New criteria for cluster identification in continuum systems.

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Two new criteria, that involve the microscopic dynamics of the system, are proposed for the identification of clusters in continuum systems. The first one considers a residence time in the definition of the bond between pairs of particles, whereas the second one uses a life time in the definition of an aggregate. Because of the qualitative features of the clusters yielded by the criteria we call them chemical and physical clusters, respectively. Molecular dynamics results for a Lennard-Jones system and general connectivity theories are presented.

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I. INTRODUCTION

Clustering plays a relevant role in condensed matter physics, particularly in relation with transition phenomena, as it has been recognized since more than sixty years ago when Bijl, Band and Frenkel (among others) introduced the concept of real clusters, in place of the mathematical ones that Mayer had considered in the virial expansion of imperfect gases.
The application of statistical mechanics formalism to describe clustering in equilibrium classical systems is mainly due to Hill\textsuperscript{5}. In Hill’s theory the concept of cluster is directly related to that of connectivity: two particles belong to the same cluster if they are connected through a path of directly connected particles. Therefore a crucial point in the identification of the clusters is the definition of directly connected particles (a bonded pair). Whereas thermodynamic properties are not affected by the particular definition used to identify the clusters, clustering and percolation properties do are very sensitive to this choice instead\textsuperscript{5}.

Hill’s definition of a bonded pair is based on an energetic criterion: two particles are bonded, in a given configuration, if their relative kinetic energy is less than minus the pair potential energy\textsuperscript{5}. Frequently, however, a geometrical criterion is used instead of the energetic one. Thus, Stillinger criterion states that two particles are bonded if they are separated by a distance shorter than certain value \(d\), which is called the connectivity distance\textsuperscript{6}.

In the past few years, several papers have renewed interest in the energetic and dynamic aspects of bonding, particularly in relation to the properties of water\textsuperscript{7}. Hydrogen-bond life times have been calculated and new connectivity criteria have been proposed for water molecules. These works suggest that a bonded pair must be defined as two water molecules that are in some appropriate geometrical arrangement at least during a time interval of the order of the estimated hydrogen-bond life times. Recently has been pointed out the necessity of including dynamical information in the definition of the clusters considered in nucleation studies\textsuperscript{8–10}. It is also expected that taking into consideration the dynamics of aggregates would improve the description of some phenomena as the conductor/insulator transitions in microemulsions\textsuperscript{11}.

Hill’s theory separates the Boltzmann factor \(e(r_1, r_2) = \exp[-\beta v(r_1, r_2)]\) into bonded (\(\dagger\)) and unbounded (\(\ast\)) terms: \(e(r_1, r_2) = e^\dagger(r_1, r_2) + e^\ast(r_1, r_2)\). In this paper we will consider only systems interacting via pairwise additive potentials and will denote with \(v(r_1, r_2)\) the pair potential. As usual \(\beta = 1/k_B T\) with \(T\) the absolute temperature and \(k_B\) the Boltzmann constant. Since \(e^\dagger(r_1, r_2)\) represents the basic probability density that two particles at positions \(r_1\) and \(r_2\), respectively, are directly connected (bonded), this separation gets a
diagrammatic expansion for the partition functions in terms of real clusters instead of the mathematical clusters of Mayer.

Fugacity and density expansions similar to those obtained by Mayer and Montroll for the ordinary pair correlation function $g(r_1, r_2)$ has been found, within Hill’s formalism, by Coniglio and collaborators for the pair connectedness function $g^+(r_1, r_2)$. This function is proportional to the joint probability density of finding two particles connected (directly or indirectly) and at positions $r_1$ and $r_2$, respectively. Moreover, by collecting nodal and non-nodal diagrams in these expansions an Ornstein-Zernike like relationship is obtained. Consequently, integral equations for $g^+(r_1, r_2)$ can be posed. These equations, as well as computer simulations, have been applied together with Stillinger criterion to study clustering and percolation in several continuum systems. They include: the ideal gas; simple hard spheres; hard spheres with (sticky) adhesion; hard spheres with square wells; hard spheres with Yukawa tails; charged hard spheres; Lennard-Jones fluids and dipolar hard spheres.

Hill’s work is the basis for all the present clustering theories in continuum systems. Nevertheless, it has some limitations. In one hand, as Hill pointed out in his paper, the essence of his theory is the concept of bonded pair. This fact limits the kind of cluster we can study. In the other hand both, the energetic and the geometrical, criteria considered by Hill yield a poor description of a “real” bond.

Let first consider the second problem. If we use an energetic criterion to define a bond, then the functions $e^+$ and $e^*$ must be momenta, as well as position, dependent. However, the functions $e^+$ and $e^*$ used by Hill are only position dependent, since the momenta have been averaged. A geometrical criterion is neither enough by itself to warrant the existence of a real bond. After a short time two neighbor particles can be much separated each other if the relative velocity is high. These features suggest that the bond definition should be modified. In Section II we introduce a bond criterion which incorporates a residence time into Stillinger criterion. We shall call “chemical clusters” the aggregates so defined. A connectivity theory, already presented in a previous paper, that allows to handle these
clusters will be reviewed in Subsection V-A.

Let us now focus on the energetic criterion and take, for example, three particles which remain next one to the others. If the potential interaction between each pair is not strong enough to form a bond then, according to Hill’s theory, we will have three clusters of one particle each. Nevertheless, since the three particles remain close each other, then the system can be considered as a single cluster of three particles “collectively or non-specifically pair-bonded”. We call this kind of aggregates “physical clusters”.

With respect to the geometrical criterion, it could happen that it does not matter how the particles interact each other, if they are close enough, then they are bonded. Thus, according to the Stillinger’s criterion, there will be three bonded pairs and the particles will form a single three-particle cluster. In this way the Stillinger’s criterion partly avoid the limitation that the energetic criterion imposes in Hill’s work. Due to this feature, Stillinger’s criterion has given good results in nucleation studies. However, it does not include dynamical information. As a consequence one could take as a single cluster two physical clusters which are close during a very short time. In Section III we will give a definition for physical clusters which adds a dynamical restriction to the Stillinger criterion. This restriction is equivalent to require a minimum lifetime for the aggregates. In Subsection V-B we present a simplified theory to obtain connectivity functions and mean cluster sizes for physical clusters.

It can be worth-mentioning that the difference between the chemical and physical clusters that we introduce is, in some sense, analogous to that existing between chemical (or specific) and physical (or non-specific) adsorption.

We remark that in this work, the time is thought in the frame of the microscopical evolution of the system whereas its macroscopic (thermodynamic) state remains unchanged.

