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Clustering and percolation theory for continuum systems: Clusters with nonspecific bonds and a residence time in their definition

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ABSTRACT

In this article, dedicated to the memory of Lesser Blum, we develop a theory for the physical clusters which were introduced some time ago in our group (J. Chem Phys. **116**, 1097–1108, 2002). The physical cluster definition establishes that a system particle belongs to the cluster if it is (nonspecifically) bonded to other particles of the cluster along a finite time period τ (the residence time). Our theory has as main ingredients the Stillinger criterion of instantaneous connectivity, that involves a connectivity distance d, the generalized time-dependent pair distribution function of Oppenheim and Bloom that acts as a classical propagator and also the cluster pair correlation function for a weaker version of the physical clusters that requires connectivity just at the extremes of the time period no matter what happens in between. With these tools we express the time dependent pair connectedness function for the physical clusters in the strong sense as a path integral. The path integral is solved by means of a perturbation expansion where the nonperturbed connectedness function coincides with the generalized pair distribution function of Oppenheim and Bloom. We apply the theory to Lennard-Jones fluids at low densities and perform molecular dynamics simulations to check the goodness of diverse functions that appear in the theory.

This work is dedicated to the memory of Lesser Blum: enlightening professor, generous colleague and unforgettable friend.

1. Introduction

Many interesting natural phenomena arise in systems whose macroscopic properties are related to the formation of aggregates of their constituent particles. We can mention, among many others, the insulator-conductor [1], the sol-gel [2] and the glassy [3,4] transitions observed in several materials; the behavior of supercooled water [5,6], aggregation and agglutination phenomena in cells and biological macromolecules and organelles [7–9], the flow of fluids in porous media [10], earthquakes and fractures in the terrestrial crust [11–13], and the large-scale structure of the Universe [14–16]. Frequently these phenomena can properly be studied by using the ideas of clustering and percolation.

A rough drawing of clustering and percolation theoretic studies shows that two main approaches have commonly been used. In one of them the system particles are restricted to occupy just the sites of given lattices (see e.g. Refs. [17,18]); in the other one they can move through continuum regions. Here we will restrict ourselves to the lattice-free (continuum) approach.

Continuum percolation is normally associated with the existence of "real" clusters that become macroscopic in size. The clusters we are talking about were already considered many years ago by Bijl [19], Band [20] and Frenkel [21] (among others) and must be distinguished from the more familiar Mayer's mathematical clusters used in the diagrammatic virial expansion of the imperfect gases [22].

Most of the present day theories of clustering and percolation are based on the work of Terrel L. Hill. In Hill ' s theory [23] the concept of cluster is directly related to that of ("instantaneous") connectivity: two particles belong to the same cluster if they are connected trough

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an instantaneous 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).

The original 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 [23]. Very frequently, however, a geometrical criterion is used instead of the energetic one. For spherically symmetric particles that interact via radial pair potentials $V(r_{12})$ where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ ($\mathbf{r}_i \equiv$ position of the center of particle i), a very common specification (Stillinger criterion) considers that two particles are bonded if they are separated by a distance smaller than certain parameter d which is called the connectivity distance [24].

In this context, the Boltzmann factor $e(r_{12}) \equiv exp[-\beta V(r_{12})]$, where $\beta = (k_B T)^{-1}$ with k_B the Boltzmann constant and T the absolute temperature can be split into bonded (†) and unbonded (*) terms: $e(r_{12}) = e^{\dagger}(r_{12}) + e^{*}(r_{12})$ and, since it is the statistical weight in the configurational integrals, all the pair functions can be separated in a similar way in "connectedness" and "blocking" parts. In particular, the pair distribution function is written: $\rho(r_{12}) = \rho^{\dagger}(r_{12}) + \rho^{*}(r_{12})$. The pair-connectedness density function $\rho^{\dagger}(r_{12})$ plays a central role in the clusters theory. This function, that was introduced some time ago by Coniglio and collaborators [25,26], very properly describes the particles distribution inside the clusters. It represents the probability density of finding two particles connected and separated by a distance r_{12}.

Fugacity and density expansions similar to those obtained by Mayer and Montroll [27] for the ordinary pair correlation function $g(r_{12})$ has been found [25,26], within Hill-Coniglio formalism, for the pair connectedness correlation function $h^{\dagger}(r_{12}) = \rho^{\dagger}(r_{12})/\rho$, where $\rho = N/V$ is the system density. Moreover, by collecting nodal and non-nodal diagrams in these expansions, an Ornstein-Zernike (OZ) like relation is obtained [25,26] from which integral equations for $h^{\dagger}(r_{12})$ can be posed [28]. This way, several approximate integral equations for the pair-connectedness function have been derived [28–34] and solved for diverse fluid models [29–42].

The cluster pair correlation function in the geometrical criterion of Stillinger $g_{Still}(r_{12}; d)$, say the density probability of finding two particles of the same cluster at a relative distance r_{12}, and the connectedness total correlation function are both the same object: $g_{Still}(r_{12}; d) \equiv h^{\dagger}(r_{12}; d)$. Thus, the mean cluster size can be obtained in the form $S(\rho) = 1 + 4\pi\rho \int_0^{\infty} g_{Still}(r_{12}; d) r_{12}^2 dr_{12}$ so that the critical percolation density ρ_p verifies $\lim_{\rho \to \rho_p} S(\rho) = \infty$. This equation expresses in mathematical language the meaning of ρ_p: the density at which a macroscopic fraction of particles first become connected.

The use of an instantaneous geometrical criterion to decide whether two particles are bonded can be meaningful in some application where the fact that particles are close together for an instant is sufficient to describe the phenomenon under study. However, in most real experiments, clusters and the involved particle-particle bonds need to last for some minimum period of time in order to allow the occurrence of the phenomenon in question. Examples where the finite value of the bond lifetime is of crucial importance to the understanding of the clustering and percolation phenomena include the formation of hydrogen bonds in liquid and glassy water [6,43].

In our group, we have taken into account this point and have considered to introduce clusters that incorporate a residence time in their definition. So, in reference [44], two new criteria for the clusters identification, which generalize the instantaneous geometric criterion of Stillinger by adding a residence time to decide when the particles belong to them, have been proposed. In the definitions we demand that, in order to belong to the cluster, a given particle must be bonded to another one of the cluster along a finite time period τ (the residence time). But, whereas in one of the criteria we require that this second particle be always the same one during the whole time interval τ, in the other criterion the second particle need not to be the same one along the residence time, but it is enough that at each instant of the complete time period it simply be any one of the cluster particles. We call the clusters so defined *chemical clusters* and *physical clusters*, respectively, in an obvious analogy with the concepts of chemical (or specific) adsorption and physical adsorption. These clusters are such that when the residence time is zero they reduce to the Stillinger clusters.

