Continuum percolation and the liquid–solid coexistence line of simple fluids.

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Abstract

We compare the percolation loci for chemical clusters with the liquid–solid transition in the temperature–density phase diagram. Chemical clusters are defined as sets of particles connected through particle-particle bonds that last for a given time $\tau$. By using molecular dynamics simulations of a Lennard–Jones system we obtain the percolation loci at different values of $\tau$ as the lines in the temperature–density plane at which the system presents a spanning cluster in 50 percent of the configurations. We find that the percolation loci for chemical clusters shifts rapidly towards high densities as $\tau$ is increased. For moderate values of $\tau$ this line coincides with the low-density branch of the liquid–solid coexistence curve. This implies that no stable chemical clusters can be found in the fluid phase. In contrast, the percolation loci for physical clusters —sets of particles that remain close together at every instant for a given period $\tau$— tends to a limiting line, as $\tau$ tends to infinity, which is far from the liquid–solid transition line.

1 Introduction

Clustering and percolation in continuum systems are concepts of great interest in many areas of physics. See for example ref. [1, 2, 3, 4, 5, 6, 7]. In a many-body disordered system, the central problem in continuum percolation consists in determining the critical density (for a given temperature) at which the system presents a cluster that spans the system volume. This, in turn, leads to the crucial question of what is a cluster. The answer to this question is many-sided. A cluster is a set of particles that can be considered as a unit separated from the rest of the system and that can manifest itself in an experiment. What we define as a cluster in a given system depends on the properties of interest. Therefore,
there is a degree of arbitrariness in the cluster definition. The main premise here is that any proposed definition allows a separation of the system into a number of disjoint sets of particles which is appropriate to describe the phenomenon under study. For example, if one intends to explain an insulator–conductor transition, and the particles of the system are the conducting objects, we should call cluster to any set of contacting particles that is not in contact with any other particle in the system \cite{4}. A good example is also found in deposited granular matter where clusters correspond to mutually stabilizing sets of particles called arches \cite{6, 7}.

The first physically sound cluster definition for a simple fluid was given by Hill \cite{8} by contrast with the mathematical clusters introduced by Mayer \cite{9}. In Hill’s theory, the concept of cluster is directly related to the idea of bonded pairs. A bonded pair is a set of two particles that are linked by some direct mechanism. Then, a cluster is defined as a set of particles such that any pair of particles in the set is connected through a path of bonded pairs. The definition of bonded pair becomes then the essential part of the theory and a number of definitions have been used. Among others, we can mention the energetic criterion and the geometric criterion for bonded pairs proposed by Hill himself \cite{8}. In the first case, two particles are considered bonded at a given time if the negative of the pair potential energy is higher than the relative kinetic energy of the pair (see for example refs. \cite{10} and \cite{11}). In the second case, two particles are bonded at a given time if they are within a distance $d$. These later geometrical clusters are referred to as Stillinger’s clusters (see for example refs. \cite{12} and \cite{13}).

In a previous paper \cite{15}, we have introduced a new definition of cluster based on Hill’s theory where the bonded pairs are defined as particles that remain within a certain distance $d$ during a time interval $\tau$. We call these clusters chemical clusters since the stability requirement on each connection remind us of a covalent bond. Note that a very similar dynamic definition was advanced previously by Bahadur and McClurg \cite{14}. In the same paper, we have also presented a different approach to cluster identification where the concept of bonded pairs is meaningless. In this case, we identify as a cluster any set of particles that remain interconnected (in the Stillinger’s sense) at every instant over a time interval $\tau$. Each particle within a given cluster may move around without forming a stable bond with any other particle whereas it stays connected to the group. We have termed these later clusters physical clusters for they exist without the presence of specific particle–particle bonds.