Since the work of Coniglio and collaborators, the central object in clustering and percolation theory of continuum systems is the cluster pair correlation function $g_\gamma(r_1, r_2)$. It is the joint probability density of finding two particles that belong to the same cluster of kind $\gamma$ ($\gamma =$Stillinger, chemical or physical) at positions $r_1$ and $r_2$, respectively. In particular, for
Stillinger clusters we have \( g_{\text{Still}}(\mathbf{r}_1, \mathbf{r}_2) = g^\dagger(\mathbf{r}_1, \mathbf{r}_2) \). From cluster correlation functions we can calculate the mean cluster size defined

\[
S_\gamma(\rho) = 1 + \frac{1}{(N - 1)} \int g_\gamma(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2,
\]

where \( N \) is the number of particles of the system and the integrations are over the whole system volume \( V \). In Eq. (1) we have explicitly indicated its dependence on the system density \( \rho = N/V \). Percolation of an ensemble of particles is concerned with the existence of clusters that become macroscopic in size. Then the percolation transition occurs at a critical percolation density \( \rho_c \) which mathematically verifies

\[
\lim_{\rho \to \rho_c} S_\gamma(\rho) = \infty.
\]

The rest of this article is arranged in the following way. In Section II and III we introduce the chemical and physical clusters, respectively. Section IV will be devoted to discuss some results from molecular dynamics simulations. In section V we present statistical mechanics theories to describe both kind of clusters. We conclude with some comments on potential applications of these new criteria.

II. CHEMICAL CLUSTERS

As it was mentioned, Stillinger’s criterion does not describe a real bond in a completely satisfactory way since it does not include any dynamical information. For example, two particles which are separated by a distance shorter than \( d \), at a given instant, are considered bonded even when their relative velocity is high enough to separate the particles in a short time. On the other hand, the analysis of the residence time of a molecule in the neighborhood of another one has produced important advances in the study of the hydrogen bond in water\(^7\)–\(^{35}\). All those facts suggest to include a residence time to describe a real bond. In this direction we propose the following bond definition:
Two particles in the system are bonded at the instant $t$ if they have been separated by a distance shorter than the connectivity distance $d$ during the time interval $[t-\tau, t]$, where $\tau$ is the residence time.

Then we define a cluster in the same way as Hill did it:

**A chemical cluster is a set of particles such that between any pair of them exists a path of bonded particles.**

As we can see, the residence time modifies the bond definition but, once the definition of a bond is given, the same connectivity rule for the cluster identification is used. We call chemical clusters to this aggregates because the stable bonds are the essence of the cluster formation, like the covalent bond is the essence in the building of molecules. In the limit case $\tau = 0$ we recover Stillinger’s definition.

The numbers $d$ and $\tau$ are two parameters of the theory that must be obtained from physical considerations on the system and the phenomenon under study. For example, in nucleation studies for Lennard-Jones fluids, where the particles interact via the pair potential

$$v(r_i, r_j) = v(r_{i,j}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{i,j}} \right)^{12} - \left( \frac{\sigma}{r_{i,j}} \right)^{6} \right],$$

is generally adopted the value $d = 1.5\sigma$. According with its role in the theory, one possible election of $\tau$ could be done on the basis of considering the mean value of the relative velocity between two atoms in the fluid at temperature $T$:

$$v_{1,2} = \sqrt{\frac{6k_B T}{m}},$$

where $m$ denotes the mass of the atoms. Thus we choose $\tau$ as the necessary time for the particles travel, in average, the connectivity distance:

$$\tau = \frac{d}{v_{1,2}} = d \sqrt{\frac{m}{6k_B T}}.$$

To have an idea of magnitude orders, let consider argon at $T = 300$ K. We have $\sigma = 3.41 \text{ Å}$, $\varepsilon = 1.65 \times 10^{-21}$J and $m = 6.62 \times 10^{-26}$ Kg, so that $d = 5.03 \text{ Å}$ and $\tau = 0.83$ ps or, in reduced units, $\tau^* \equiv \tau\sigma^{-1}\sqrt{\varepsilon/m} \approx 0.39; d^* = d/\sigma = 1.5$. 
It should be remarked that this estimation for \( \tau \) is just an example. The residence time will depend on the system and the particular phenomenon to be studied and can be determined by very different causes. In section VI we briefly comment on the application of chemical clusters to the case of water in oil microemulsions. There we discuss in particular on the determination of the parameters.

III. PHYSICAL CLUSTERS

Here, we will consider how to identify physical clusters, i.e. those aggregates in which specific bonds between pairs of particles are not necessary for the clusters existence. As we have mentioned, this kind of clusters could be of interest in the simulation of nucleation process. The Stillinger’s criterion and some other improved criteria are currently used in those studies.\(^8\)

We propose, in order to define physical clusters, a criterion in which the dynamics of the system is implicitly involved:

A set of particles form a physical cluster in the instant \( t \) if all they remained connected during the whole time interval \([t - \tau, t]\).

Here the term “connected” must be understood in the Hill-Stillinger sense, i.e. two particles are connected if between them there exists a path of directly connected particles. Two particles being directly connected if they are at a distance shorter than \( d \).

The previous definition is incomplete. It must be accompanied by the additional condition that those particles of the system which do not belong to a given cluster can not contribute to the connectivity of that cluster. Actually, the best way of stating the criterion is operationally. In this vein it is convenient to introduce the concept of fragmentation event. A fragmentation event occurs when a cluster breaks up into two or more connected subaggregates.

Suppose we identify the system clusters at \( t - \tau \) according to the ( “instantaneous”) Stillinger’s criterion. Select one of these clusters. When the system evolves from \( t - \tau \)
to $t$, their particles eventually connect and disconnect several times. If we consider just those particles which had belonged to the selected Stillinger cluster at $t - \tau$ and consider the successive fragmentation events then, after the period $[t - \tau, t]$, the particles will lie in several subaggregates. Each subaggregate forms a physical cluster at time $t$.

In Fig. 1 we show a simple example where the differences among Stillinger, chemical and physical clusters can be appreciated. At the initial time $t - \tau$ we show the instantaneous Stillinger clusters (a). At the final time $t$ we identify Stillinger (b), physical (c) and chemical clusters (d). We can see that physical clusters are smaller in size and longer in life than Stillinger ones, which are instantaneous. Thus, physical clusters would be more stable entities than Stillinger ones. However, physical clusters do not need pair-bonded particles to exist whereas these last are essential for defining chemical clusters. In Fig. 1, particles 1 and 3 form a physical cluster of two particles, but they do not form a chemical cluster: although they are directly connected at $t$ they were not at $t - \tau$.

An estimation of the characteristic time $\tau$ and the connectivity distance $d$ is necessary for physical clusters as well as for chemical clusters. In our calculations on Lennard-Jones systems, we use the same value of $d$ that for the chemical clusters. In order to select a value for $\tau$ it is necessary to estimate the mean life time of an aggregate. Nevertheless, we are interested in comparing the results of the two different criteria. Thus, we will use the same value of $\tau$ for both, chemical and physical criteria.

IV. MOLECULAR DYNAMICS

A. Chemical clusters

In order to show the implications of using the residence time restriction in the bond definition we have simulated by molecular dynamics (MD) a system of particles which interact through a Lennard-Jones potential. Monte Carlo simulation can not be used because the trajectory of the particles is required.
We use a leap-frog algorithm with velocity correction to simulate a system at constant volume and temperature. To identify the chemical clusters we modify the standard MD code in such a way that the resulting algorithm is as follow:

1) All initial conditions are set for the MD ($t = t_0$).