In previous works we have exhaustively studied the chemical clusters for the Lennard-Jones fluid using molecular dynamics simulations [44]. This way we could observe the close relation between the percolation loci and the low-density branch of the liquid-solid coexistence curve [45]. Also, for the chemical clusters we have posed an Ornstein-Zernike like equation for the connectedness function $g^{\dagger}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2; d, \tau)$ which is proportional to the joint probability density of finding two particles at positions $\mathbf{r}_1$ and $\mathbf{r}_2$ with momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, respectively, and belonging to the same chemical cluster [44,46]. We have closed this equation with a Percus-Yevick like relation for the connectedness functions together with the condition that the direct bond between each pair of cluster particles lasts during the whole residence time τ and have solved the resulting integral equation for $g^{\dagger}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2; d, \tau)$ using an orthogonal polynomial approach [47]. This function is related to the pair correlation function for chemical clusters $g_{Chem}(r_{12}; d, \tau)$ according to $g_{Chem}(r_{12}; d, \tau) = \int \rho(\mathbf{r}_1, \mathbf{p}_1)\rho(\mathbf{r}_2, \mathbf{p}_2) g^{\dagger}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2; d.\tau) d\mathbf{p}_1 d\mathbf{p}_2$ where $\rho(\mathbf{r}_1, \mathbf{p}_1)$ is the one point density function.

We have performed molecular dynamics simulations for the physical clusters in Lennard-Jones fluids too [44]. The results in this case suggest [45] that physical clusters are more accurate for describing the gas-liquid coexistence than the chemical clusters are. In Ref. [44], we have tried to develop also a theory for the pair correlation function of physical clusters $g_{Phys}(r_{12}; d, \tau)$ for systems of spherically symmetric particles. However, as a previous step, we had to consider a weaker version of them, say $g_{Phys;W}(r_{12}; d, \tau)$, where we require that, in order that a given particle belongs to the cluster, it is sufficient that it be bonded (in the Stillinger sense) to others of the cluster just at the origin t and the end $t + \tau$ of the time period, no matter what happens in between. For $g_{Phys;W}(r_{12}; d, \tau)$ an integral equation determined by an OZ like relation with closures that involve the functions $g_{Still}(r_{12}; d)$ and $G(\mathbf{r}_{12}, \mathbf{r}'_{12}, \tau)$ was solved for the ideal gas. The generalized time-dependent pair distribution function $G(\mathbf{r}_{12}, \mathbf{r}'_{12}, t)$, which is a central object in our theory of physical clusters, was introduced by Oppenheim and Bloom in relation with the nuclear spin relaxation in fluids [48,49]. It is the joint probability density of finding two particles in relative position $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ at an initial time and in relative position $\mathbf{r}'_{12} = \mathbf{r}'_2 - \mathbf{r}'_1$ at a time t later.

The aim of the present work is to follow developing a theory for the physical clusters and their application to Lennard-Jones fluids. To this end, in the next Section, we consider the generalized time-dependent pair distribution function that we will need further. Following previous works [48–51], we present an approximated theoretic expression for $G(\mathbf{r}_{12}, \mathbf{r}'_{12}, \tau)$ to be used along the paper and compare them with molecular dynamics calculations. Section 3 is devoted to the weak criterion for physical clusters. We consider two approximations for $g_{Phys;W}(r_{12}; d, \tau)$. One [44] is the already mentioned integral equation defined by an OZ like relation with closures that involve the functions $g_{Still}(r_{12}; d)$ and $G(\mathbf{r}_{12}, \mathbf{r}'_{12}, \tau)$. The other one is the integral $g_{Phys;W}(r_{12}; d, \tau) = \int h_W^{\dagger\dagger}(\mathbf{r}_{12}, \mathbf{r}'_{12}; \tau) d\mathbf{r}'_{12}$ where the function $h_W^{\dagger\dagger}(\mathbf{r}_{12}, \mathbf{r}'_{12}; \tau)$, that accounts for the joint probability density that two particles which are initially connected at a relative position $\mathbf{r}_{12}$ will be also connected at a relative position $\mathbf{r}'_{12}$ at a time τ later, is given by a simple product relation that involves again the functions $g_{Still}(r_{12}; d)$ and $G(\mathbf{r}_{12}, \mathbf{r}'_{12}, \tau)$. We perform molecular dynamics runs to analyze the goodness of both approximations for Lennard-Jones fluids and, very especially of $h_W^{\dagger\dagger}(\mathbf{r}_{12}, \mathbf{r}'_{12}; \tau)$ at very short residence

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times because, in Section 4, we will use $h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};\epsilon)$ for small ϵ to calculate $g_{Phys}(r_{12};d,\tau)$. The idea is to divide the finite interval τ into subintervals of length $\epsilon=\tau/n(n\to\infty)$; to assume that for residence times ϵ small enough the connectedness function for strong physical clusters, $h^{\dagger\sim\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};\epsilon)$, is well approximated by $h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};\epsilon)$ and finally to pose a path integral for $g_{Phys}(r_{12};d,\tau)$ in the whole residence time τ. After comparison of $g_{Phys}(r_{12};d,\tau)$ so obtained with simulation results, the paper is closed by giving some conclusions in Section 5.

2. Generalized time-dependent pair distribution function

The generalized time-dependent pair distribution function of Oppenheim and Bloom [48,49] $G(\mathbf{r}_{12},\mathbf{r}'_{12},\tau)$ plays a fundamental role in our theory of physical clusters, so we will study it with some detail. We briefly review the semiclassical approach of Borysow et al. [51] that gives theoretic expressions which allow to calculate it with diverse degree of approximation. Besides, we also consider the calculation of $G(\mathbf{r}_{12},\mathbf{r}'_{12},\tau)$ from molecular dynamics trajectories in order to compare with the theoretic results.

