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Percolation Line and Response Functions in Simple Supercritical Fluids

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RESEARCH ARTICLE

Percolation Line and Response Functions in Simple Supercritical Fluids

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The question of a physical relevance (meaning) of the percolation line in simple supercritical fluids has been addressed using both extensive Monte Carlo simulations and accurate analytic equations of state. Thermodynamic and structural properties of two qualitatively different fluids, the Lennard-Jonesium (continuous model) and square-well fluid (stepwise model), have been studied in vicinity of their percolation lines over a range of pressures in order to find potential changes which may take place when an infinite cluster is detected in the system. Two different criteria for the occurrence of an infinite cluster, physical and configurational criteria, have also been used to assess their effect on the observed properties. It is found that the lines of extremes of various response functions run close to the percolation lines. Accounting for uncertainties in the definition of bonds and determination of the percolation line one may conjecture that extremes in some response functions occur when crossing the percolation line.

Keywords: Percolation line; Response functions; Supercritical fluids

1. Introduction

At certain thermodynamic conditions the molecules in bulk fluids may form aggregates (clusters) and/or a network whose occurrence affect considerably the behaviour of fluids. Formation or disruption of an infinite cluster of molecules (percolation transition) is then marked by a dramatic changes of certain properties of the system. Typical examples are a rapid change of electric conductivity of aqueous solutions [1, 2], metal-nonmetal transition in supercritical fluids [3], or a sudden change of electric and dielectric properties of composites [4]. Percolation seems to be also a necessary condition for physical gelation [5].

Although the above examples refer to fluids, the concept of percolation originated in studies of lattice systems mimicking the crystalline phase for which the notions as, e.g., bond or the nearest neighbor are rather natural and for which also a number of theoretical results have been obtained [6, 7]. One of the most important of them is a universality which says that although the percolation threshold is system dependent, there are scaling functions and parameters which are universal for all systems of a given dimensionality and symmetry. However, when dealing with fluids (continuous systems referred to also as correlated systems) the situation is

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1 much less clear and a number of fundamental problems as, e.g., the definition of
2 cluster itself, are encountered. Consequently, practically no theoretical results are
3 available for fluids and various conjectures on percolation in fluids represent a mere
4 extension of the results obtained originally for lattice systems.

5
6 When dealing with fluids, the first problem to be addressed is the definition of
7 cluster itself (i.e., a group of particles that are connected by an unbro-
8 ken path of interparticle bonds) because there is no unambiguous criterion of
9 particle connectivity. Then, in addition to determining the occurrence of clusters
10 of various size, the ultimate goal of the percolation theory is to find the perco-
11 lation threshold, i.e., the thermodynamic state at which a percolating (infinite)
12 cluster occurs. Since molecular simulations are the only currently available tool
13 the problem arises how to estimate the percolation threshold from simulations on
14 finite systems. As regards the former problem, the most common way is to use a
15 local concept, i.e., to define a cluster by means of bonds between pairs of molecules
16 and the entire problem is then reduced to the problem of an appropriate defini-
17 tion of bonds. With the latter problem we dealt recently and concluded that, for
18 supercritical fluids, the so-called wrapping probability (the cluster wraps the
19 system if it is possible to get, starting from any particle of the cluster
20 and moving along interparticle bonds, to an image of that particle in an-
21 other replica [8]) provided a more accurate estimate of the percolation threshold
22 when compared to the crossing probability (the cluster crosses the system if
23 the maximal distance between some pairs of its particles is equal to or
24 greater than the box length) [9, 10]. Finally, we have also addressed recently
25 the problem of potential universality for supercritical fluids and showed that the
26 results exhibited not only strong temperature dependence but also dependence on
27 the nature of the systems considered [11]. In other words, the percolation thresh-
28 old in real fluids *cannot* be characterized by universal exponents of usual random
29 percolating systems.