2) The NEIGHBORS routine is called. It generates a table with all direct connections -in the Stillinger sense- between the atoms. The positions of the particles at $t = t_0$ are used in that operation.

3) The MD algorithm is carried out with a very short time step $\Delta t$ until a pair of atoms disconnect in the Stillinger sense ($t = t_1$).

4) The REDUCTION routine is called. It checks and deletes from the neighbors list the direct connections that have disappeared. The position of the particles at $t = t_1$ are used in this step.

5) If $t_1 - t_0 < \tau$ go back to step 3, else go to step 6.

6) All clusters are separated by using the remaining neighbors list. At this point the neighbors list only contain the direct connections which survived a time $\tau$ from $t = t_0$, e.g. the list of chemical bonds.

7) All interesting information is saved (coordinates, cluster list, etc.)

8) Initial conditions are set from the last configuration. Return to step 2.

Steps 1 to 8 are the loop for the chemical cluster identification corresponding to the final configuration at time $t = t_1$.

In step 2 NEIGHBORS routine makes a list with the same structure of the Verlet’s neighbors list, but a cut off equal to the connectivity distance $d$ is used.

In step 3 the leap-frog algorithm is carried out with a time step $\Delta t$ short enough as to allow that no more than one disconnection occurs. We chose $\Delta t$ to find a disconnection in each $3\Delta t$ intervals in average.

In step 4 the neighbors list created in 2 is reduced by deleting the disappeared connections. The new connections created in the system are discarded. Because in the last $\Delta t$ interval more than one disconnection can occur, we check all connections in step 4 and any
disappeared connection is deleted from the neighbor list.

After the time interval $t_1 - t_0$ grows (by successive iterations) beyond $\tau$, a list of chemical bonds (as defined in section II) remains in the neighbors list. Any standard algorithm for cluster identification can be used to separate each cluster knowing the bonded pairs. We have used Stoddard’s one.

B. Physical clusters

For physical clusters we use a similar method to that applied in the case of chemical cluster. Nevertheless, the clustering steps are modified to achieve the desired definition. The complete algorithm is:

1) All initial conditions are set for the MD ($t = t_0$).

2) Stillinger clusters are tabulated by standard routines. The positions of the particles at $t = t_0$ are used in that operation.

3) The MD algorithm is carried out in very short time steps $\Delta t$ until a pair of atoms disconnect in the Stillinger sense ($t = t_1$).

4) The DIVISION routine is called. It checks each cluster in the table made in step 2 and breaks up those clusters which were fragmented as a result of the disconnection in step 3. The cluster table is updated.

5) If $t_1 - t_0 < \tau$ go back to step 3, else go to step 6.

6) Save the interesting information. The cluster table contains all the set of particles which are in agreement with the physical cluster definition of section III.

7) Initial conditions are set from the last configuration. Return to step 2.

Steps 1 to 7 are the loop to identify the physical clusters for the final configuration at time $t = t_1$.

In step 4 a clustering count must be done separately over each initial cluster identified in 2. In this way the connections formed between different clusters in the time interval $[t_0, t_1]$ are not included in the count.
C. Results

In this section we show the results obtained by molecular dynamics simulation for a Lennard-Jones fluid with the pair potential given by Eq.(3). Our aim is not to exhaust the study of the various aspects of the clustering that we will consider but instead is simply to remark the qualitative differences they show for the three kinds of clusters: Stillinger, chemical and physical.

We will express all quantities in reduced units: $\rho^* = N\sigma^3/V$, $T^* = k_B T/\varepsilon$, $t^* = \tau \sigma^{-1} \sqrt{\varepsilon/m}$ and $d^* = d/\sigma$ for density, temperature, residence and life time, and connectivity distance respectively. We have used the leap frog algorithm with velocity corrections at half step to produce a molecular dynamics with constant number of particles $N$, volume $V$ and temperature $T$. 500 particles were placed in a cubic box with periodic boundary conditions and 1000 configurations were generated after stabilization to calculate time averages. We use a cut off equal to $2.7\sigma$ for the pair potential interaction and a tail correction for the remaining interaction. Because we use the same number of particles in all simulations, scaling laws were not used to extrapolate in the limit $N \to \infty$. The time step is varied between $\Delta t^* = 0.00001$ and $\Delta t^* = 0.0001$ depending on temperature to get a connection or disconnection approximately every three time steps. The parameters for the cluster identifications were chosen $d^* = 1.5$ and $\tau^* = 0.5$ for chemical and physical clusters. In order to compare the results with the standard Stillinger criterion we use the same connectivity distance $d^* = 1.5$ for the three criteria.

In Fig. 2 the correlation functions for Stillinger clusters $g_{\text{Still}}(r_{1,2})$, chemical clusters $g_{\text{Chem}}(r_{1,2})$ and physical clusters $g_{\text{Phys}}(r_{1,2})$ are shown. We have used free boundary conditions in the calculation of the correlation functions for clusters. It means that neither real position nor nearest image of a particle but the image belonging to the proper aggregate through the replicas is used.

If two particles are separated by a distance shorter than the connectivity distance, then they belong to the same Stillinger cluster with certainty. Thus, for $r_{1,2} < d$, the function...
\( g_{\text{Still}}(r_{1,2}) \) coincides with the ordinary radial distribution function \( g(r_{1,2}) \) as it can be appreciated in Fig. 2. The observed discontinuity at \( r_{1,2} = d \) for all cluster definitions is typical: the probability for two particles to be connected at \( r_{1,2} > d \), even for \( r_{1,2} \rightarrow d^+ \), depends on the presence of an intermediate third particle and thus the probability of belonging to the cluster notably diminishes. The function \( g_{\text{Still}}(r_{1,2}) \) is long ranged because the density of the system considered in the figure coincides with the percolation density for Stillinger clusters at the given temperature. The mean Stillinger cluster size \( S_{\text{Still}} \) diverges at this density.

As it is expected \( g_{\text{Chem}}(r_{1,2}) \) and \( g_{\text{Phys}}(r_{1,2}) \) are smaller than \( g_{\text{Still}}(r_{1,2}) \) for all \( r_{1,2} \) because a dynamical restriction is required in addition to the geometrical one. Comparing \( g_{\text{Chem}}(r_{1,2}) \) against \( g_{\text{Phys}}(r_{1,2}) \) in Fig. 2, we see that \( g_{\text{Chem}}(r_{1,2}) \) is above \( g_{\text{Phys}}(r_{1,2}) \) for every \( r_{1,2} \). That is just what one expect when the same value for \( \tau \) is used in both, chemical and physical clusters definition, because a life time restriction on the aggregate is a condition weaker than imposing a residence time restriction on the bond.