2.1. Theory

As was mentioned, the function $G(\mathbf{r}_{12},\mathbf{r}'_{12},\tau)$ gives the joint probability density of finding two particles in relative position $\mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1$ at an initial time and in relative position $\mathbf{r}'_{12}=\mathbf{r}'_2-\mathbf{r}'_1$ at a time t later . It can be written as [50]

$$G(\mathbf{r}_{12},\mathbf{r}'_{12};t)=\frac{1}{N}\left\langle\sum_i^N\sum_{j\neq i}^N\delta\left[\mathbf{r}_{12}-\mathbf{r}_{ij}(0)\right]\delta\left[\mathbf{r}'_{12}-\mathbf{r}_{ij}(t)\right]\right\rangle, \tag{1}$$

where $\mathbf{r}_{ij}(t)=\mathbf{r}_i(t)-\mathbf{r}_j(t)$; $\delta(x)$ is the Dirac delta function and $\langle.\rangle$ means a canonical average carried out over all initial configurations. Since the system is in equilibrium, $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ is invariant under time translation. The function $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ verifies

$$G(\mathbf{r}_{12},\mathbf{r}'_{12};t=0)=g(r_{1,2})\delta(\mathbf{r}'_{12}-\mathbf{r}_{12}) \tag{2}$$

and

$$\int G(\mathbf{r}_{12},\mathbf{r}'_{12};t)d\mathbf{r}'_{12}=g(r_{1,2}), \tag{3}$$

where $g(r_{12})$ denotes the ordinary pair correlation function.

Here we use for $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ a semiclassical approach in the stationary phase approximation as developed by Borysow et al. [51]. We write:

$$G(\mathbf{r}_{12},\mathbf{r}'_{12};t)=\left(\frac{2\pi\hbar^2\beta}{\mu}\right)^{3/2}\times \times K(\mathbf{r}',\mathbf{r}_{12};t-i\hbar\beta)K(\mathbf{r}_{12},\mathbf{r}'_{12};-t) \tag{4}$$

with $\mu=m/2$ the reduced mass (m the particles mass). In this equation appears the Feymann propagator defined, in terms of the Hamiltonian H of relative motions, as

$$K(\mathbf{r}_{12},\mathbf{r}'_{12};t)=\left\langle\mathbf{r}'_{12}\left|\exp(-iHt/\hbar)\right|\mathbf{r}_{12}\right\rangle. \tag{5}$$

The propagator $K(\mathbf{r}_{12},\mathbf{r}'_{12},t)$ can be written as a Feymann path integral

$$K(\mathbf{r}_{12},\mathbf{r}'_{12};t)=\int d\mathbf{r}_F\exp\left[\frac{i}{\hbar^2}S(\mathbf{r}_F)\right]. \tag{6}$$

The integral must be performed over all the paths that link $\mathbf{r}_{12}$ and $\mathbf{r}'_{12}$ in time t and $S(\mathbf{r}_F)$ denotes the action along them. In the semiclassical limit only classically allowed paths are considered. Here we assume that there is only one such a classical path. The stationary phase approximation then gives the VanVleck formula (the WKB or semiclassical approximation to the propagator):

$$K(\mathbf{r}_{12},\mathbf{r}'_{12};t)=\left(\frac{\mu}{2\pi\hbar}\right)^{3/2}\left[Det\frac{\partial^2S(\mathbf{r}_{12},\mathbf{r}'_{12},t)}{\partial\mathbf{r}_{12}\partial\mathbf{r}'_{12}}\right]^{1/2} \times\exp\left[\frac{i}{\hbar^2}S(\mathbf{r}_{12},\mathbf{r}'_{12},t)\right], \tag{7}$$

where $S(\mathbf{r}_{12},\mathbf{r}'_{12},t)$ is the classical action connecting $\mathbf{r}_{12}$ and $\mathbf{r}'_{12}$.

In turn, the classical action is solution of the Hamilton-Jacobi equation

$$\frac{\partial S}{\partial t}+\frac{1}{2\mu}\left(\nabla_{\mathbf{r}'_{12}}S\right)^2+V(\mathbf{r}'_{12})=0. \tag{8}$$

For short enough time the action can be written

$$S=S_0-tS_1-t^3S_2+\cdots \tag{9}$$

where S_0 is the action for free particles and S_1 and S_2 are time independent. Introducing Eq. (9) into Eq. (8) and collecting terms with the same power in t we obtain:

$$S_0(\mathbf{r}_{12},\mathbf{r}'_{12};t)=\frac{\mu(\mathbf{r}_{12}-\mathbf{r}'_{12})^2}{2t}, \tag{10}$$

$$S_1(\mathbf{r}_{12},\mathbf{r}'_{12})=\frac{1}{|\mathbf{r}_{12}-\mathbf{r}'_{12}|}\int_{\mathbf{r}_{12}}^{\mathbf{r}'_{12}}V(r)d\mathbf{r} \tag{11}$$

and

$$S_2(\mathbf{r}_{12},\mathbf{r}'_{12})=\frac{1}{|\mathbf{r}_{12}-\mathbf{r}'_{12}|^3}\times\int_{\mathbf{r}_{12}}^{\mathbf{r}'_{12}}\frac{1}{2\mu}\left[\nabla S_1(\mathbf{r}_{12},\mathbf{r}'_{12})\right]^2(\mathbf{r}-\mathbf{r}_{12})^2d\mathbf{r}. \tag{12}$$

Replacing in Eq. (4) the propagators by the expression of Eq. (7) with $S(\mathbf{r}_{12},\mathbf{r}'_{12},t)$ given by Eqs. (9)–(12), remembering that $\mu=m/2$ and doing $\hbar\to0$ we obtain

$$G(\mathbf{r}_{12},\mathbf{r}'_{12};t)=\left(\frac{m\beta}{4\pi t^2}\right)^{3/2}\exp\left[-\beta m(\mathbf{r}_{12}-\mathbf{r}'_{12})^2/4t^2 -\beta S_1(\mathbf{r}_{12},\mathbf{r}'_{12})-\beta3t^2S_2(\mathbf{r}_{12},\mathbf{r}'_{12})\right]. \tag{13}$$

If Eqs. (11) and (12) are replaced by

$$S_1(\mathbf{r}_{12},\mathbf{r}'_{12})\approx V(r'_{12})\quad\text{and}\quad S_2(\mathbf{r}_{12},\mathbf{r}'_{12})\approx\frac{1}{3m}\left[\nabla_{\mathbf{r}_{12}}V(r_{12})\right]^2, \tag{14}$$

respectively, then $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ in the so called constant acceleration approximation (CAA) is obtained [48,50]:

$$G(\mathbf{r}_{12},\mathbf{r}'_{12};t)=e^{-\beta V(r_{12})}\left(\frac{m\beta}{4\pi t^2}\right)^{3/2} \times\exp\left\{-\frac{\beta m}{4t^2}\left[\mathbf{r}'_{12}-\mathbf{r}_{12}+\frac{2}{m}\nabla_{\mathbf{r}_{12}}V(r_{12})t^2\right]^2\right\}, \tag{15}$$

which is accurate to low densities and short times. Observe that if we apply Eq. (3), then the pair correlation function $g(r_{12})=$

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$exp[-\beta V(r_{12})]$ for dilute fluids is, in fact, obtained. Also the condition given by Eq. (2) is easily verified.

