spatial location of patchy interactions can be properly addressed. On the basis of recent investigations²⁶, it has been suggested that in network forming liquids the slowing down on approaching the glass transition can be interpreted as the molecular counterpart of the gelation process in colloidal systems with limited valence. It has also been suggested that the bond–energy sets a well defined energy scale in all microscopic processes and induces an Arrhenius dependence of the T dependence of all characteristic times³¹. Limited valence gels, similarly to network forming liquids, are expected to be strong in Angell's classification³².

Primitive models are relevant not only in the study of liquids, but more generally in the study of colloidal systems, especially when the solvent properties are neglected and colloidal particles are represented as units interacting via an effective potential³³. Also in colloidal physics, despite the severe approximations, simple hard-sphere and square-well models^{34–36} have been of significant utility in deepening our understanding of the essence of the equilibrium liquid state and of the glass transition. The relevance of these models to colloidal physics is expected to grow in the near future, when the newly synthesized colloidal particles with patterns of sticky patches on their surfaces will be produced in large quantities^{37–39}. Indeed, recent developments in colloidal science are starting to provide particles with specific directional interactions⁴⁰. In the same way as sterically stabilized colloids have become the ideal experimental model for realizing the hard-sphere fluid, novel physical chemical techniques will soon make available to the community colloidal analogs of several molecular systems. A colloidal water is probably not far from being realized.

In this manuscript I discuss recent works on primitive models, inspired by Nezbeda's models for associated liquids¹⁰, designed to mimic the behavior of colloidal particles with limited valence, highlighting the most relevant results arising from these studies.

2. EMPTY LIQUIDS

Primitive models have been recently studied numerically and theoretically – via the Wertheim theory^{7,8} – to investigate the relation between the gas–liquid phase separation phenomenon and the number of inter-particle attractive interactions (bonds)⁴¹, with the aim of investigating how the liquid

phase appears. By calculating the phase diagram of hard-sphere particles whose surface is decorated by a small number of identical short-ranged square-well attraction sites (sticky spots)⁴², it has been shown that on decreasing the number of sticky sites, the critical point moves toward smaller densities and T values. When binary mixtures of particles with two and three sticky spots are considered (so that the average valence per particles can be varied continuously down to two) the critical point shifts continuously toward vanishing density, making it possible to realize equilibrium liquid states with arbitrary small density (empty liquids), a case which can not be realized via spherical potentials.

The main point raised by these studies is that attraction, by itself, is not sufficient to induce a gas–liquid phase separation at low temperatures, unless the potential offers the possibility of forming an extended set of bonded particles, i.e. of generating a branched percolating network. An interesting extension of this idea has been recently reported in refs^{43,44} for a primitive model of particles with two types of bonds (A and B), whose relative bonding free energy can be varied interpolating between different types of condensation, based on the structure of the underlying networks: linear chains, hyperbranched polymers, or dimers. In the first two cases the size of aggregates goes to infinity as the limit of infinite chains or hyperbranched polymers is approached, also yielding a vanishing critical density^{43,44}.

These studies show that liquid phases of vanishing density can be generated once small fraction of branching points are present in the system. This means that with the new generation of non-spherical sticky colloids, it should be possible to realize “empty liquids”⁴², i.e. states with temperature lower than the liquid–gas critical temperature with an arbitrarily small occupied packing fraction. This shift of the critical point in density and temperature with the number of patches indicates substantial changes in the phase diagram with branching: the reduction of the number of bonded nearest neighbours is accompanied by an enlargement of the region of stability of the liquid phase in the T –density plane. This fact could favor the establishment of homogeneous disordered materials at small density, i.e. equilibrium disordered states – in which particles are interconnected in a persistent gel network – can be reached at low T . At such low T , the bond-lifetime will become comparable to the experimental observation time.