In Fig. 3 we present the system coexistence curve obtained by Panagiotopoulos together with the percolation curves for the various cluster definitions. These curves separate the phase diagram in two parts: percolated (high densities) and non-percolated (low densities); and intersect the coexistence curve.

To determine if a given configuration is percolated we look for a cluster which span through the replicas. For a given temperature we increase the density until get 50\% of percolated configurations. In that case we say that the percolation density was reached. We observe that the percolation curve for physical clusters is slightly less steep than for the Stillinger ones. Nevertheless, it is at higher densities as is expected.

In the other hand, the percolation curve for chemical clusters is at higher densities than for the physical ones and has a pronounced temperature dependence. We will discuss in section VI how this temperature dependence of chemical clusters makes them special candidates to describe the metal-insulator transition in water in oil microemulsions.

Fig. 4 shows the size distribution function for Stillinger clusters \( n_{\text{Still}}(s) \), chemical clus-
ters $n_{\text{Chem}}(s)$ and physical clusters $n_{\text{Phys}}(s)$. These functions measure the number of clusters of size $s$ per particle. For both, chemical and physical clusters, the number of small clusters is larger than for the Stillinger ones. In the displayed example, $T^* = 1.4$ and $\rho^* = 0.155$, the biggest chemical clusters are approximately of size 60, the biggest physical clusters are of size 200 and the biggest Stillinger clusters are of size 400. The lifetime restriction in the physical clusters avoid the unphysical big aggregates yielded by the Stillinger criterion. This fact suggest that physical clusters could be useful in nucleation studies of saturated vapors.

In Fig. 5 the curves $n_{\text{Still}}(s)$, $n_{\text{Chem}}(s)$ and $n_{\text{Phys}}(s)$ are shown at the corresponding percolation density for each cluster definition. At the percolation density we obtain the power law

$$n(s) = As^{-z},$$

where the exponent has an universal value. Heyes and Melrose got for Stillinger clusters in a Lennard-Jones system $z = 2.1 \pm 0.1$. We found, averaging over all temperatures, $z_{\text{Still}} = 2.05 \pm 0.05$, $z_{\text{Chem}} = 2.14 \pm 0.05$, $z_{\text{Phys}} = 2.30 \pm 0.05$. As we can see, for chemical clusters we have, within the statistical errors, a similar exponent that for the Stillinger ones, whereas for physical clusters we observe that the exponent value differs. We obtained the value of $z_{\text{Phys}}$ for physical cluster with a longer lifetime, $\tau^* = 1.0$, at $T^* = 1.4$, for which percolation density is $\rho_p^* = 0.2 \pm 0.01$ and $z_{\text{Phys}} = 2.41 \pm 0.04$. This show that the critical exponent $z$ is very sensitive to the lifetime selected for physical clusters.

Looking for structural information of the clusters we have calculated its moments of inertia. Surprisingly, we get elongated clusters, no matter which definition is used. Two of the principal moments of inertia ($I_1$ and $I_2$) are always similar between them and larger than the third one ($I_3$). This result was explained by Laría and Vericat when small clusters are under consideration. However, they got approximately spherical big clusters for dipolar hard spheres. In Fig. 6 the ratio $(I_1 + I_2)/(2I_3)$ is plotted as function of the cluster size for each cluster definition. Physical clusters are the more spherical ones, with a more near one ratio. Because big clusters are rare we average $(I_1 + I_2)/(2I_3)$ for all clusters bigger than 20
particles size obtaining \((I_1 + I_2)/(2I_3) = 2.52\). This is far away from the spherical value.

The origin of the difference between our result and the result obtained by Laría and Vericat lies in the fact that we use free boundary conditions in the calculation of the inertia matrix. Unphysical structures are simulated when periodic boundary conditions are used as in the Laría and Vericat work.

Recently, non-spherical clusters in nucleation studies have received special interest. An experimental result shows that spherical particles aggregate in non-spherical clusters at the liquid-solid transition. However, spherical clusters are expected for the gas-liquid transition. Our simulation results show that at liquid densities non-spherical clusters are the more frequent case.

We give here a very simple explanation, based on steric considerations, for the existence of non-spherical clusters. For simplicity, suppose a quasi-circular two-dimensional cluster [see Fig. 7(a)]. If we add a particle in the accessible surface of the cluster a symmetry break down will occur. Now, the accessible surface is greater on the right side of the cluster [see Fig. 7(b)]. This increases the probability that a second particle added at random lands in the right side of the cluster. So, the cluster tends to grow in an elongated structure. Nevertheless, this process cannot go on for ever. If the cluster is very elongated, the lateral accessible surface [top and bottom part in Fig. 7(c)] is very big. Then, the probability that a new particle added at random lands in the lateral region dominate. The mean shape of a cluster will balance the two competing effects. Suppose a cluster with the shape of a spherical caped cylinder (cylinder length \(L\) and caps radius \(R\)) (see Fig. 8). The balance of the mentioned competing effects means that the lateral surface of the cylinder has to be equal to the surface of the caps. So, we chose \(L = 2R\). A solid revolution ellipsoid with semiaxis \(R\) and \(2R\) has a moments of inertia ratio \((I_1 + I_2)/(2I_3) = 2.5\), which is quite similar to the value obtained from our simulations for clusters bigger than 20 particles.

Another structural parameter is the radius of gyration \(R_g\). It is defined for a cluster of size \(s\) as.
\[ R_g^2 = \frac{1}{s} \sum_{i=1}^{s} |r_i - r_{cm}|^2 \]  

(5)

where \( r_i \) is the position of the ith particle in the cluster and \( r_{cm} \) is the position of the centre of mass of the cluster.

\[ r_{cm} = \frac{1}{s} \sum_{i=1}^{s} r_i \]  

(6)

In Fig. 9 we present the radius of gyration as a function of the size of the cluster at the percolation density for each cluster definition. As usual \( R_g \) follows the power law

\[ R_g \propto s^{1/D_f} \]  

(7)

where \( D_f \) is the fractal dimension of the clusters. In our simulation that power law applies only for clusters bigger than 5 particles size. The fractal dimension is the same for all clusters definitions. The chemical and physical clusters are more compact than Stillinger clusters because they have a smaller radius of gyration. In the calculation of \( R_g \) we used free boundary conditions as for all the previous structural quantities.

V. THEORY

A. Chemical clusters

In this section we will summarize the main results of the theory that we have developed elsewhere to describe the clustering and percolation for chemical clusters.