We also note that for the ideal gas, where $V(r_{12}) = 0$, we have

$$G(\mathbf{r}_{12}, \mathbf{r}'_{12}; t)_{free} = \left(\frac{m\beta}{4\pi t^2}\right)^{3/2} \times \exp\left[-\frac{\beta m(\mathbf{r}_{12} - \mathbf{r}'_{12})^2}{4t^2}\right], \tag{16}$$

a well known result [50].

2.2. Molecular dynamics

Here we describe the molecular dynamics (MD) simulations that we have performed, using the package GROMACS [52,53], in order to evaluate the theoretical generalized time-dependent distribution function $G(\mathbf{r}_{12}, \mathbf{r}'_{12}; t)$. We also will use the runs to evaluate, in the next Section, the pair correlation and other related functions of physical clusters in the weak sense whereas that in Section 4 the MD trajectories will be used to calculate the corresponding functions for the strong criterion of the physical clusters.

We consider $N = 64000$ particles of mass m interacting through a Lennard-Jones potential

$$V(r_{12}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{12}}\right)^{12} - \left(\frac{\sigma}{r_{12}}\right)^{6}\right] \tag{17}$$

with the parameters adequate for argon [54]: $m = 6.62 \times 10^{-26}$kg, $\varepsilon/k_B = 119.8$K and $\sigma = 3.401$Å. The particles are placed into a cubic box with sides of length $L = 74.46\sigma$, so we are taking a system of reduced density $\rho^* = 0.155(\rho^* = \rho\sigma^3 = (N/L^3)\sigma^3)$. The temperature we consider is, in reduced units, $T^* = 1.4(T^* = k_BT/\varepsilon; T = 167.72$K) stabilized by velocity rescaling [55].

The position and velocities of the N particles are followed by standard MD simulation methods [56,57] in the NVT ensemble using leap-frog integrator with an integration step $\Delta t = 0.002$ ps and an interaction cut-off distance $r_c = L/4$. For the trajectories the usual periodic boundary conditions are used.

In the calculation of $G(\mathbf{r}_{12}, \mathbf{r}'_{12}; t)$, in particular, a problem with the periodic conditions arise. The point is that in order to evaluate it we need to follow the trajectories of pairs of particles and can occur that whereas one of the particles of a given pair remains at certain time inside the simulation box, the other one leaves it. When the boundary conditions return this particle inside the box a discontinuity in the relative motion of both particles can be produced. To avoid this inconvenient, Balucani and Vallauri [58] consider an auxiliary separate record with the coordinates of the particles not modified by the periodic conditions. Another solution, that is what we use here, takes advantage of the relatively great number of particles that we are considering (64000 against the 108 of Ref. [58]). Thus, in addition to the box of side L we define a second cubic box of side $L/4$ at the center of that, so the volume of the new box is 1/64 of the volume of the big one. The initial position of at least one of the particles of the pairs to be followed is in the small box. The small box will contain in average $N' \sim 1000$ particles a number still large enough as to have good statistics. On the other hand, if we study $G(\mathbf{r}_{12}, \mathbf{r}'_{12}; t)$ for times t not too much large, as will be the case here, the pairs of particles one of which is initially inside the small box and the second is at a distance $r_{ij} < r_c$ have to travel a distance greater than $(L/8)\sigma$ in order to arrive to the big box surface, so, for the times we are considering here, most of them will not have sufficient time to reach the surface of the big box and corrections by periodic conditions will be unnecessary.

The procedure to calculate $G(\mathbf{r}_{12}, \mathbf{r}'_{12}; t)$ is as follows. First we take a particle i of the small box and count the number of particles j that fall at the initial time into the spherical shell between the spheres of radius $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $r_{ij} + \delta r_{ij} (r_{ij} < r_c)$ centered at the position of particle i. The volume of the shell is: $\delta V(0) = (4\pi/3)\left[(r_{ij} + \delta r_{ij})^3 - r_{ij}^3\right]$. We repeat the procedure for all the particles i in the small box. Then, we leave the pairs (i,j) evolve during time t and count, of all the particles j, those that fall in the volume delimited between spheres of radius r'_{ij} and $r'_{ij} + \delta r'_{ij}$ $\left(r'_{ij} < r_c\right)$ centered at particle i and the angles θ' and $\theta' + \delta\theta'$, where θ' is the angle between $\mathbf{r}'_{ij}$ and $\mathbf{r}_{ij}$:

$$\delta V'(t) = \frac{2\pi}{3}\left[\cos(\theta') - \cos(\theta' + \delta\theta')\right] \times \left[\left(r'_{ij} + \delta r'_{ij}\right)^3 - r'^3_{ij}\right]. \tag{18}$$

Note that, because we can assume that the vector $\mathbf{r}_{ij}$ is placed along the axis z of coordinates, the angle θ' between the vectors $\mathbf{r}_{ij}$ and $\mathbf{r}'_{ij}$ coincides with the polar angle of $\mathbf{r}'_{ij}$ in spherical coordinates.

If we denote with $n[\delta V'(t)|\delta V(0)]$ the number of pairs whose second particle falls, at time t, inside the volume $\delta V'(t)$, assuming that initially the first particle was in the volume $\delta V(0)$, then we have for $r_{12} < r_c, r'_{12} < r_c$:

$$G(\mathbf{r}_{12}, \mathbf{r}'_{12}; t) = \frac{n\left[\delta V'(t)\middle|\,\delta V(0)\right]}{N'\delta V(0)\delta V'(t)}. \tag{19}$$

2.3. Results

To visualize in some way on the paper the function $G(\mathbf{r}_{12}, \mathbf{r}'_{12}; t)$ is necessary to restrict ourself to sections of the full hypersurface that represents it. In particular, in order to take an idea about how well works the approximation given by Eq. (15), we consider in Fig. 1 the radial function $g_2(r'_{12}, t)$, defined by [58]

$$g_2(r'_{12}, t) = 8\pi^2\rho \int_{0.9\sigma}^{2.1\sigma} dr_{12} r_{12}^2 \times \int_0^{\pi} d\theta \sin\theta G(\mathbf{r}_{12}, \mathbf{r}'_{12}; t),$$

for $t = 0.1$, 0.2, 0.3 and 1.0 ps (0.047, 0.094, 0.141 and 0.47, respectively, in reduced units $t^* = t\sigma^{-1}\sqrt{\varepsilon/m}$). There the corresponding curves calculated using Eq. (15) (lines) are compared with those given by molecular dynamics simulations as described in the previous subsection (symbols). We observe that, for the relatively small density considered, the approximation given by Eq. (15) compares well just at very short times as we must expect from Eq. (9).