30
31
32 **There are two other important issues related to supercritical fluids.**
33 **The first one is the question where the percolation line terminates with**
34 **lowering temperatures. Theoretical arguments suggest that it should**
35 **terminate at the critical point [12] but vast majority of simulation results**
36 **have not indicated any such tendency. Surprisingly, this important issue**
37 **has in fact gained only little attention and we are aware of only two**
38 **papers confirming the theoretical arguments for continuous models, for**
39 **supercritical Lennard-Jonesium (LJ) [14, 15]. With respect to the above**
40 **mentioned ambiguities one reason may be an inappropriate choice for**
41 **the bond definition or/and estimation of the percolation threshold.**

42
43 **There are two other important issues related to supercritical fluids.**
44 **The first one is the question where the percolation line (i.e., the loci**
45 **of the state points where the percolation transition/threshold occurs)**
46 **terminates with lowering temperatures; in other words, what is the re-**
47 **lation between the percolation and the critical point. This topic has**
48 **been comprehensively reviewed by Coniglio [12]. With respect to the**
49 **mentioned ambiguous criterion of the interparticle connectivity, there**
50 **cannot be an unambiguous percolation line and, consequently, no its**
51 **unique relation to the critical point. For example, it has been already**
52 **well-known that application of a simple geometric definition of cluster**
53 **tends to produce a percolation line ending below the critical temper-**
54 **ature in the low-density region (e.g., [13]). On the other hand, we are**
55 **aware of two papers which, using a 'proper' definition of cluster for a**
56 **continuous model, supercritical Lennard-Jonesium (LJ), confirm that**
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1 the percolation line terminates at the critical point [14, 15]. It is also
2 known that the percolation line can be moved to the left or right side
3 from the critical point by using different (more sophisticated) criteria
4 (see, e.g., [16, 17]). On top of that, another problem in interpreting
5 the percolation line and its termination arises when an inappropriate
6 method for the estimation of the percolation threshold is used.

7
8 The second issue is related to the fundamental question one should ask at the
9 very beginning when studying percolation in supercritical fluids: Does the percola-
10 tion threshold have any physical significance for supercritical fluids or is it only a
11 pure mathematical construction extending otherwise meaningful results? Dramatic
12 changes in the properties of fluids are observed primarily on mixtures (aqueous so-
13 lutions, colloids) but what about pure supercritical fluids? This applies particularly
14 to models with continuous intermolecular potentials. Based on physical intuition,
15 one can understand that for models with a stepwise interaction potential as, e.g.,
16 the square-well (SW) potential or primitive models of associating or polar fluids
17 [18–20], the occurrence of an infinite cluster may give rise to some changes in the
18 thermodynamic or structural properties of the system. But what about continuous
19 models as, e.g., the LJ potential? To our best knowledge, we are not aware of any
20 result reporting observable changes in their properties related to the percolation.
21 However, this does not seem to be the case of water which in fact has attracted
22 a good deal of attention. Quite recently Bernabei et al. [21], combining neutron
23 diffraction experiments with molecular simulation and the questionable assumption
24 of universality, determined the percolation line for supercritical water and reported
25 certain changes in the 3-dimensional arrangements of water molecules when cross-
26 ing the percolation line. Partay and Jedlovsky [22] simulated recently supercritical
27 SPC/E water and suggested that the percolation line might coincide with an ‘imag-
28 inary’ extension of the vapour-liquid (V-L) line in the pressure-temperature plane
29 to the supercritical temperatures.