For a system of \( N \) classical particles interacting via a pair potential \( v(r_i, r_j) \) we define a density correlation function \( \rho(r_1, r_2, p_1, p_2) \) which is \( N(N-1) \) times the probability density of finding two particles at phase space points \( (r_1, p_1) \) and \( (r_2, p_2) \) respectively:

\[
\rho(r_1, r_2, p_1, p_2) = \frac{N(N-1)}{h^{3N}N!Q_N(V, T)} \times \int \prod_{i=1}^{N} \exp\left[-\beta \frac{P_i^2}{2m_i}\right] \prod_{i=1}^{N} \prod_{j>i}^{N} \exp[-\beta v(r_i, r_j)] d^{N-2}r d^{N-2}p.
\]  

(8)
Here $h$ is the Planck constant and $Q_N(V,T)$ the canonical partition function of the system. Then, in the same spirit of Hill and Coniglio et. al. we separate $\exp[-\beta v(r_i,r_j)]$ into connecting and blocking parts

$$\exp[-\beta v(r_i,r_j)] = f^\dagger(r_i,r_j,p_i,p_j) + f^*(r_i,r_j,p_i,p_j) + 1 \quad (9)$$

Here $f^\dagger(r_i,r_j,p_i,p_j)$ represent the basic probability density that two particles at configuration $(r_i,r_j,p_i,p_j)$, are bonded. The shorthand notation $f^\gamma(r_i,r_j,p_i,p_j) \equiv f^\gamma_{i,j}$ ($\gamma = \dagger, *$) will be sometimes used.

Substitution of Eq.(9) in Eq.(8) yields

$$\rho(r_1,r_2,p_1,p_2) = \frac{N(N-1)}{h^{3N}N!Q_N(V,T)} \exp[-\beta v(r_1,r_2)] \quad (10)$$

where the sum is carried out over all possible arrangements of products of functions $f^\dagger_{i,j}$ and $f^*_{k,l}$.

It should be noted that the functions $f^\dagger_{i,j}$ and $f^*_{i,j}$ can depend on momenta as well as on the positions of the two particles, but the sum of $f^\dagger_{i,j}$ and $f^*_{i,j}$ must be momenta independent in order that Eq.(9) be satisfied. Except by this last condition, the functions $f^\dagger_{i,j}$ and $f^*_{i,j}$ are otherwise arbitrary for thermodynamic purposes. Obviously we choose them in such a way that the desired definition of bonded particles is achieved:

$$f^\dagger(r_i,r_j,p_i,p_j) = \begin{cases} \exp[-\beta v(r_i,r_j)] |r_{i,j}(t)| < d & \forall t \leq \tau \\ 0 & \text{otherwise} \end{cases} \quad (11)$$

$$f^*(r_i,r_j,p_i,p_j) = \begin{cases} -1 & |r_{i,j}(t)| < d & \forall t \leq \tau \\ \exp[-\beta v(r_i,r_j)] - 1 & \text{otherwise} \end{cases} \quad (12)$$

where $r_{i,j}(t)$ is the relative position of particles $i$ and $j$ at time $t$. We see that, in fact, Eq.(9) is satisfied by Eqs. (11) and (12). Explicitly, time is introduced here by taking the set $\{r^N, p^N\}$ as initial conditions in $t = 0$ and solving the equation of motion of the particles under their mutual interaction.
In order to exactly calculate \( r_{ij}(t) \) for any \( t \) we must solve a many body problem. An approximation can be obtained by reducing it to a two-body problem. This can be done by taking the effective force \( -\nabla v^{\text{eff}}(r_i, r_j) \) composed of the direct force exerted by particle \( j \) on \( i \) \( -\nabla v(r_i, r_j) \) plus the conditional average force exerted by the remaining particles in the system on the particle \( i \). The last is an average over all configurations of the \( N - 2 \) particles keeping \( i \) and \( j \) fixed. Thus
\[
-\nabla v^{\text{eff}}(r_i, r_j) = -\nabla v(r_i, r_j) + \left\langle -\sum_{k \neq i,j} \nabla v(r_i, r_k) \right\rangle_{N-2}.
\]
It can be shown that this approximation corresponds to take \( v^{\text{eff}}(r_i, r_j) = -\ln[g(r_i, r_j)]/\beta \).
This way \( r_{i,j}(t) \) is obtained in terms of just the initial values \( r_i, r_j, p_i \) and \( p_j \).

Equation (11) states that two particles \( i \) and \( j \) are bonded if they are separated by a distance shorter than \( d \) during a time interval longer than \( \tau \). This coincides with the definition introduced in section II for chemical clusters.

Each term in the integrand of Eq.(11) can be represented as a diagram consisting of two white \( e_1 \) and \( e_2 \)-points, \( N - 2 \) black \( e_i \)-points and some \( f_{i,j}^\dagger \) and \( f_{i,j}^* \) connections except between the white points. Here we take \( e_i \equiv \exp[-\beta \frac{p_i^2}{2m}] \). White point are not integrated over whereas black points are integrated over their positions and momenta. All the machinery normally used to handle standard diagrams in classical liquid theory can be now extended to treat these new kind of diagrams. By following the Coniglio recipe to separate connecting and blocking parts in correlation functions i.e. \( g(r_1, r_2) = g^\dagger(r_1, r_2, p_1, p_2) + g^*(r_1, r_2, p_1, p_2) \), we obtain an Ornstein-Zernike like integral equation for \( g^\dagger(r_1, r_2, p_1, p_2) \)
\[
g^\dagger(r_1, r_2, p_1, p_2) = c^\dagger(r_1, r_2, p_1, p_2)
+ \int \rho(r_3, p_3)c^\dagger(r_1, r_3, p_1, p_3)g^\dagger(r_3, r_2, p_3, p_2)dr_3dp_3.
\]
\[
\rho(r_1, p_1) = \frac{1}{N - 1} \int \rho(r_1, r_2, p_1, p_2) dr_2 dp_2.
\] (14)

The function \( c^\dagger(r_1, r_2, p_1, p_2) \) denotes the sum of all the non-nodal diagrams in the diagrammatic expansion of \( g^\dagger(r_1, r_2, p_1, p_2) \). We remember that a nodal diagram contains at least a black point through which all paths between the two white points pass.

For homogeneous systems we have

\[
g^\dagger(r_1, r_2, p_1, p_2) = c^\dagger(r_1, r_2, p_1, p_2) + \frac{\rho}{(2\pi mk_BT)^{3/2}} \times \int \exp[-\beta \frac{p^2}{2m}] c^\dagger(r_1, r_3, p_1, p_3) g^\dagger(r_3, r_2, p_3, p_2) dr_3 dp_3.
\] (15)

To get an integral equation from Eq. (13) is necessary a closure relation between \( g^\dagger(r_1, r_2, p_1, p_2) \) and \( c^\dagger(r_1, r_2, p_1, p_2) \). We take the Percus-Yevick approximation \( g(r_1, r_2) \exp[\beta v(r_1, r_2)] = 1 + N(r_1, r_2) \), where the function \( N(r_1, r_2) \) is the sum of the nodal diagrams in the expansion of \( g(r_1, r_2) \). Separation into connecting and blocking parts i.e. \( g(r_1, r_2) = g^\dagger(r_1, r_2, p_1, p_2) + g^\star(r_1, r_2, p_1, p_2) \) and \( N(r_1, r_2) = N^\dagger(r_1, r_2, p_1, p_2) + N^\star(r_1, r_2, p_1, p_2) \), yields

\[
g^\dagger(r_1, r_2, p_1, p_2) = \left[ f^\star(r_1, r_2, p_1, p_2) + 1 \right] [g^\dagger(r_1, r_2, p_1, p_2) - c^\dagger(r_1, r_2, p_1, p_2)]
\] (16)

\[+ \exp[\beta v(r_1, r_2)] g(r_1, r_2) f^\dagger(r_1, r_2, p_1, p_2).\]

Eq. (13) closed by Eq. (16) gives an integral equation for \( g^\dagger(r_1, r_2, p_1, p_2) \).

