

# Percolation line of stable clusters in supercritical fluids

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We predict that self-bound clusters of particles exist in the supercritical phase of simple fluids. These clusters, whose internal temperature is lower than the global temperature of the system, define a percolation line that starts at the critical point. This line should be physically observable. Possible experiments showing the validity of these predictions are discussed.

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Recent studies [1] of the supercritical phase of fluids reveal new and unexpected phenomena that concern a variety of domains, ranging from fundamental problems in cluster physics [2] to industrial applications [3]. A question relevant to many of these domains is the possible existence of clusters of particles. We predict in this Letter that self-bound clusters of particles exist in the supercritical phase of simple fluids and that these clusters define a physically observable percolation line that starts at the critical point.

Clusters of particles in the supercritical phase have been considered in the past, mainly from a theoretical point of view [4,5]. However, these clusters are mathematical objects, introduced to match the percolation threshold with the thermodynamical critical point. Furthermore, any critical percolation line defined by these clusters has been considered as unphysical and efforts have been made to eliminate them by a proper redefinition of the clusters [6,7].

The results presented here are based on extensive numerical calculations [8] of the cluster size distributions obtained from canonical Monte Carlo and microcanonical Molecular Dynamics simulations of systems of  $N \leq 11664$  particles which interact through the Lennard-Jones potential:  $V(r_{ij}) = 4\epsilon[(r_0/r_{ij})^{12} - (r_0/r_{ij})^6]$ . The cutoff distance of the potential is fixed at  $3r_0$  and particles are confined in a cubic box with periodic boundary conditions. The phase diagram of this fluid is represented in figure 1 [9,10]. This phase diagram as well as the results we will show below are insensitive to this particular choice of the potential and can be considered generic for simple fluids.

We assume that the system is at equilibrium when mean potential (kinetic) energy reaches a stable value in the canonical (microcanonical) ensemble. In the latter we take 2/3 of the mean kinetic energy as a measure of the temperature of the system.

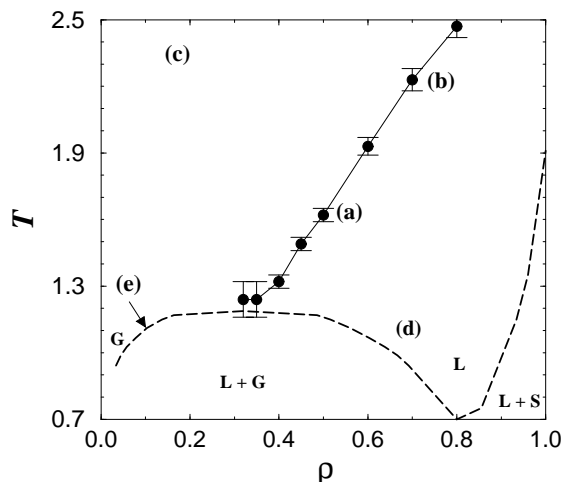


FIG. 1. Phase diagram of the Lennard-Jones fluid. The dashed line indicates the boundaries of the gas (G), liquid (L) and solid phases (S) [9,10]. The continuous line (main purpose of this Letter) is the critical percolation line calculated with the condition of stability of clusters. Temperature  $T$  and density  $\rho$  are in units of  $\epsilon$  and  $r_0^{-3}$  respectively.

The cluster size distributions are calculated once thermal equilibrium is reached. Physical clusters are defined according to a prescription proposed by Hill [11]: At a given time, two particles are linked if their potential energy exceeds their relative kinetic energy. A set of linked particles forms a cluster. We have checked that using this procedure, for equilibrium configurations, most clusters are stable by particle emission, namely the kinetic energy of each particle relative to the center of mass of the cluster is less than the sum of the potential energies due to the other particles of the cluster.

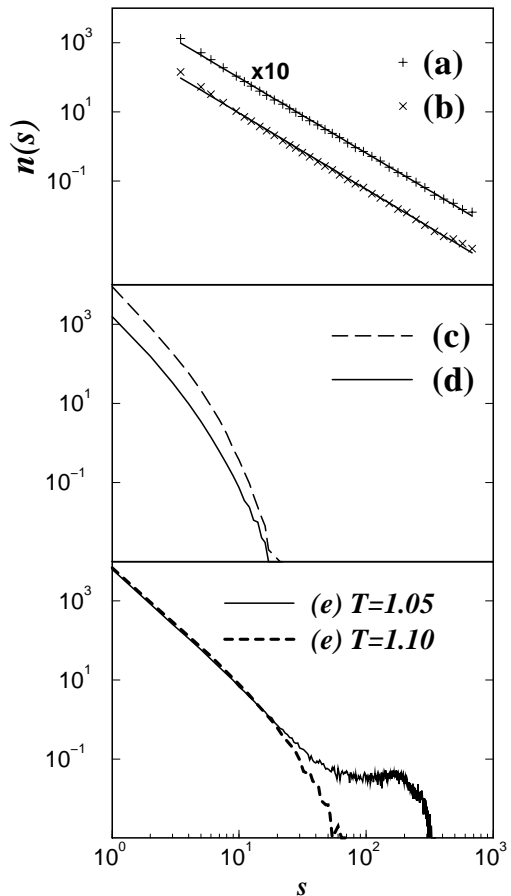


FIG. 2. Cluster size distributions  $n(s)$  at points (a)-(b), (c)-(d) and (e) of the phase diagram of figure 1. For curve (d), the contribution of the largest cluster  $S_{max}$  is sharply peaked beyond the boundaries of the figure.