30
31 To summarize, the problem of the physical meaning of the percolation threshold
32 in supercritical fluids, including water, has not been settled yet and the present
33 paper attempts to address this issue and related problems. Percolation transition
34 is not a genuine transition in the thermodynamic sense but may be viewed as a
35 sort of a geometrical transition since a certain restructuring (rearrangement) does
36 take a place when crossing the percolation line. We will therefore try to detect and
37 characterize such changes and their relation to the thermodynamic behaviour of
38 the fluid. Since the commonly used correlation functions are rather insensitive to
39 tiny structural changes, we use the Voronoi polyhedra tessellation. As for ther-
40 modynamic properties, it is known that the so called thermodynamic response
41 functions (derivatives of the state functions with respect to temperature, e.g., the
42 isobaric heat capacity) [23] exhibit extremes at a certain temperature, $T_m(P)$, for
43 pressures greater than the critical one, P_c . This behaviour must/should be related
44 to some structural changes in the system, potentially to percolation as suggested
45 recently by Partay and Jedlovsky [22]. We will therefore focus on the response
46 functions and extend their notion by considering the first-order derivatives also of
47 the state variables (as, e.g., the isothermal compressibility) which exhibit extremes
48 in temperature at a given pressure as well. After providing all the necessary def-
49 initions in the next section, we then determine the percolation line in two most
50 common but qualitatively different simple fluid models, the LJ and the SW fluid.
51 Further, two different definitions are used to consider two molecules to be bonded
52 or not, the usual configuration criterion (also referred to as the Stillinger criterion)
53 and the physical criterion (also referred to as the Hill criterion). Based on our own
54 previous results [9, 10], we consider only wrapping clusters to identify the occur-

rence of an infinite cluster in the system and no assumption of universality is used. The obtained results are then summarized and discussed in section 4.

2. Basic definitions and computational details

The two common simple fluid models considered, the LJ and SW models, are defined by the following intermolecular potentials,

$$u_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

and

$$\begin{aligned} u_{\text{SW}}(r) &= +\infty && \text{for } r < \sigma \\ &= -\epsilon && \text{for } \sigma \leq r < \lambda\sigma \\ &= 0 && \text{for } r \geq \lambda\sigma, \end{aligned} \quad (2)$$

respectively. The depth of the potential, ϵ , and parameter σ are used henceforth to define the dimensionless temperature, $T^* = k_{\text{B}}T/\epsilon$, pressure, $P^* = P\sigma^3/\epsilon$, and density, $\rho^* = N\sigma^3/V$, where k_{B} is the Boltzmann's constant, T is the temperature, P is the pressure, N is the number of particles, V is the volume of the system, and ρ is the number density. The range of the SW interaction has been set to $\lambda = 1.5$ which also defines the range within which two particles are considered bonded (configuration criterion). In the case of the LJ fluid, we choose from various possibilities for the configuration criterion for the limit of bonding the point of inflection of $u(r)$, $r_b/\sigma = (26/7)^{1/6}$, used already in previous studies, see e.g. [24]. The energy-based Hill clusters are defined by means of the relative kinetic energy with respect to their interaction energy [25, 26]: If \mathbf{v}_i and \mathbf{v}_j are the velocity vectors of particles i and j , resp., and m is their mass, then they are considered to be bonded if

$$\frac{m}{4}(\mathbf{v}_j - \mathbf{v}_i)^2 \leq -u_{ij} \quad (3)$$

We used the common Metropolis Monte Carlo (MC) simulation in a N-V-T ensemble [27] both for the location of the percolation threshold and for the investigation of other structural properties; for the application of the energy criterion the velocity components have been assigned to every particle at random from the Gaussian distribution characterized by the temperature of the system (for further details see the previous paper [11]). The correlation functions and the structure factors were determined at several state points around every detected percolation threshold point and further structural analysis was carried out by means of the Voronoi tessellation [28, 29] over a wide range of densities. The extension of the V-L line to the supercritical temperatures has been determined by an extrapolation of the Clausius-Clapeyron equation $\ln P = a - b/T$, where a and b are fitted parameters for the model considered.

The response functions we consider here are the coefficient of thermal expansivity,

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P, \quad (4)$$

1 the coefficient of isothermal compressibility,

$$2 \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T, \quad (5)$$

3 and the isobaric heat capacity,

$$4 c_P = \frac{1}{N} \left(\frac{\partial H}{\partial T} \right)_P, \quad (6)$$

5 where H is enthalpy. These functions exhibit various extremes or even singularities
6 (as, e.g., the heat capacity at the critical point) or change sign (as, e.g., the thermal
7 expansivity which indicates an anomaly in the isobaric temperature dependence
8 of density). The loci of the extremes of the response functions as functions of
9 temperature at constant pressures form in the $P - T$ plane a line which we are
10 going to refer to as the 'response function extremes line (RFEL)'. To determine the
11 response functions and RFEL's, for the LJ fluid we use the most accurate equation
12 of state (EOS) available to date, Kolafa-Nezbeda equation [30], and for the SW
13 fluid a generalized EOS developed by Patel et al. [31].