From the function \( g^\dagger(r_1, r_2, p_1, p_2) \) we define the pair correlation function for chemical clusters

\[
g_{\text{Chem}}(r_1, r_2) = \int \rho(r_1, p_1) \rho(r_2, p_2) g^\dagger(r_1, r_2, p_1, p_2) dp_1 dp_2.
\] (17)

It is the joint probability density of finding two particles that belong to the same chemical cluster at positions \( r_1 \) and \( r_2 \), respectively.

Then, the mean cluster size \( S_{\text{chem}} \) is given by Eq. (1) and the percolation density is calculated from Eq. (2) with \( \gamma = \text{Chem} \):

\[
S_{\text{Chem}} = 1 + \frac{1}{(N - 1)} \int g_{\text{Chem}}(r_1, r_2) dr_1 dr_2,
\]
\[ \lim_{\rho \to \rho_c} S_{Chem}(\rho) = \infty. \]

**B. Weak criterion for physical clusters**

In order to treat the physical clusters within a theoretical framework we will restrict ourself to a weak version of the definition introduced in section III. The weak criterion is established as follows

Two particles of the system belong to the same physical cluster at the time \( t \) if at that time exists a path of directly connected particles which link them, and all particles forming the path, including the two particles under study, were connected in time \( t - \tau \).

Connected and directly connected are understood in the Stillinger sense. The difference with the strong criterion established in Section III is that in the weak version we require that the particles be connected just at the extremes of the time interval and not during the whole interval. The idea for the future is to use the results obtained from this definition within a path-integral like formalism in order to describe clusters according to the strong criterion.

Consider the function \( H(r_1, r_2) \) introduced by Xu and Stell in their “percolation in probability” theory. This function measures the basic conditional probability for two particles to be directly connected if they are at positions \( r_1 \) and \( r_2 \), respectively. The role of this function within Hill formalism is that of an auxiliary function in the Boltzmann factor separation into bonded and unbounded terms:

\[ e^b_{i,j} = H(r_i, r_j) e(r_i, r_j) \]

\[ e^s_{i,j} = [1 - H(r_i, r_j)] e(r_i, r_j). \]

Each choice of \( H(r_i, r_j) \) corresponds to a different bond definition. For example, for the Stillinger’s definition of directly connected particles we have
\[ H(r_1, r_2) = H(r_{1,2}) = \begin{cases} 1 & r_{1,2} \leq d \\ 0 & r_{1,2} > d \end{cases} . \]

To define bonded particles according with the weak criterion of physical clusters, we use:

\[ H(r_1, r_2) = H(r_{1,2}; \tau) = \begin{cases} \frac{N h^\dagger(r_{1,2}; \tau)}{\rho g(r_{1,2})} & r_{1,2} \leq d \\ 0 & r_{1,2} > d \end{cases} , \tag{19} \]

where \( h^\dagger(r_{1,2}; \tau) \) is the probability density of finding two particles connected at time \( t - \tau \) and in relative position \( r_{1,2} \) at time \( t \). Clearly, this selection of \( H(r_{1,2}; \tau) \) considers as bonded any two particles which are separated by a distance shorter than \( d \) and have been connected (directly or not) at time \( t - \tau \). We explicitly include \( \tau \) in the functions to stress the life time dependence.

Once the direct bond is defined, a connectivity Ornstein-Zernike relation between the pair correlation function \( g_{\text{phys}}(r_{1,2}; \tau) \) and the direct correlation function for physical clusters \( c_{\text{phys}}(r_{1,2}; \tau) \) can be obtained in the standard form \(^{46,47} \):

\[ g_{\text{phys}}(r_{1,2}; \tau) = c_{\text{phys}}(r_{1,2}; \tau) + \rho \int c_{\text{phys}}(r_{1,3}; \tau) g_{\text{phys}}(r_{3,2}; \tau) \, dr_3. \tag{20} \]

The function \( g_{\text{phys}}(r_{1,2}; \tau) \) is \( N(N - 1) \) times the probability density of finding two particles in positions \( r_1 \) and \( r_2 \) and belonging to the same physical cluster.

In order to solve equation (20) a closure relation is needed. For \( r_{1,2} \leq d \), we see that \( g_{\text{phys}}(r_{1,2}; \tau) \) is exactly equal to \( \frac{N}{\rho} h^\dagger(r_{1,2}; \tau) \), because the conditional probability density that two particles belong to the same physical cluster under the assumption they were connected at \( t - \tau \) is equal to one if they are separated by a distance shorter than \( d \). For \( r_{1,2} > d \) we can use the Percus-Yevick connectivity closure \(^{47} \).

The calculation of \( h^\dagger(r_{1,2}; \tau) \) remains to be discussed. Consider the temporal correlation function introduced by Oppenheim and Bloom in the study of nuclear spin relaxation \( G(r'_{1,2}, r_{1,2}, t) \). This function is the probability density of finding two particles in relative position \( r'_{1,2} = r_2' - r_1' \) at an initial time and in relative position \( r_{1,2} = r_2 - r_1 \) at time \( t \) later. It is given by
\[ G(r'_{1,2}, r_{1,2}, t) = \frac{1}{N(N-1)} \]
\[ \times \left\langle \sum_{i}^{N} \sum_{j \neq i}^{N} \delta \left[ r'_{1,2} - (r_i(0) - r_j(0)) \right] \delta \left[ r_{1,2} - (r_i(t) - r_j(t)) \right] \right\rangle, \]

where \( \delta(x) \) is Dirac’s delta function and \( \langle \cdot \rangle \) mean an average over all initial configurations in the canonical ensemble. In the case of an ideal gas, i.e. non-interacting particles of mass \( m \), \( G(r'_{1,2}, r_{1,2}, t) \) is exactly given by

\[ G(r_{1,2}, r'_{1,2}, t) = \rho N \left( \frac{\beta m}{4\pi \tau^2} \right)^{3/2} \exp \left[ -\frac{\beta m(r_{1,2} - r'_{1,2})^2}{4\tau^2} \right]. \] (22)

For systems with non-null interaction some approximations for \( G(r'_{1,2}, r_{1,2}, t) \) have been reported.\(^48\)–\(^50\).