Some preliminary studies of the properties of chemical and physical clusters in Lennard–Jones systems where presented in ref. \cite{15}. Moreover, an integral equation theory was presented there —and later on successfully used \cite{16}— to calculate the cluster pair correlation function for chemical clusters. Also, a first theoretical attempt to treat the case of physical clusters was advanced in ref. \cite{15}. In this paper, we present the results of an exhaustive investigation of the percolation of chemical clusters for a variety of values of $\tau$. We have encountered that chemical clusters percolate at progressively higher densities as $\tau$ grows from zero. Beyond a moderate value of $\tau$, the percolation line coincides with the low-density branch of the liquid–solid coexistence curve. This represents, to our
knowledge, the first application of continuum percolation where the percolation line coincides to such degree with a coexistence line of a simple fluid. We also show that the percolation line for physical clusters, although it moves towards higher densities as $\tau$ grows, reaches a maximum density within the fluid phase beyond which the system percolates irrespective of how large is $\tau$. From these findings, we conclude that stable chemical clusters cannot exist in a simple fluid although physical cluster do exist at relatively high densities. We also point out that transient chemical clusters (by contrast with stable clusters) may help to explain differences in experiments carried out on the same system when probing different timescales.

2 Stillinger’s clusters

In a many-body system, two particles at time $t$ are considered to form a bonded pair (in the Stillinger’s sense) of proximity $d$, if they are within a distance $d$ from each other at time $t$. Then, a set of particles at time $t$ is called a Stillinger’s cluster of proximity $d$, if every particle in the set is connected through a path of pair-bonded particles and no other particle in the system is bonded to any of them. This cluster definition is a basic standpoint for the following more realistic definitions.

3 Chemical clusters

Two particles at time $t$ are considered to form a bonded pair of lifespan $\tau$ and proximity $d$, if they were within a distance $d$ from each other over the entire time interval $[t - \tau, t]$. Then, a set of particles at time $t$ is called a chemical cluster of lifespan $\tau$ and proximity $d$, if every particle in the set is connected through a path of pair-bonded particles and no other particle in the system is bonded to any of them. A chemical cluster with lifespan $\tau \gg \tau_0$ is called a stable chemical cluster. Here, $\tau_0$ means any time long enough for the cluster to be detected by an experimental setup. A chemical cluster of lifespan $\tau = 0$ and proximity $d$ corresponds to a Stillinger’s cluster of proximity $d$.

We would not normally expect to find stable chemical clusters in a simple fluid since particles do not tend to form stable particle–particle bonds. However, if we use an experimental technique able to resolve short times, we might be able to detect the presence of ephemeral (small $\tau$) chemical clusters. Moreover, if interactions are significantly stronger and dynamics significantly slower, as is the case in colloidal systems, most experiments are able to detect the existence of chemical clusters (see for example the relation between percolation of chemical clusters and the sol-gel transition [17]). Of course, chemical clusters are easily detected in true chemical bonding (e.g. polymerisation) and in strongly interacting molecules (e.g. hydrogen bonding [18]).
4 Physical clusters

Suppose that we identify a given set of particles at time \((t - \tau)\) as a Stillinger’s cluster of proximity \(d\). We then focus on this set of particles alone. As the system evolves in time, the particles of this Stillinger’s cluster approach other particles in the system, which we will disregard in our analysis. Eventually, the original Stillinger’s cluster fragments into two or more disconnected subclusters — in the Stillinger’s sense. Each of these subclusters can be now considered individually, disregarding the remaining particles in the system — even those that were part of the parent cluster and now belong to a different subcluster. Again, during the evolution, each subcluster may fragment. If we continue this analysis systematically until time \(t\) is reached \(i.e.\) over a period of time \(\tau\), each final subcluster, which is a product of numerous fragmentation events, is called a physical cluster of lifespan \(\tau\) and proximity \(d\). A physical cluster with lifespan \(\tau \gg \tau_0\) is called a stable physical cluster. Again, \(\tau_0\) represents a time long enough for the cluster to be detected by an experimental setup. A physical cluster of lifespan \(\tau = 0\) and proximity \(d\) corresponds to a Stillinger’s cluster of proximity \(d\).

We expect to find stable physical clusters in a simple fluid. In fact, any sample of liquid should correspond to a single physical cluster.

5 Molecular dynamics

The molecular dynamics (MD) simulation technique used to identify both chemical and physical clusters was introduced and described in ref. [15]. This technique is a slight modification of a standard \(NVT\) MD simulation \([19]\) where bonded pairs (for chemical cluster) and entire Stillinger’s clusters (for physical clusters) are tracked down along a time interval of length \(\tau\). We report results for a Lennard–Jones system, \(i.e.\) particles that interact through

\[ v(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]. \]  \(1\)

Quantities are then expressed in Lennard–Jones reduced units in the rest of the paper: \(\sigma\) for length, \(\sigma\sqrt{m/\varepsilon}\) for time, and \(\varepsilon\) for energy. Quantities in reduced units are indicated with an asterisk.