24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

3. Results and discussion

Following the strategy outlined above we determined from simulations two types of
the percolation line corresponding to the two different definitions of bonds (config-
urational and physical) and the results are shown in figures 1 and 2. As it is seen,
both lines follow a different course. Although it may seem that at least the Hill's
percolation line tend to go to the critical point, the detailed examination shows
that this is not the case. And as for the Stillinger's percolation line, it evidently
goes away from the critical point.

As already mentioned, the primary property of the fluids **from onto** which all
other properties **reel off are superimposed** is the structure. As regards structural
characteristics, we have not found any significant (reasonably detectable) changes
in the course of either correlation functions or the structure factors that might
indicate a structural rearrangement. From a number of various characteristics of
the Voronoi tessellation (volumes of Voronoi polyhedra, etc.) we examined, the
most interesting seems the skewness of the distribution of the number of nearest
neighbors (in terms of the Voronoi tessellation) for one simple reason: this function
exhibits, as a function of density ρ at a given temperature T , a maximum, see
figure 3, and the line connecting these extremes (skewness extreme line; SEL)
originates from (vicinity of) the critical point.

Examination of figures 1 and 2 reveals two different patterns of the behaviour
not in the dependence on the fluid model but in dependence on the thermodynamic
property considered. Quantities directly related to the structure are the coefficient
of isothermal compressibility and the skewness of the distribution of the number of
nearest neighbors. As we see, the line of extremes of the former quantity runs very
close to the SEL and both also follow (approximately) the course of the percolation
line based on the configurational definition all along the considered temperature
range. The former coincidence expresses the fact that the coefficient of isothermal
compressibility reflects the response of density to the applied pressure which may
give rise, at certain conditions, to a structural rearrangement (repacking) of the
molecules and the same applies to the skewness. Since the percolation line involves

1 explicitly the bonding in the geometrical sense (proximity of molecules), it is un-
2 derstandable that the structural rearrangement may simultaneously give rise to
3 establishing of an infinite network, i.e., percolation.

4 Quite different pattern of behaviour we find in the case of the other two RFELs.
5 First, the RFEL's of the isobaric heat capacity and of the coefficient of thermal
6 expansivity are not monotonous functions of pressure and may thus hardly be
7 related to any percolation line, which are monotonous, over a wide range of pres-
8 sures/temperatures. Second, both these functions are derivatives with respect to
9 temperature and involve thus, implicitly, the effect of the change in energy. If any
10 percolation line is to be related to them then it is the percolation line based on
11 the Hill's criterion which is thus in this case more appropriate. In fact, for the SW
12 fluid this percolation line runs, in the vicinity of the critical point, quite close to
13 their RFELs.
14

15 The last curve shown in figures 1 and 2 is the extension of the V-L line. In
16 principle, this line does not have any physical meaning and, as we see, it cannot
17 be related to any pattern of the behaviour of the quantities shown in these figures.
18

19 As a counterpart to the $P - T$ diagram used in discussions of any transition, we
20 show in figure 4 the above discussed quantities also in the $T - \rho$ plane which is a
21 common practice when dealing with percolation. In this case it is even more difficult
22 to find a common pattern for the percolation lines and other characteristics of the
23 considered fluids. In fact, the results are different for each fluid with the exception
24 of the percolation line given by the configurational definition of the bond: In both
25 cases the percolation line ends anywhere but in the critical point. Some relation
26 between the Hill's percolation line and the energy dependent quantities (α_P and
27 c_P) can be detected for the SW fluid over an extended range of the supercritical
28 temperatures but no such pattern is observed for the LJ fluid.
29
30

31 4. Conclusions

32 Percolation is a phenomenon which is known to affect considerably the properties of
33 the solid phase but whether the same applies also to the fluid phase remains still an
34 open question. We have investigated the behaviour of certain thermodynamic and
35 structural properties of two simple supercritical fluids and found out two different
36 types of their behaviour, both with respect to the lines of percolation and among
37 themselves.
38