3. GELATION AND GLASS TRANSITION

As discussed in the previous section, the study of primitive models of associating fluids have provided evidence that small valence systems are characterized by a gas–liquid coexistence whose width shrinks on decreasing valence. Note that this phenomenon is never observed if the particle–particle interaction potential has a dominant spherical component, since in this case, the region of gas–liquid phase coexistence extends, at low T , to large densities, when each particle is able to make contacts with the largest number of possible neighbors. In the case of limited valence, instead, fully-bonded states – i.e. configurations where all possible bonds in the system are formed – do not require large local densities. This has a profound consequence on the collective behavior of low-valence systems at low temperature, since in a large region of densities (larger than the density of the coexisting liquid branch) it is possible to reach low temperature states (if crystallization can be avoided) in an homogeneous condition, without encountering any phase separation. At low temperatures, a dynamic arrest phenomenon takes place even if the density of the system is rather small. Differently from the phase-separation induced glass formation⁴⁵, in small valence colloidal system it becomes possible to approach dynamic arrest continuously from equilibrium, generating a state of matter as close as possible to an ideal gel²⁸. Dynamic arrest here is induced not by packing (as it is typical of glasses) but by the formation of a long-lived network of bonds, which determine a long-lived connectivity pattern in the system. The dynamics of these system has been investigated in ref.⁴⁶

In small valence systems, beside high density arrest driven by packing, it is thus possible also to observe arrest at low densities, driven by the formation of bonds. One interesting open question concerns the interplay between these two different mechanisms of formation of disordered rigid-like structures. Recent theoretical studies⁴⁷, based on replica theory, suggest that packing is associated to a finite Kauzmann temperature T_K , while bonding is characterized by $T_K = 0$, where T_K indicates the temperature at which the entropy of the deeply supercooled liquid has only a vibrational component associated to the exploration of the configuration space of the lowest disordered ground state. Experimentally, T_K is evaluated by equating the extrapolated entropy of the glass with the entropy of the crystal, assuming – as a first approximation – that the vibrational properties of the glass and of the crystal are similar. This is consistent with the fact that the low-density fully-bonded ground-state configuration has a non-vanishing statistical weight at low T and it can even be accessed in simulations. More-

over, this would correspond to a super-Arrhenius T dependence of the viscosity for packing driven arrest and to a strong-liquid behavior for the bond driving one⁴⁸. Unfortunately, with present time computational resources, the investigation of the region of T and densities where the two mechanisms compete is not practicable and this remains an open question for future studies.

4. CONNECTIVITY PROPERTIES

Primitive models of low-valence associated liquids provide also an interesting case for studying the clustering process. Indeed, recent studies have shown that for these systems it is possible to derive a fully predictive parameter-free theory of equilibrium self-assembly by combining the Wertheim theory for associating liquids with the Flory–Stockmayer approach⁴⁹ for chemical gelation. This is possible due to the fact that often the location of the interacting sites on the particle⁵⁰ or the small valence⁵¹ favors the formation of branched loopless clusters. The reason for the formation of loopless clusters can be found in the different entropic cost of closing a loop of bonds, which becomes larger and larger on increasing the length of the chains connecting the branching points when the valence is progressively reduced.

Under these conditions, except for a small region close to the percolation locus, the associating system is properly described by mean field theory and both its thermodynamic (via the Wertheim theory^{7,8}) and its connectivity (via the Flory–Stockmayer theory) properties can be accurately modeled. When this is the case, the Wertheim theory can be used to provide accurate estimates of the density and T dependence of the number of bonds in the system and the Flory–Stockmayer theory can then be used to estimate the cluster size distributions, their moments (fraction of particles in the infinite cluster, mean cluster size) as well as the percolation locus. Moreover, extending the Flory predictions also beyond percolation (in the so-called post-gel Flory assumption), these properties can be estimated down to complete bonding. In this limit, an accurate description of the low T fully bonded network can be provided⁴⁶.