The mean cluster size distributions  $n(s)$  ( $s = 1, 2, \dots, N$ ) calculated at the points (a, b, c, d, e) of the phase diagram are displayed in figure 2. One remarks

that at points (a) and (b) the distributions can be fitted (for  $s > 3$ ) by the same power law distribution  $n(s) \sim s^{-\tau}$  with  $\tau = 2.20 \pm 0.05$ . In fact, the same power law behavior is found along the full line of figure 1. This line  $T_p(\rho)$  is defined as the locus of points where  $m_2$  reaches its maximum value [12]. The  $m_k$  are the usual moments of  $n'(s)$  [7], where  $n'(s)$  is the distribution of finite size clusters, excluding the largest one. We find that to the right of this line there exists a percolating cluster. Its size  $S_{max}/N$  vanishes as  $(T_p(\rho) - T)^\beta$ . In the vicinity of that line the moments behave as  $m_2 \sim |T - T_p(\rho)|^{-\gamma}$  and  $m_3/m_2 \sim |T - T_p(\rho)|^{-1/\sigma}$ . The values we find for these exponents are in agreement with those of random percolation theory (see table 1.) A more rigorous determination of the ratios of critical exponents can be made using finite size scaling relations. As a function of the size  $N$  of the system, one expects just on the critical line the behaviors:  $S_{max} \sim N^{1-\beta/3\nu}$ ,  $m_2 \sim N^{\gamma/3\nu}$ ,  $m_3/m_2 \sim N^{1/3\sigma\nu}$ ,  $\langle S_{max}^2 \rangle - \langle S_{max} \rangle^2 \sim N^{1+\gamma/3\nu}$  [13], where  $\nu$  is the critical exponent associated to the two-point correlation function [7]. These quantities, corresponding to point (b) of the phase diagram, are displayed as a function of  $N$  in figure 3. One observes that beyond  $N \approx 50$  the expected power law behavior is very well satisfied. The values we find for the ratios of critical exponents are also in good agreement with those of random percolation (table 1.). We get the same agreement at other points of the line. These results strongly suggest that *clusters of self-bound sets of particles define a critical percolation line (CPL), characterized by the universal exponents of random percolation*. In addition, the present numerical calculations show that, within the uncertainties inherent to the finite size of the system and to the critical slowing down, this percolation curve ends at the (thermodynamical) critical point  $(T_c, \rho_c)$ . Just at this point, for the same technical reasons, we are unable to calculate accurately the corresponding critical exponents. Extrapolating the exact results of Kasteleyn-Fortuin [14] and Coniglio-Klein for the lattice gas model [4], one expects to get at the (thermodynamical) critical point (and only at this point) the critical exponents of the Ising model.

	Percolation	Present Work
$\beta$	0.41	$0.4 \pm .1$
$\gamma$	1.80	$1.6 \pm .3$
$\sigma$	0.45	$0.44 \pm .05$
$\tau$	2.18	$2.20 \pm .05$
$\beta/\nu$	0.47	$0.48 \pm .02$
$\gamma/\nu$	2.05	$2.0 \pm .05$
$1/\sigma\nu$	2.53	$2.60 \pm .05$

TABLE I. *Critical exponents associated with the cluster size distributions, in 3d Random Percolation [7] and present work.*

At  $\rho < \rho_c$  or  $T < T_c$  we do not see any signal of critical (percolation) behavior. The distribution  $n(s)$  decreases much faster than  $s^{-2.2}$  and clearly deviates from a power law form. However, a “macroscopic” cluster appears as soon as one penetrates into the two-phase region. This is clearly seen in figure 2, where we plot two distributions  $n(s)$  around point (e) of the phase diagram, with temperatures of  $T = 1.10$  and  $T = 1.05$ , just above and below the liquid-gas coexistence curve. This sharp signal corresponds very well to the crossing of the coexistence curve. Indeed, small change in  $T$  induces a drastic change in  $n(s)$  for large  $s$  [15].

We have checked that all the above findings do not depend on the specific definition of stable clusters: Using two different definitions, [16,17], both based on minimization procedures of the interaction energy between different clusters, we get cluster distributions that are almost identical [18].

It is interesting to emphasize that the CPL, characterized by the critical exponents of random percolation, is found, on a deterministic dynamical framework, *without* any explicit reference to a random (site or bond) percolation mechanism. This is even more striking when using definitions [16,17], for which clusters result from a global energy balance (and not simply from a bond activation prescription).