39 Arguing that the percolation in the fluid is connected, in some way, to a struc-
40 tural rearrangement of the molecules in the system, then the configuration criterion
41 seems the most appropriate. The thermodynamic property reflecting such a struc-
42 tural change is the coefficient of isothermal compressibility whose RFEL (**the line
43 connecting the state points at which the given response function, as a
44 function of temperature T at constant pressure P , reaches its maximum**)
45 follows very closely the course of the SEL (**the line connecting the state points
46 at which the skewness of the distribution of the number of nearest neigh-
47 bors in terms of the Voronoi tessellation, as a function of density ρ at
48 constant T , reaches its maximum**) and both follow, approximately, also the
49 course of the configuration percolation line in the $P - T$ plane. The other case in-
50 volves properties which are, either explicitly or implicitly, associated with changes
51 in energy, the coefficient of the thermal expansivity and the isobaric heat capacity.
52 Their RFELs fall into the region of the percolation line defined by the Hill's crite-
53 rion. However, with respect to the behaviour of the RFEL's no simple conclusion
54 can be drawn.
55

56 Some authors [22, 23] argue that the line which may indicate a structural change
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in supercritical fluids may be an extension of the **vapour-liquid (V-L)** line. However, we have not found any evidence for this surmise, except for very close proximity of the critical point; in fact, outside the critical region the V-L line runs away from both the percolation lines and also away from the RFELs and SEL. Nonetheless, with respect to ambiguity of the definition of the percolation line [17] such a connection cannot be, in principle, excluded.

To summarize, we have attempted to find a link between the percolation and observable changes in the thermodynamic behaviour of supercritical fluids considering two types of simple fluids. With respect to the mentioned ambiguity in the definition of cluster (and percolation) in fluids, only indications of such a potential link between the percolation and extremes of (at least some) response functions have been found, at least in the vicinity of the critical point. For a more definite result at least other classes of fluids must be also considered, particularly associating fluids (e.g., water and methanol) and, for completeness, also strongly polar fluids (e.g., acetone). Thus, the problem of the physical relevance of the percolation line in supercritical fluids remains still open and deserves further investigations.

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LIST OF FIGURES

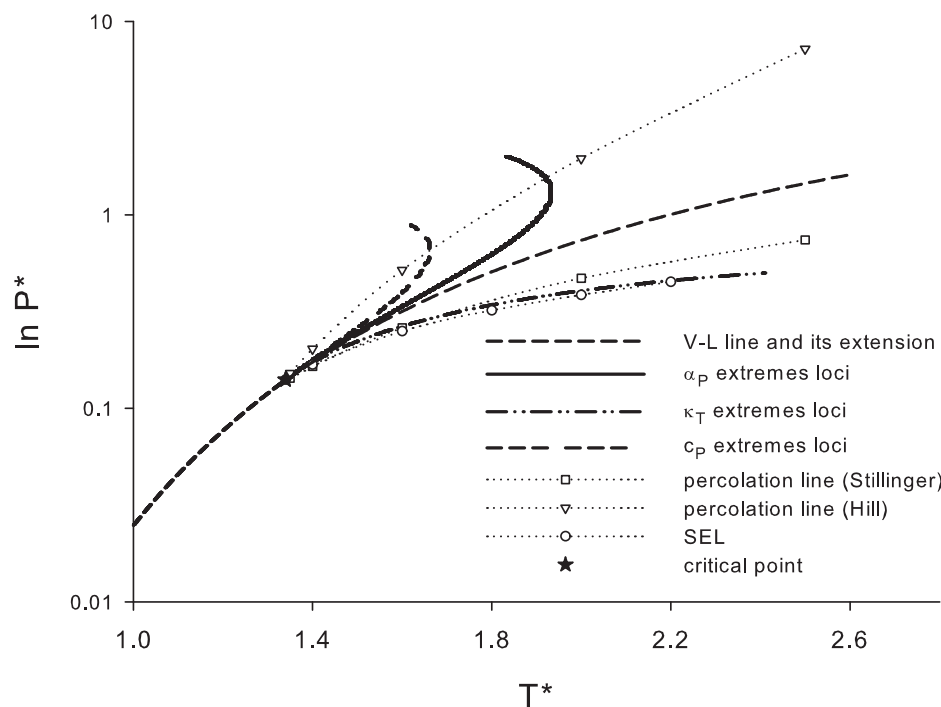


Figure 1. Percolation lines, loci of the extremes of the response functions, and the skewness extreme line in the supercritical Lennard-Jones fluid.