The results that we present in the following section are based on a leapfrog MD simulation of 500 particles in a cubic box with periodic boundary conditions. A cut-off distance equal to \(2.7\sigma\) was used in the Lennard–Jones pair potential. We have set the proximity value to \(d^* = 1.5\). This value was chosen because it corresponds roughly to the maximum distance at which two Lennard–Jones particles attract most strongly. Besides, at \(d^* = 1.5\) lies the boundary between the first and the second neighbour shell in the supercooled liquid state \([20]\). This can be considered the maximum distance for which a particle should be considered directly connected from a geometrical point of view.
Figure 1: Temperature–density phase diagram for the Lennard–Jones fluid and percolation loci for chemical clusters. Solid squares (with trend line) correspond to the coexistence curve for gas–liquid and liquid–solid transition. Open symbols (with dotted trend line) correspond to the percolation loci for chemical clusters with proximity $d^* = 1.5$ and lifespan $\tau^* = 0$ (circles), 0.5 (pentagons), 1.0 (squares), 5.0 (diamonds), 8.0 (down triangles), and 10.0 (up triangles).

In most cases, quantities are averaged over $10^3$ configurations generated after stabilization. A few simulations performed with 4000 particles yielded results indistinguishable from those obtained with the 500-particle-system. A system is said to be in a percolated state if a cluster that spans the periodic replicas is present 50 percent of the time [21]. Then, a percolation transition curve (the percolation loci), which separates the percolated and the non-percolated states of the system, can be drawn above the gas–liquid coexistence curve in the $T - \rho$ phase diagram.

6 Results

In fig. 1 we show the phase diagram of the Lennard–Jones fluid in the $T - \rho$ plane. The gas–liquid coexistence curve corresponds to the Gibbs ensemble Monte Carlo (MC) simulation results from Panagiotopoulos [22] and the liquid–solid coexistence line corresponds to the MC calculations of Hansen and Verlet [23]. The percolation line for chemical clusters of proximity $d^* = 1.5$ and lifespan $\tau^* = 0, 0.5, 1, 5, 8$ and 10 are also shown in fig. 1. The special case with $\tau^* = 0$ corresponds to instantaneous Stillinger's clusters. As we can see, the percolation line shifts towards high values of $\rho$ as $\tau$ is increased. This is to be expected in a simple liquid because, for a given temperature, the density needs to be increased.
Figure 2: Temperature-density phase diagram for the Lennard–Jones fluid and percolation loci for physical clusters. Solid squares (with trend line) correspond to the coexistence curve for gas–liquid and liquid–solid transition. Open symbols (with dotted trend line) correspond to the percolation loci for physical clusters with proximity $d^* = 1.5$ and lifespan $\tau^* = 0$ (circles), 1 (pentagons), 5 (squares), 10 (diamonds), 100 (down triangles), 1000 (up triangles). The solid vertical line corresponds to the critical density $\rho_f$ (see text).

in order to promote caging and so extend the lifespan of particle–particle bonds.

Interestingly, for $\tau^* \gtrsim 8.0$ we find that the percolation line coincides with the liquid branch of the liquid–solid transition curve. Rigorously speaking, if $\tau^* \gtrsim 8$, any state of the system to the left of the liquid–solid coexistence line is non-percolated whereas any state in the solid side of the phase diagram is percolated. The reason for this resides in the fact that simple liquids have to make a transition to a crystalline state in order to generate long-lasting particle–particle bonds. In a crystalline state the neighbours of each particle remain the same for extremely long periods of time. Of course, a similar effect can be achieved in a glassy state, but we are only concerned with equilibrium states here. From this result we can say that stable ($\tau \gg \tau_0$) chemical cluster do not exist in the fluid phase of a simple liquid. It is worth mentioning that using different values of $d$ (at least in the range $1.25 < d^* < 2.0$) shifts all the percolation curves but they still converge to the liquid–solid transition line for large $\tau$. Larger values of $d$ requires larger values of $\tau$ to achieve convergence.