3. Physical clusters: weak criterion

In order to treat the physical clusters within a theoretical framework first we will restrict ourself to a weaker version. The weak criterion is established as follows [44]:

Two particles of the system belong, at a time t, to the same physical cluster (of connectivity distance d and residence time τ) if at the initial time t there exists a path of directly connected particles which links them and at time t + τ later all the particles forming the path, including the two particles under consideration, are also connected.

Here connected and directly connected are understood in the Stillinger sense with connectivity distance d. The difference with the strong criterion that we will establish in Section 4 is that in the weak version we require that the particles be connected at the extremes of the time interval no matter if they are connected or not in between.

3.1. Theory

We start considering the function $H(\mathbf{r}_1, \mathbf{r}_2)$ introduced by Xu and Stell in their "percolation in probability" theory [34]. This function measures the basic conditional probability for two particles to be

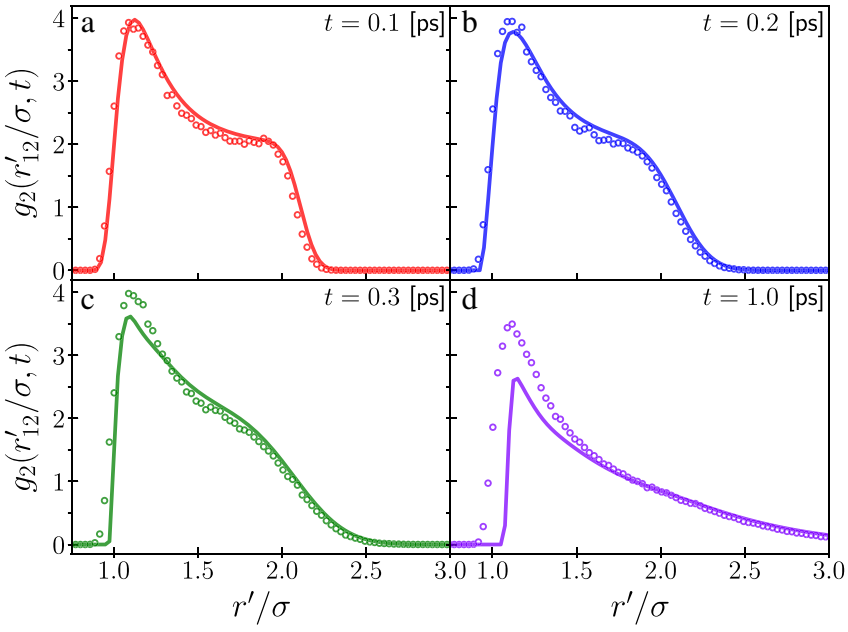

Fig. 1. The function $g_2(r'_{12}, t)$ (see text) for different values of the time t. Solid lines: theoretic result with $G(\mathbf{r}_{12}, \mathbf{r}'_{12}; t)$ calculated in the CAA (Eq. (15)). Open circles: from MD simulations.

directly connected if they are at positions $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. The role of this function within Hill's formalism is that of an auxiliary function in the Boltzmann factor separation $e(\mathbf{r}_i, \mathbf{r}_j) = e^{\dagger}(\mathbf{r}_i, \mathbf{r}_j) + e^{*}(\mathbf{r}_i, \mathbf{r}_j)$ into bonded and unbonded terms:

$$e^{\dagger}_{i,j} = H(\mathbf{r}_i, \mathbf{r}_j) e(\mathbf{r}_i, \mathbf{r}_j)$$
$$e^{*}_{i,j} = [1 - H(\mathbf{r}_i, \mathbf{r}_j)]\, e(\mathbf{r}_i, \mathbf{r}_j). \tag{20}$$

Each choice of $H(\mathbf{r}_i, \mathbf{r}_j)$ corresponds to a bond definition. For example, for Stillinger definition of directly connected particles we have

$$H(\mathbf{r}_1, \mathbf{r}_2) = H(r_{1,2}) = \begin{cases} 1 & r_{1,2} \le d \\ 0 & r_{1,2} > d \end{cases}.$$

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

$$H(\mathbf{r}_1, \mathbf{r}_2) = H(r_{1,2}; \tau) = \begin{cases} \frac{h^{\bullet\dagger}(\mathbf{r}_{1,2}; d, \tau)}{g(r_{1,2})} & r_{1,2} \le d \\ 0 & r_{1,2} > d \end{cases}, \tag{21}$$

where $h^{\bullet\dagger}(\mathbf{r}_{1,2}; d, \tau)$ is the probability density of finding two particles in relative position $\mathbf{r}_{1,2}$ at time t and connected at time $t + \tau$.

Clearly, this election of $H(r_{1,2}; \tau)$ considers as bonded any two particles which are connected (directly or not) at time $t + \tau$ and were separated by a distance smaller than d at t. We explicitly include τ in the functions to stress the life time dependence and calculate $h^{\bullet\dagger}(r_{1,2}; d, \tau)$ as

$$h^{\bullet\dagger}(\mathbf{r}_{1,2}; d, \tau) = \int \frac{g_{Still}\left(r'_{1,2}, d\right)}{g\left(r'_{1,2}\right)} G\left(\mathbf{r}_{1,2}, \mathbf{r}'_{12}; \tau\right) d\mathbf{r}'_{1,2} \tag{22}$$

It is worth noting that, according to the definition of $h^{\bullet\dagger}(\mathbf{r}_{1,2}; \tau)$, in the initial time t the particles can be connected or not, but they must be in relative position $\mathbf{r}_{1,2}$, whereas at the final time $t + \tau$ they must be connected whatever the relative position is.