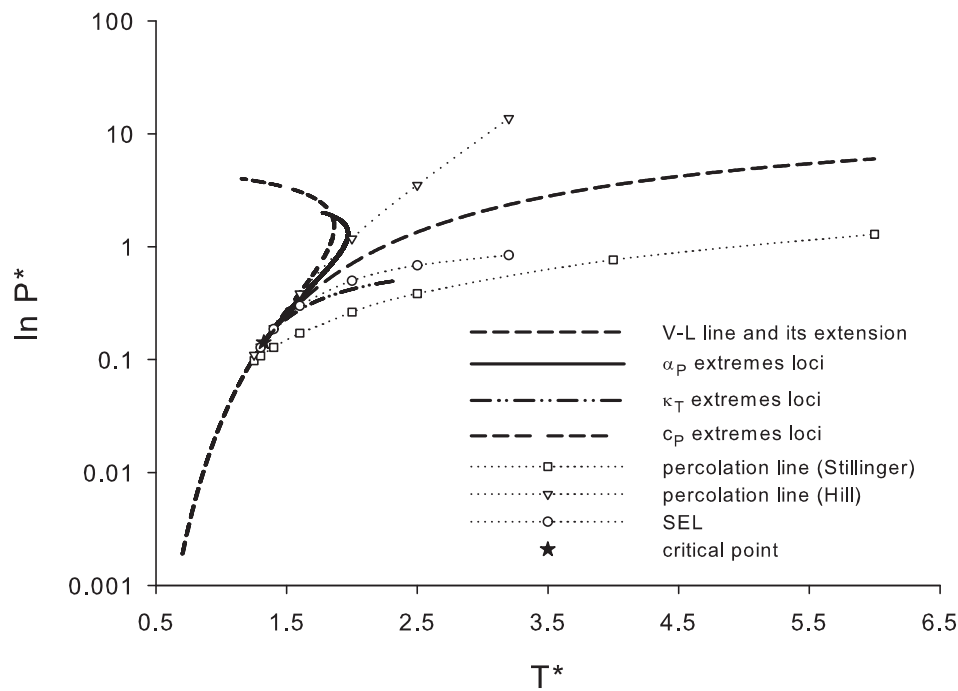


Figure 2. The same as figure 1 for the square-well fluid.