5. BONDING KINETICS

As a last example of application of primitive models applied to patchy colloids, I discuss the kinetics of formation of branched loopless structures. Numerically, this is made possible by event driven algorithms²⁵ which al-

low us to follow the entire aggregation kinetic after a temperature jump from the high temperature unassembled state to the low temperature clustered state. The mean-field nature of the aggregation process (i.e. the absence of loops of bonds in the finite size clusters) makes it possible to provide not only an accurate description of the equilibrium properties of the system, but also of their kinetics. Indeed, it has been recently shown^{50–52} that it is possible to combine the appropriate Smoluchowski rate equations, including condensation and fragmentation terms, with the thermodynamic perturbation theory of Wertheim, to provide a parameter-free description of the assembly process, even in the limit of irreversible aggregation (low T), bridging physical and chemical gelation in low-valence particle systems by properly relating aging (or curing) time with temperature.

The numerical studies^{50–52}, based on event driven dynamics, show that the formation of a branched network proceeds via a sequence of equilibrium steps, even in the deep quench limit, where the model behaves as in a irreversible (or chemical) gelation process. This means that during the kinetic of formation of the bonded structure – i.e. during the progressive increase of the number of bonds – the structure of the clustering system evolves in such a way that, at each aging (or curing) time, the cluster size distribution is identical to the one that would be found in equilibrium at a T such that the number of bonds is identical. Such mapping between equilibrium and aging properties in small valence systems makes it possible to convert aging time with an effective temperature and envisage the evolution of a chemical gel as a progressive cooling of the corresponding physical model, i.e., as a progressive path in the phase diagram of the physical model. An interesting case is offered by the possibility that during the formation of a chemical gel the corresponding thermodynamic path crosses the gas–liquid coexistence, resulting in an inhomogeneous arrested structure. The stability and structural properties of the final state of the chemical gels will be in this case connected to the thermodynamic properties and the phase diagram of the corresponding physical model. Small limited-valence colloidal systems⁵³ are thus excellent candidates for testing the analogies between equilibrium and aging properties and the connection between gel stability and colloidal gas–liquid phase separation.

We recall that the aggregation process of spherically interacting particles does not take place along a sequence of equilibrium steps, as clearly revealed by the fractal structure of the aggregates resulting from diffusion-limited or reaction-limited aggregation processes⁵⁴. Even when aggregation is not irreversible, as in the case of depletion interactions, aggregation proceeds driven by a phase-separation process⁴⁵ and the structure of the system

is not homogeneous. The small valence and the formation of loopless clusters is a pre-requisite for the possibility of establishing a mapping between time in aging and temperature in equilibrium. The other important condition for the validity of the mapping is the possibility of neglecting the diffusional component in the aggregation and fragmentation rates, i.e. the so-called chemical limit of the aggregation process⁵⁵. Note that the chemical limit is set not by the presence of an activation energy for bonding (as in the case of most aggregation processes where the barrier arises from electrostatic repulsion) but again by an entropic barrier for bonding, set by the difficulty in interacting with the right orientation to form a bond. Once more, the validity of the chemical limit is enhanced by the small valence, which makes harder to properly orient the colliding clusters for bond formation.

6. CONCLUSIONS

Primitive models continue to provide a simplified, but realistic, description of disordered systems, both of their static and dynamic properties. After the several applications in the late eighties to fluids in general and associated liquids in particular, in which Ivo Nezbeda has been one of the most active players, these models are now significantly contributing in the understanding of colloidal systems in which the hypothesis of short interaction range and limited valence are in principle realizable. Beside providing information on specific systems, these studies are providing new insights into fundamental questions on the fluid state of matter, for example on the onset of the liquid phase and on the differences/analogies between gels and glasses. Some of these studies have been discussed in this article.

I acknowledge support from ERC-226207-PATCHYCOLLOIDS. I also wish to thank my collaborators E. Bianchi, S. Corezzi, C. De Michele, F. Romano, J. Russo, P. Tartaglia, E. Zaccarelli who have contributed to the ideas discussed in this article.

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