Now we define

\[ h^\dagger(r_{1,2}; \tau) = \int \frac{g_{\text{Still}}(r'_{1,2})}{g(r'_{1,2})} G(r'_{1,2}, r_{1,2}, \tau) dr'_{1,2}, \] (23)

where \( g_{\text{Still}}(r'_{1,2}) \) is the pair correlation function for Stillinger clusters and \( g(r'_{1,2}) \) is the ordinary pair correlation function. The function \( h^\dagger(r_{1,2}; \tau) \) is proportional to the probability density of finding two particles connected at time \( t - \tau \) and in relative position \( r_{1,2} \) at time \( t \). Note that in the final time \( t \) the particles can be connected or not, but they must be in relative position \( r_{1,2} \), whereas in the initial time they must be connected whatever the relative position is.

We have applied the previous formalism to an ideal gas. In this case \( g(r_{1,2}) \equiv 1 \) and \( G(r_{1,2}, r'_{1,2}, \tau) \) is given by Eq.(22).

The correlation function for Stillinger clusters \( g_{\text{Still}}(r_{1,2}) \) was obtained, for this system, by Chiew and Glandt in the Percus-Yevick approximation \( [c^\dagger(r_{1,2}) = 0 \text{ for } r_{1,2} > d] \).\(^15\)

We used this solution to obtain \( h^\dagger(r_{1,2}; \tau) \) from equation (23). As we have mentioned, \( g_{\text{Phys}}(r_{1,2}; \tau) \) is known exactly for \( r_{1,2} \leq d \). To close equation (20) we take the approximation: \( c_{\text{Phys}}(r_{1,2}; \tau) = 0 \text{ for } r_{1,2} > d \). By using the Baxter’s factorization method\(^2\) and the Perram’s algorithm\(^3\) we have solved the integral equation for \( g_{\text{Phys}}(r_{1,2}; \tau) \) in \( r_{1,2} > d \).
In order to analyze the approximations we have introduced in our theoretical approach, we have also simulated by molecular dynamics the non-interacting system and have obtained the pair correlation function for physical clusters defined in the weak sense. The simulation algorithm to identify the weak physical clusters is slightly different from that considered in Subsection IV-B for the strong criterion. It is carried out as follow:

1) Identify a Stillinger cluster at \( t - \tau \).

2) Move the particles of this cluster to the new positions in \( t \) without using periodic boundary conditions. In an ideal gas periodic boundary conditions are unphysical.

3) Identify the Stillinger clusters in the new configuration for the particles selected in 1.

These clusters are the physical clusters.

4) Repeat from 1 until cover all initial Stillinger clusters.

Fig. 10 shows the function \( g_{\text{Phys}}(r_{1,2}; \tau) \), obtained from our theory and simulation for the weak physical clusters at reduced density \( \rho^* = \rho d^3 = 0.2 \) and various reduced life times \( \tau^* = \tau/(d\sqrt{\beta m}) \). When \( \tau^* \to 0 \) we recover the Stillinger clusters \( g_{\text{Phys}}(r_{1,2}; \tau = 0) = g_{\text{Still}}(r_{1,2}) \).

In Fig. 11 we present the mean cluster size for the physical clusters as a function of \( \tau^* \) for various values of \( \rho^* \) obtained from Eq.(1) with \( \gamma = \text{Phys} \):

\[
S_{\text{Phys}} = 1 + \frac{1}{(N - 1)} \int g_{\text{Phys}}(r_1, r_2) dr_1 dr_2.
\]

At low densities, \( \rho^* < 0.3 \), the theory fits very well the simulation results. For higher densities the approximations used for \( g_{\text{Still}}(r_{1,2}) \) and \( c_{\text{Phys}}(r_{1,2}; \tau) \) for \( r_{1,2} > d \) lead to poor results.

VI. COMMENTS

A. Summary and further developments

In this work we have introduced two criteria for the cluster identification in continuum systems. Both criteria are based in the dynamics of the system. The first one uses a residence time in the definition of the bond between pairs of particles, the second one uses a life time...
in the definition of an aggregate. Due to the qualitative features of the clusters yielded by the criteria we call them chemical and physical clusters, respectively.

The main results that show the differences between chemical, physical and the traditional Stillinger clusters are collected below.

**Physical clusters:**

a) The percolation curve presents a slope similar to the corresponding curve for Stillinger clusters. However, this curve locates at higher densities than for the Stillinger case.

b) The clusters are more spherical than the Stillinger ones for sizes smaller than 20 particles. For clusters bigger than 20 particles size, physical and Stillinger clusters have the same shape and are always elongated.

c) Big clusters are rare in comparison with Stillinger clusters. At percolation density a power law is followed by the cluster size distribution, but with a strongly $\tau$-dependent critical exponent.

d) The fractal dimension of the clusters is the same that for Stillinger clusters but the physical ones are more compact.

**Chemical clusters:**

a) The percolation curve present a small slope as compared with the corresponding Stillinger curve. If the same value of $\tau$ is used for physical and chemical clusters, then the percolation curve appears at higher densities in the chemical case.

b) The sphericity of the chemical clusters is in between the physical and the Stillinger ones.

c) At the percolation density a power law is followed by the cluster size distribution with an almost $\tau$-independent critical exponent.

d) The fractal dimension of the clusters is the same that for Stillinger clusters but the chemical ones are as compact as the physical clusters.

The definitions used in this work restricts us to use molecular dynamics simulation, because the trajectory of the particles must be known. To determine which particle belong to a given clusters at a given time $t$ simulations need to be run between $t - \tau$ and $t$ in very
short time steps. This takes a large computing time. Thus, approximate theories are very much desirable to be developed.

The solution of Eq. (13) for chemical clusters is a very difficult task. Tensors of rank 9 must be used to store correlation functions and a double convolution has to be solved. Recently, F. Lado has developed a method to calculate the pair correlations for a polarizable Lennard-Jones system which is based on expanding the relevant functions in orthogonal polynomials. The integral equation he has to solve is similar to Eq. (13) but with \( p_1 \) and \( p_2 \) representing the induced dipolar moments of the particles 1 and 2 respectively. We are currently working in the application of Lado’s code to the chemical clustering problem for Lennard-Jones particles.

In the theory for physical clusters the main difficulty is to have a good approximation for \( G(r_{1,2}, r_{1,2}, t) \) and \( g_{\text{Still}}(r_{1,2}) \). In one hand, the present theories to calculate the correlation function for Stillinger clusters do not provide it for densities higher than the percolation density. Because percolation densities are higher for physical than for Stillinger clusters the theory developed here is unable to give results for densities close to the “physical” percolation density. In other hand, approximations for \( G(r_{1,2}, r_{1,2}, t) \) in interacting systems are available just for the limiting cases \( t \approx 0 \) and \( t \approx \infty \).

Because the theory developed for physical clusters correspond to a weak criterion, an improved theory to describe the physical clusters introduced in section III is desirable. We hope that using a path integral approach in the interval \( [t - \tau, t] \), where the weak criterion is used in each step of the path, the “strong” criterion could be reached.