Our findings on the properties of the chemical cluster percolation line for large $\tau$ suggests that we could use this analysis to predict the liquid–solid transition line using a relatively simple simulation technique and the appropriate cluster identification criterion. Previously, much effort have been made to find a match between percolation and the gas–liquid transition, especially in the
two-state magnetic lattice model of a fluid [24]. This studies have been unsuccessful so far, which can be appreciated in the type of device (ghost spin) needed to prevent inconsistencies in the theory [24]. As we can see, chemical clusters are a more realistic definition of clusters and shows that the percolation line should describe the liquid–solid transition rather than the gas–liquid transition. Whether there exists a suitable definition of cluster that yields a match between percolation and gas–liquid transition is still unresolved.

For the sake of completeness, the percolation behaviour of physical clusters is shown in fig. 2. In contrast with chemical clusters, physical clusters percolate at moderate densities (far from the liquid–solid transition) even at very large values of $\tau$ ($\tau^* \simeq 10^3$). In fact, the percolation curve seems to converge to a limiting line beyond which the system is always percolated no matter how large is $\tau$. This suggest that there exist a critical density $\rho_f$ ($\rho_f^* \simeq 0.573$) in the supercritical phase above which physical clusters percolates irrespective of the temperature and the required lifespan [25]. This line is sketched in fig. 2, and it can be thought of as a dividing line between a gas-like phase (to the left of $\rho_f$) and a liquid-like phase (to the right of $\rho_f$). Within the gas-like phase, physical clusters percolate only at finite lifespan. In the liquid-like phase physical clusters always percolate the system. Within the liquid-like phase — except in a small neighbourhood around $\rho_f$ — nearly all particles in the system remain interconnected in a single large physical cluster, i.e., no fragmentation takes places within any finite time interval.

The main objection we have to this separation into liquid-like and gas-like regions of the supercritical phase is that states that we would normally assign to a liquid reside in the gas-like side of the phase diagram. The density $\rho_f$ is certainly higher than the thermodynamic critical density $\rho_c$. All the states comprised between the gas–liquid coexistence curve, the vertical line that passes through $\rho_f$ and the horizontal line that passes through $T_c$ (the thermodynamic critical temperature) are in a liquid state. According to our physical cluster properties, however, they should be in a gas-like state. Interestingly, a different separation of the supercritical phase proposed by Fisher and Widom [26] does also meet the gas–liquid coexistence line at a density above $\rho_c$ [27]. However, the Fisher–Widom line does not coincide with the dividing line we present here.

7 Conclusions

In this work, we have shown that chemical clusters and physical clusters defined in ref. [15] have very different behaviour at large lifespan. In particular, chemical clusters present a percolation curve that coincides with the low-density branch of the liquid–solid transition curve for any $\tau$ beyond a moderate value. Physical clusters, in contrast, present a percolation curve that converges to a vertical line in the $T - \rho$ plane located at moderate densities when $\tau$ tends to infinity.

The percolation properties of chemical clusters suggest that we can predict the liquid–solid transition in a simple fluid by calculating the percolation line at moderate lifespan values. An integral equation theory for chemical clusters has
been developed previously [15, 28]. Moreover, a numerical technique has been used recently [16] to solve the equations, but only at small values of $\tau$. This technique may allow us to predict the position of the liquid–solid coexistence line without the need of free energy calculations by setting $\tau$ to larger values ($\tau^* \gtrsim 8.0$).

It is important to notice that it is not possible to find stable (long lifespan) chemical clusters in the fluid phase of a simple fluid. As soon as we exceed a moderate value of $\tau$ we require the system to crystallise in order to find chemical clusters of lifespan $\tau$. This finding seems rather intuitive; however, until now, percolation models were not consistent with this picture.

For small values of $\tau$, we find a family of percolation curves for chemical clusters ranging from the classical instantaneous (Stillinger’s) cluster percolation up to the liquid–solid transition. Each of these percolations curves may be observable as viscoelastic sol–gel-like transitions measured at different shear frequencies [17]. Indeed, working at very high shear frequencies will result in a sol–gel transition line at relatively low densities. High frequencies probe short timescales and any ephemeral (small $\tau$) stress-bearing percolating cluster will develop a dominating elastic response in the system. Conversely, working at very low frequencies will result in a sol–gel transition line at relatively high densities. Low frequencies probe long timescales and the particle–particle bonds have to last long enough (large $\tau$) for any percolating cluster to develop a dominating elastic response.

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