For completeness we remember that we can calculate $g_{Still}(r_{1,2}; d)$ in the Perscus-Yevick approximation as solution of the connectivity OZ relation [26,59]

$$g_{Still}(r_{1,2}; d) = c_{Still}(r_{1,2}; d) + \rho \int c_{Still}(r_{1,3}; d) g_{Still}(r_{3,2}; d) d\mathbf{r}_3, \tag{23}$$

with the closures

$$g_{Still}(r_{1,2}; d) = g_{PY}(r_{1,2}) \quad \text{for} \quad r_{1,2} \le d, \tag{24}$$

where $g_{PY}(r_{1,2})$ is the ordinary (or thermic) pair correlation as obtained in the Percus-Yevick approximation [59] and [26]:

$$c_{Still}(r_{1,2}; d) = (1 - \exp[\beta V(r_{12})])\, g_{Still}(r_{1,2}; d) \quad \text{for} \quad r_{1,2} > d. \tag{25}$$

Once the direct bond is defined, a connectivity Ornstein-Zernike relation between the pair correlation function $g_{Phys,W}(r_{1,2}; \tau)$ and the direct correlation function for weak physical clusters $c_{Phys,W}(r_{1,2}; \tau)$ can be obtained, in a similar way as for $g_{Still}(r_{1,2}; d)$ and $c_{Still}(r_{1,2}; d)$, in the form:

$$g_{Phys;W}(r_{12}; d, \tau) = c_{Phys,W}(r_{1,2}; d, \tau) + \rho \int c_{Phys,W}(r_{1,3}; d, \tau) g_{Phys,W}(r_{3,2}; d, \tau) d\mathbf{r}_3. \tag{26}$$

The function $g_{Phys,W}(r_{1,2}; \tau)$ is proportional to the probability density of finding two particles in positions $\mathbf{r}_1$ and $\mathbf{r}_2$ and belonging to the same weak physical cluster.

To transform the OZ relation (26) into an integral equation a closure is needed. We see that

$$g_{Phys,W}(r_{1,2}; d, \tau) = h^{\bullet\dagger}(\mathbf{r}_{1,2}; d, \tau) \quad \text{for} \quad r_{1,2} \le d, \tag{27}$$

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because the conditional probability density that two particles belong to the same weak physical cluster, under the assumption that they are connected at time $t+\tau$, is equal to one if they were at a distance smaller than d at time t. For $r_{1,2} > d$ we use the Percus-Yevick connectivity closure:

$$c_{Phys,W}(r_{1,2};d,\tau) = (1-\exp[\beta V(r_{12})]) \times g_{Phys,W}(r_{1,2};d,\tau) \quad \text{for} \quad r_{1,2} > d. \tag{28}$$

A second approximation for $g_{Phys,W}(r_{1,2};d,\tau)$ that we propose is based in the connectedness function $h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau)$, that accounts for the joint probability density that two particles which are initially connected at a relative position $\mathbf{r}_{12}$ will be also connected at a relative position $\mathbf{r}'_{12}$ at a time τ later. It can be approximated as

$$h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau) \approx \left[\frac{g_{Still}(r_{1,2},d)}{g(r_{1,2})}\right] \times G(\mathbf{r}_{12},\mathbf{r}'_{12};\tau) \left[\frac{g_{Still}\left(r'_{1,2},d\right)}{g\left(r'_{1,2}\right)}\right]^{\gamma}, \tag{29}$$

where

$$\gamma = \frac{(\tau/\tau_0)^2}{1+(\tau/\tau_0)^2} \tag{30}$$

is a switching function. For $\tau = 0$ Eq. (30) yields $\gamma = 0$ and we obtain the exact value $h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau = 0) = g_{Still}(r_{1,2};d)\delta(\mathbf{r}_{12}-\mathbf{r}'_{12})$ (see Eq. (2)), whereas for very large τ we have $\gamma = 1$ and $h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau) = [g_{Still}(r_{1,2},d)/g(r_{1,2})]\, G(\mathbf{r}_{12},\mathbf{r}'_{12};\tau)\left[g_{Still}\left(r'_{1,2},d\right)/g\left(r'_{1,2}\right)\right]$. This last expression is also correct since the connectivity status of two particles at instants separated by a time interval τ are, for large enough τ, independent events. The constant τ_0 in Eq. (30) denotes the critical time around which the transition from coincident ($\gamma = 0$) to completely independent ($\gamma = 1$) events occurs. A lower bound for τ_0 is $d/\langle|\mathbf{v}_2-\mathbf{v}_1|\rangle$ with d the connectivity distance and $\langle|\mathbf{v}_2-\mathbf{v}_1|\rangle$ the mean relative velocity between pairs of particles.

The cluster pair correlation for weak physical cluster is thus given by

$$g_{Phys,W}(r_{1,2};d,\tau) = \int h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau)\, d\mathbf{r}'_{12} \tag{31}$$

With $g_{Phys,W}(r_{1,2};d,\tau)$ calculated by any of both approximations we obtain the mean cluster size in the form

$$S(\rho) = 1 + 4\pi\rho \int_0^{\infty} g_{Phys,W}(r_{1,2};d,\tau) r_{12}^2 dr_{12} \tag{32}$$

3.2. Molecular dynamics

To analyze the approximations that we have introduced in our theoretical approach, we have calculated the pair correlation function for physical clusters defined in the weak sense from molecular dynamics trajectories obtained as described in the previous Section. The simulation algorithm to identify the weak physical clusters is slightly different from that considered for the strong criterion (see Subsection 4.2). It is carried out as follows [44]:

1) Identify a Stillinger cluster at $t-\tau$.
2) Move the particles of this cluster to the new positions in t.
3) Identify the Stillinger clusters in the new configuration for the particles selected in **1.**
   These clusters are the physical ones in the weak sense.
4) Repeat from **1** until cover all initial Stillinger clusters.

3.3. Results

In Fig. 2 we consider the curves we obtain for $g_{Phys,W}(r_{1,2};d,\tau)$ in the Percus-Yevick approximation defined by Eqs. (26)–(28) with $h^{\bullet\dagger}(\mathbf{r}_{1,2};d,\tau)$ given by Eq. (22) where we use for $g_{Still}(r_{1,2},d)$ that obtained of solving the Percus-Yevick integral equation (formulas (23), (24) and (25)) whereas that $G(\mathbf{r}_{1,2},\mathbf{r}'_{12};\tau)$ is treated in the CAA discussed in the previous section. The system density and temperature, as well as the particle mass and the potential parameters are the same ones considered in Subsection 2.2. The two parameters that characterize the clusters are the connectivity distance d and residence time τ. We take, in reduced units, $d^* = d/\sigma = 1.325$ and $\tau^* = \tau\sigma^{-1}\sqrt{\varepsilon/m} = 0, 0.047, 0.094, 0.47$. The panel **a** is devoted to the cluster pair correlation function for the Stillinger criterion ($\tau = 0$). For completeness we also show the corresponding ordinary (thermal) pair correlation function calculated in the PY approximation too. In all the cases, to solve the involved integral equations we have used the hybrid method of Labík and collaborators [60]. The overestimation of PY connectedness correlations with respect to MD ' s was already observed for extended hard spheres by DeSimone et al. [33] and is a point to take into account in the comparison of the MD results with ours. The dependence of the PY $g_{Phys,W}(r_{1,2};d,\tau)$ with $G(\mathbf{r}_{1,2},\mathbf{r}'_{12};\tau)$ specially for $r_{1,2} \leq d$ (see Eqs. (27), (22)) and the differences observed between the $G(\mathbf{r}_{1,2},\mathbf{r}'_{12};\tau)$ calculated using MD and using the CAA expression for times not short enough (Fig. 1), manifest into a correspondent difference between PY and MD curves at $\tau^* = 0.47$ (panel **d**).