**B. Potential applications**

Water in oil microemulsions are formed by mixing water, oil and a surfactant. Surfactant configuration favors the formation of inverted micelles with water inside and oil external to spherical structures. When the micellar concentration is low, the system is a poor electrical conductor. Nevertheless, when the concentration of micelles increases beyond a critical value
a conducting behavior is present. This conductor-insulator transition has been explained by a continuum percolation model. When an aggregate of micelles spans the system, charge carriers hop from micelle to micelle in the aggregate and the system becomes a conductor. The process of passing a charged carrier from a given micelle to another one to which the former is directly connected requires some time. One can think of at least two ways of modeling this feature. In one of them the real pair attraction between micelles is exaggerated using, for example, sticky potentials to mimic the real intermicellar bonds. In the other one, we consider a pair potential closer to the real one and require the two micelles be connected during a time longer than $\tau$. This last point of view agrees with the idea of a chemical cluster.

Most of the work on conductor/transition in microemulsions has followed the first approach. Thus, the percolation curve for Stillinger clusters in a sticky hard spheres system was shown to fit the experimental conductor-insulator curve for water/decane/sodium-bis(2-ethylhexil)sulfosuccinate. The curve has a peculiar behavior: it presents a small slope as compared with any other system. This behavior coincides with that presented by the chemical clusters in a Lennard-Jones system as we expect from the considerations above: the sticky spheres can be defined as bonded by just requiring a geometrical restriction in a given instant. As the interaction potential is infinitely deep at contact no residence time is necessary to impose in order to ensure a real bond. However, a continuum pair potential is a more realistic interaction for micelles and, in that case, the Stillinger criterion is not able to describe the conductor-insulator transition for water in oil microemulsions. In conclusion, the hopping time, e.g. the minimum time two micelles have to be close in order for a charge carrier to hop between them, seems to be necessary if realistic intermicellar pair potentials are going to be considered. The chemical clusters provide an accurate model to describe the conductor-insulator transition in this case. The values of $d$ and $\tau$, for a chemical bond in Section II, can be used for water-in-oil microemulsions as the maximum distance and minimum time required to allow charge carriers to hop between two given micelles.

As we mentioned, the concept of cluster is of fundamental importance in nucleation
studies on saturated vapors. These theories concern the growth of liquid-density-aggregates in a saturated vapor, which are the seed of a liquid phase. A comparative study of different clustering criteria was done recently by Senger et al. The most frequently used criterion for clusters identification in nucleation studies is the Stillinger criterion and some improved versions of it. Nevertheless, this criterion can wrongly consider as part of a cluster some gas particles which are close to the cluster for a short time. In this way the cluster density will be lower than the density of the cluster obtained by considering that those particles do not belong to it. Also, the Stillinger criterion consider two physical clusters, which are close together for a very short time, as a single cluster. And a single cluster formed of two real clusters joined by only a point during just a very short period of time, will have a density of particles that is lower than the corresponding density inside each of the two separated clusters.

Several modifications have been used to avoid this unphysical cluster counting. However, the inclusion of dynamical information in the identification of clusters has been proposed as essential in selecting long-lived clusters in nucleation studies. Although we have studied systems which are in equilibrium, it is possible to use the previous clusters definitions in computer simulations of non-equilibrium systems also. We hope the physical clusters introduced in this work could contribute to a more appropriate identification of the relevant clusters in nucleation because their existence depends on a life time restriction.

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Figures Captions

Figure 1: Physical cluster identification. a) Position of the particles at $t - \tau$. The two Stillinger clusters are painted in different ways. b) Position of the particles at $t$. The
two new Stillinger clusters are painted in different ways. c) As in (b) but the four physical clusters are painted in different ways. d) As in (b) but the five chemical clusters are shown.

**Figure 2:** Correlation function for the clusters at $T^* = 1.4$ and $\rho^* = 0.155$. Circles, triangles and diamonds correspond to Stillinger, chemical and physical clusters respectively. The dotted line is the (ordinary) radial distribution function. The selected density is the percolation density for Stillinger clusters.

**Figure 3:** Percolation curve for the Lennard-Jones fluid. Circles, triangles and diamonds correspond to Stillinger, chemical and physical clusters respectively. Solid squares correspond to the coexistence curve\textsuperscript{39}

**Figure 4:** Log-Log plot of the cluster size distribution. Solid, dotted and dashed line correspond to Stillinger, chemical and physical clusters respectively. $T^* = 1.4$ and $\rho^* = 0.155$ in all cases.

**Figure 5:** Log-Log plot of the cluster size distribution. Circles, triangles and diamonds correspond to Stillinger, chemical and physical clusters respectively. In each case the percolation density for $T^* = 1.4$ was chosen. The $z$ values were obtained by linear regression.

**Figure 6:** Ratio between the largest ($I_1$ and $I_2$) and smaller ($I_3$) moments of inertia as function of the cluster size. Circles, triangles and diamonds correspond to Stillinger, chemical and physical clusters respectively. The horizontal solid line is the averaged value over all clusters larger than 20 particles size.

**Figure 7:** Two dimensional aggregates.

**Figure 8:** Average shape of a big cluster.

**Figure 9:** Log-Log plot of the radius of gyration as a function of the cluster size at $T^* = 1.4$ and percolation density. Circles, triangles and diamonds correspond to Stillinger, chemical and physical clusters respectively. The fractal dimension was obtained by linear regression.

**Figure 10:** $g_{\text{phys}}(r_{1,2}; \tau)$ vs. $r_{1,2}$ for $\rho^* = 0.2$, theory (solid line) and simulation (symbols). Diamonds, circles, triangles and squares correspond the $\tau^* = 0, 0.1, 0.316$ and 1.0 respectively. Note the scale change at $r_{1,2}/d = 1$. 

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Figure 11: Inverse of the mean cluster size for physical clusters as a function of $\tau^*$, theory (solid line) and simulation (symbols). Squares, circles and triangles correspond to $\rho^* = 0.2, 0.3$ and 0.5 respectively.
(a) 

(b) 

(c) 

(d)
$T^* = 1.4$  
$\rho^* = \rho_p^*$  
$z_{\text{Still}} = 2.05 \pm 0.02$  
$z_{\text{Chem}} = 2.12 \pm 0.02$  
$z_{\text{Phys}} = 2.31 \pm 0.03$
\( (I_1 + I_2)/(2 I_3) \)

\( \rho^* = 0.155 \)
\( T^* = 1.4 \)

Cluster size
$T^* = 1.4$

$\rho^* = \rho_p^*$

$D_{f(\text{Still})} = 2.09 \pm 0.06$

$D_{f(\text{Chem})} = D_{f(\text{Phys})} = 2.19 \pm 0.06$

$R_g(s)$ vs. $s \ (\text{cluster size})$
$g_{\text{Phys}}(r, \tau)$

$r/d$

0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
1.05
1.10
1.15
1.20
1.25
1.30
1.35
1.40
1.45
1.50
1.55
1.60
1.65
1.70
1.75
1.80
1.85
1.90
1.95
2.00
2.05
2.10
2.15
2.20
2.25
2.30
2.35
2.40
2.45
2.50
2.55
2.60