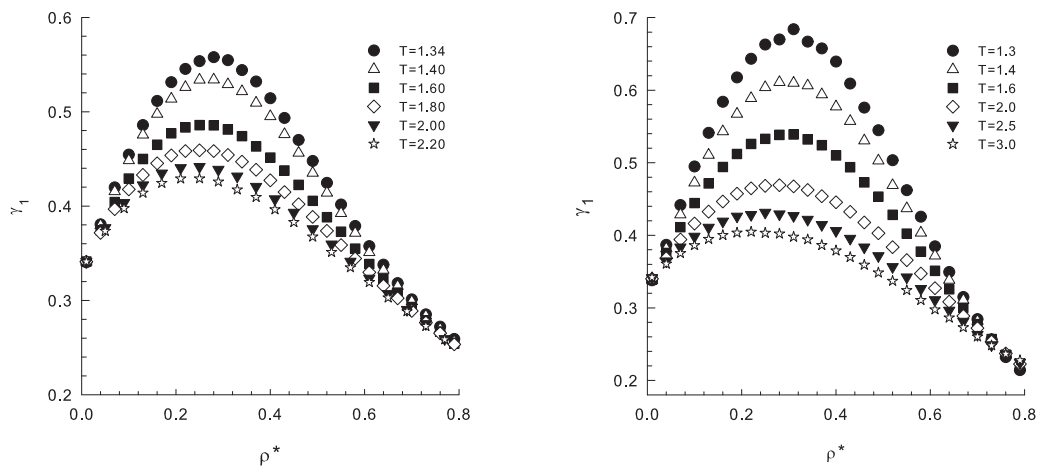


Figure 3. The skewness, γ_1 , of the distribution of the number of nearest neighbors (in terms of the Voronoi tessellation) as a function of density at given temperatures for the Lennard-Jones (left) and square-well (right) fluids.

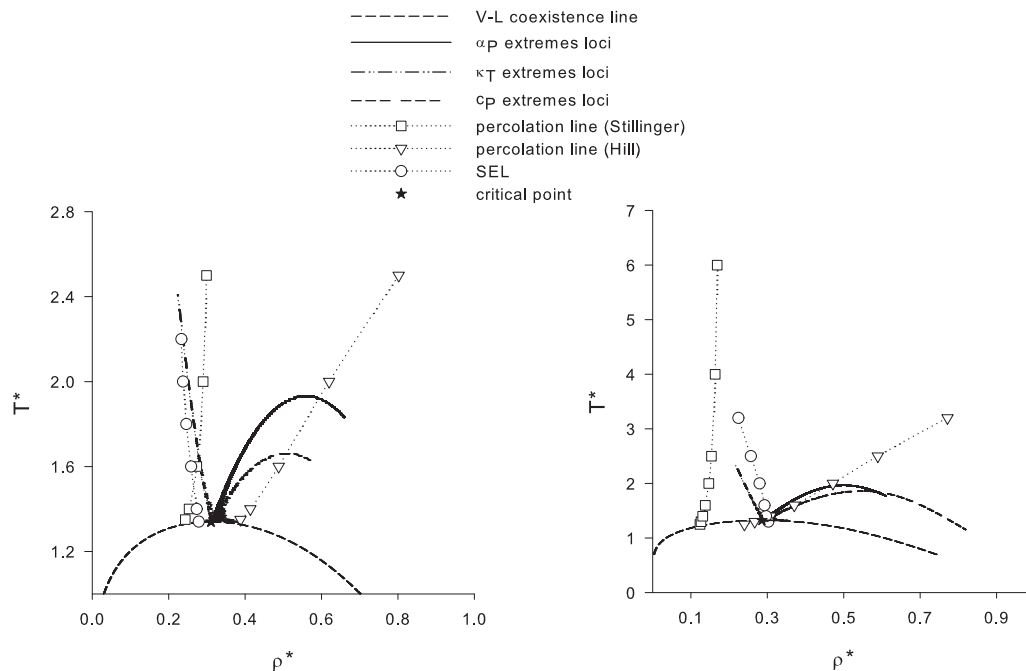


Figure 4. Percolation lines, loci of the extremes of the response functions, and the skewness extreme line in the supercritical Lennard-Jones (left) and square-well (right) fluid.

September 2, 2010

Professor George Jackson
Editor, Molecular Physics
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Re: revised MS: TMPH-2010-0312

Dear Professor Jackson,

A revised version of the above specified paper has just been uploaded. The referee asked for a minor revision and the paper has been revised accordingly.

Most changes take place in the Introduction. Specifically:

1. Wrapping and crossing probabilities are explicitly defined.
2. Percolation line is defined.
3. As for the term 'Response function', which is clearly defined in the paper, this is not our 'invention'. It's used in the field and a reference has been added for further details.
4. One paragraph dealing with the connection between the percolation line and the critical point has been completely reformulated and extended, and additional references added.

Structural properties are discussed in terms of the skewness for reasons which are discussed in the paper in details.

The acronyms used in the Conclusions has been detailed again for better readability.

All the changes to the MS are highlighted by color: the green color indicates the new text, red color the text which must be deleted.

I believe that after these changes the paper will be acceptable for publishing in Mol Phys.

With best regards,

Jiri Skvor