The curves for $g_{Phys,W}(r_{1,2};d,\tau)$ calculated using the approximation given by Eqs. (29)–(31) are displayed in Fig. 3 together with the corresponding ones obtained from the MD trajectories. In Eq. (30) we take for $\tau_0 = d\sqrt{m/6k_BT}$ in reduced units $\tau_0^* = 0.46$. We observe that for the shortest time $g_{Phys,W}(r_{1,2};d,\tau)$ and $g_{Still}(r_{1,2},d)$ practically fix together. This fact is observed for the MD as well as for the theoretic curves (remember the above-mentioned difference between MD and PY Stillinger connectedness correlations). For larger times the two curves start to separate, the curve for the weak clusters taking smaller values as it should be. For even larger times the approximation is not more valid.

4. Physical clusters: strong criterion

The strong criterion for the physical clusters reads:

A set of particles form a physical cluster (of connectivity distance d and residence time τ) at the instant t if all they remained connected during the whole time interval $[t, t+\tau]$.

Here the term "connected" must be also understood in the Hill-Stillinger sense with connectivity distance d, 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 smaller 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 cannot 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 sub-aggregates.

Suppose we identify the system ("instantaneous") Stillinger clusters at t. Select one of these clusters. As the system evolves from t to $t+\tau$, the particles in it will connect and disconnect themselves

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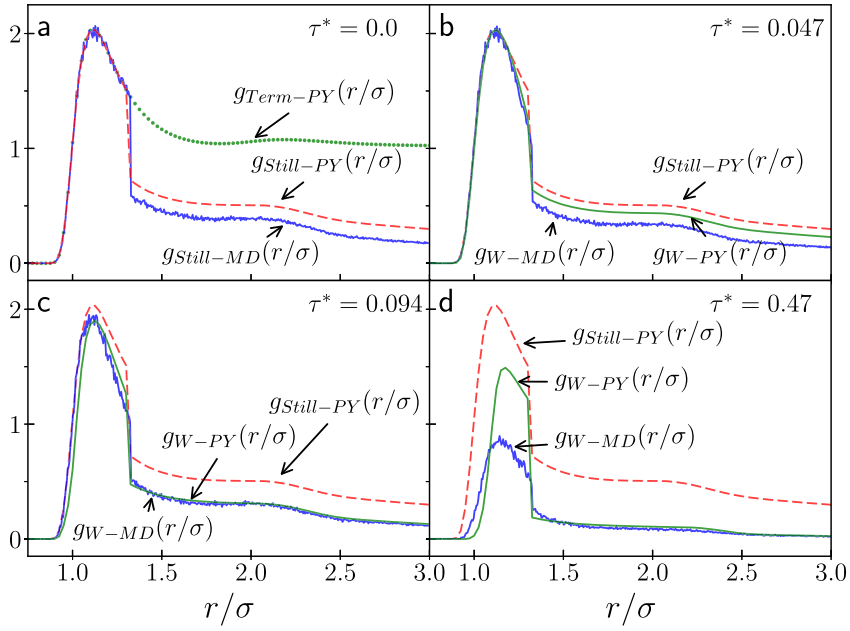

Fig. 2. Clusters pair correlation functions for physical clusters in the weak version $g_{Phys;W}(r;d,\tau)$ calculated in the Percus-Yevick aproximation and from MD simulations. For $\tau = 0$ (panel **a**) the physical clusters reduces to the Stillinger clusters.

several times. If we watch just those particles which have belonged to the initially selected Stillinger cluster and consider the successive fragmentation events then, after the period $[t, t+\tau]$, the particles will be in several sub-aggregates. Each sub-aggregate forms a physical cluster.

4.1. Theory

We will calculate the function $h^{\dagger\sim\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau)$ which accounts for the joint probability density that two particles which are initially connected at a relative position $\mathbf{r}_{12}$ will be also connected at a relative position $\mathbf{r}'_{12}$ at a time τ later, being connected during the whole time interval. It is clear that, for very small τ, is

$$h^{\dagger\sim\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau) \underset{\tau \text{very small}}{\approx} h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau), \tag{33}$$

where the connectedness function for weak clusters $h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau)$ was defined in Subsection 3.1 (see Eq. (29)).

It is convenient to redefine the parameter associated with time: $\hat{t} = t^2, \hat{\tau} = \tau^2$ and to introduce hated functions such that

$$\hat{f}\left(\mathbf{r}_{12},\mathbf{r}'_{12};d,\hat{t}=t^2\right) = f(\mathbf{r}_{12},\mathbf{r}'_{12};d,t). \tag{34}$$

So, from Eq. (15) we have:

$$\hat{G}\left(\mathbf{r}_{12},\mathbf{r}'_{12};\hat{t}\right) = e^{-\beta V(r_{12})}\left(\frac{m\beta}{4\pi\hat{t}}\right)^{3/2} \times \exp\left\{-\frac{\beta m}{4\hat{t}}\left[\mathbf{r}'_{12}-\mathbf{r}_{12}+\frac{2}{m}\nabla_{\mathbf{r}_{12}}V(r_{12})\,\hat{t}\right]^2\right\}. \tag{35}$$

Now break up the interval $[0,\hat{\tau}]$ into $n\,(\to\infty)$ divisions of length $\epsilon = \hat{\tau}/n$. Taking into account Eqs. (33), (29) and (30) we have

$$\hat{h}^{\dagger\sim\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\epsilon) \approx \hat{h}_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\epsilon) \approx \left[\frac{g_{Still}(r_{1,2},d)}{g(r_{1,2})}\right]\hat{h}^{\sim\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\epsilon), \tag{36}$$

with

$$\hat{h}^{\sim\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\epsilon) \approx \hat{G}(\mathbf{r}_{12},\mathbf{r}'_{12};\epsilon)\left[\frac{g_{Still}\left(r'_{1,2},d\right)}{g\left(r'_{1,2}\right)}\right]^{\epsilon/\tau_0^2} \tag{37}$$