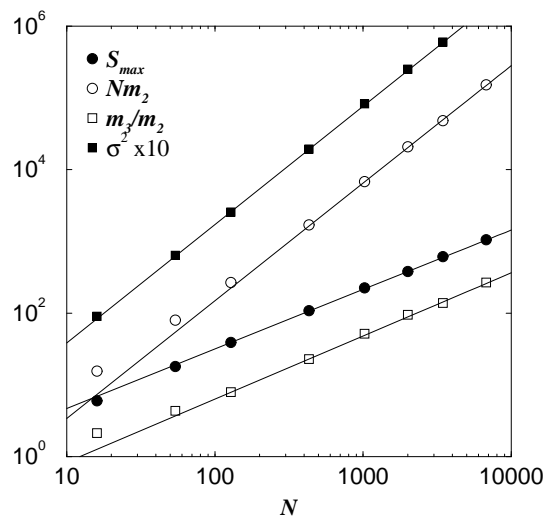


FIG. 3. *Finite size scaling behavior of  $S_{max}$ ,  $m_2$ ,  $m_3/m_2$  and  $\sigma^2 = \langle S_{max}^2 \rangle - \langle S_{max} \rangle^2$  calculated at point (b) of the phase diagram. The straight lines are the best fits in the range  $50 < N < 11664$ .*

At this point, a question that arises naturally is the link between this CPL and the critical percolation line of references [4,5]. We recall that the latter is found in the lattice gas model when choosing the Coniglio and Klein definition of clusters [4]. In ref. [19] it was shown that this definition is (nearly) equivalent, in a lattice gas model, to a condition of stability of clusters by monomer emission.

In this sense, the CPL can be seen as a generalization to a realistic fluid.

It is also interesting to recall that, when defining clusters with a real space criteria, for instance as sets of particles that are two by two at a distance less than some distance  $d_c$ , a percolation line also exists [3,20,21], but its position depends crucially on the choice of  $d_c$ . However, this percolation line may be relevant in situations in which physical clusters are sets of particles close in *real* space, for example in conductivity experiments in which neighboring atoms exchange electrons in overlapping orbits.

As a natural consequence of the definition of clusters based on a stability condition, we find that the internal “effective temperature”  $T_{eff}$  of clusters [22] is always less than the global temperature  $T$  of the system. Using the molecular dynamics calculation, we find that  $T_{eff}$  grows as a function of  $s$  from zero for  $s = 1$ , to a limiting value for  $s \gtrsim 100$ . In the supercritical phase, this limiting temperature, that depends essentially on the density of the system, ranges between  $T_{eff} = 0.7$  and  $T_{eff} = 1.0$ , i.e. small clusters behave as “solid-like crystals” while the large ones behave as “liquid-like droplets”, as can be seen considering the complete phase diagram. We have also observed that along the CPL the total energy of the system remains almost constant. The origin of this energy invariance, that results from a subtle balance between internal, center of mass kinetic energies and inter-cluster potential energies, is not understood.

Finally, we briefly discuss the possibilities to observe experimentally the CPL. Notice first that this line should not be confused with the Fisher-Widom line [23], or with the extrapolation of the rectilinear diameters line [24]. Those two lines divide the supercritical region into a gas like and a liquid like domain with probably no relevance on clustering.

Many experiments dealing with critical behavior of binary fluids (which belong to the same universality class as liquid-gas and  $3d$  Ising model) have been performed [25]. Observations of concentration fluctuations in the mixture of isobutyric acid and water have been done in the vicinity of the critical point [26] and a fractal dimension  $D_f = 2.8 \pm 0.1$  of clusters has been determined. The value we determine along the CPL is  $D_f = 1/\sigma\nu = 2.60 \pm 0.05$ . However, the relationship between these clusters, defined from persistent density fluctuations and the stable clusters is not yet clear. Work is in progress in this direction. The mobility of  $H^+$  ions in the same binary mixture has also been studied very recently [27]. The sharp decrease of the ion mobility observed for  $T > T_c$  as the critical concentration is exceeded, has been associated to the appearance of a percolation line of dynamical clusters. The position of this curve in the  $\rho - T$  plane would suggest however a closer connection with clustering in real space [21].

In a different domain, early experiments on the effusion

of a fluid through a pin hole [28] have shown the presence of stable clusters (dimers and trimers) in the gas phase. In these experiments, the mass yield of escaped clusters with a given velocity can be related to the moments  $m_k$  of the cluster size distribution  $n'(s)$ . Unfortunately, the interesting regime, namely the crossing of the CPL has not yet been explored. It should also be possible to isolate stable clusters by a sudden disassembly of a piece of fluid into droplets, like in the fragmentation of atomic nuclei or atomic aggregates [29,30]. Several experiments [12,29] show indeed, as a function of the excitation energy, an evolution of the fragment size distributions  $n(s)$  that suggests a crossing of the CPL. However, due to the small size of the system, the results are still inconclusive.

In summary: Large scale and long time Monte Carlo and Molecular Dynamics calculations suggest that energetically stable clusters are present in a supercritical simple fluid. These clusters, that are cooler than the system, percolate below a critical line that ends at the (thermodynamical) critical point. Various experiments, within the reach of present day experimental techniques, are suggested to show the presence of these stable clusters and the existence of this critical percolation line.

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