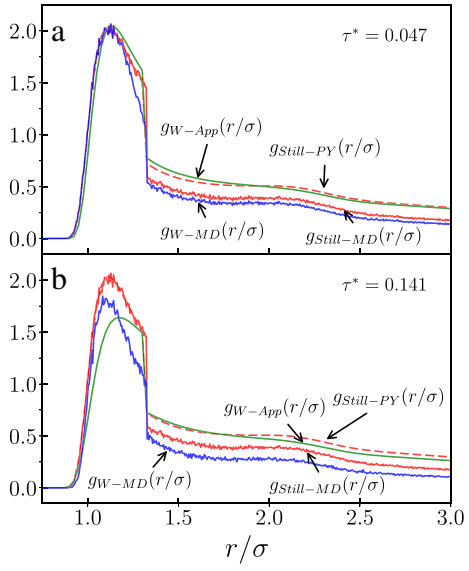

Fig. 3. Clusters pair correlation functions for physical clusters in the weak version $g_{Phys;W}(r;d,\tau)$ calculated using the approximation given by Eqs. (29)–(31) and from MD simulations.

where we consider that, for small τ, Eq. (30) gives $\gamma \approx (\tau/\tau_0)^2$. Taking into account that for ϵ very small is

$$\left[\frac{g_{Still}\left(r'_{1,2},d\right)}{g\left(r'_{1,2}\right)}\right]^{\epsilon/\tau_0^2} \approx \exp\left[-\frac{g_{Still}\left(r'_{1,2},d\right)}{g\left(r'_{1,2}\right)}\frac{\epsilon}{\tau_0^2}\right]$$

we have

$$\hat{h}^{\sim\dagger}\left(\mathbf{r}_{12},\mathbf{r}'_{12};d,\epsilon\right) \approx \hat{G}\left(\mathbf{r}_{12},\mathbf{r}'_{12};\epsilon\right) \times \exp\left[-\frac{g_{Still}\left(r'_{1,2},d\right)}{g\left(r'_{1,2}\right)}\frac{\epsilon}{\tau_0^2}\right]. \quad (38)$$

The composition property for propagators allows to write

$$\hat{h}^{\sim\dagger}\left(\mathbf{r},\mathbf{r}';d,n\epsilon=\hat{\tau}\right) = \int\int\cdots\int \hat{h}^{\sim\dagger}(\mathbf{r},\mathbf{r}_1;d,\epsilon)\hat{h}^{\sim\dagger}\left(\mathbf{r}_1,\mathbf{r}_2;d,\epsilon\right)\cdots\hat{h}^{\sim\dagger}\left(\mathbf{r}_{n-1},\mathbf{r}';d,\epsilon\right) d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_{n-1} \quad (39)$$

where we define $\mathbf{r}_{\alpha-1}=\mathbf{r}_{\alpha,\alpha+1}(\alpha=2,\cdots,n)$ and $r=\mathbf{r}_0=\mathbf{r}_{12},\mathbf{r}'=\mathbf{r}_n=\mathbf{r}'_{12}$. In the limit $\epsilon\to 0$, this equation can be written symbolically as a path integral:

$$\hat{h}^{\sim\dagger}(\mathbf{r},\mathbf{r}';d,\hat{\tau}) = \int \Phi\left[\mathbf{r}\left(\hat{\tau}'\right)\right]\mathfrak{D}\left[\mathbf{r}\left(\hat{\tau}'\right)\right] \quad (40)$$

with

$$\Phi\left[\mathbf{r}\left(\hat{\tau}'\right)\right] = \lim_{\substack{\epsilon\to\infty\\ n\epsilon=\hat{\tau}'}} \hat{h}^{\sim\dagger}(\mathbf{r},\mathbf{r}_1;d,\epsilon)\hat{h}^{\sim\dagger}(\mathbf{r}_1,\mathbf{r}_2;d,\epsilon)\cdots\hat{h}^{\sim\dagger}\left(\mathbf{r}_{n-1},\mathbf{r}';d,\epsilon\right) \quad (41)$$

and

$$\mathfrak{D}\left[\mathbf{r}\left(\hat{\tau}'\right)\right] = \lim_{n\to\infty} d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_{n-1}. \quad (42)$$

From Eqs. (35) and (38) we can write $\Phi\left[\mathbf{r}\left(\hat{\tau}'\right)\right]$ in the form

$$\Phi\left[\mathbf{r}\left(\hat{\tau}'\right)\right] = \exp\left\{-\beta\int_0^{\hat{\tau}}\left(\frac{m}{4}\left[\mathbf{r}\left(\hat{\tau}'\right)\right]^2 + W_0\left[\mathbf{r}\left(\hat{\tau}'\right)\right] + W\left[\mathbf{r}\left(\hat{\tau}'\right)\right]\right)d\hat{\tau}'\right\} \quad (43)$$

where $W_0\left[\mathbf{r}\left(\hat{\tau}'\right)\right]$ is such that

$$\hat{G}\left(\mathbf{r}_{12},\mathbf{r}'_{12};\hat{\tau}\right) = \int \Phi_0\left[\mathbf{r}\left(\hat{\tau}'\right)\right]\mathfrak{D}\left[\mathbf{r}\left(\hat{\tau}'\right)\right] \quad (44)$$

with

$$\Phi_0\left[\mathbf{r}\left(\hat{\tau}'\right)\right] = \exp\left\{-\beta\int_0^{\hat{\tau}}\left(\frac{m}{4}\left[\mathbf{r}\left(\hat{\tau}'\right)\right]^2 + W_0\left[\mathbf{r}\left(\hat{\tau}'\right)\right]\right)d\hat{\tau}'\right\} \quad (45)$$

and $W\left[\mathbf{r}\left(\hat{\tau}'\right)\right]$ is given by

$$W\left(r'_{1,2}\right) = \frac{1}{\tau_0^2\beta}\frac{g_{Still}\left(r'_{1,2},d\right)}{g\left(r'_{1,2}\right)}, \quad (46)$$

where $\tau_0 = d/\langle|\mathbf{v}_2-\mathbf{v}_1|\rangle$. We observe that $W\left(r'_{1,2}\right)$ is "globally" more small (<1) when the region in which $g_{Still}(r,d)\neq g(r)$ is larger, say for d small (see Eq. (24) and Fig. 2). According to Eq. (37), we have ($W=0$)

$$\hat{h}^{\sim\dagger}\left(\mathbf{r},\mathbf{r}';d,\hat{\tau}\right) = \hat{h}_0^{\sim\dagger}\left(\mathbf{r},\mathbf{r}';\hat{\tau}\right) = \hat{G}\left(\mathbf{r},\mathbf{r}';\hat{\tau}\right). \quad (47)$$

Therefore we are in position to solve the path integral (Eqs. (40), (42) and (43)) by perturbation expansion. To second order in the perturbation W we have:

$$\begin{aligned}\hat{h}^{\sim\dagger}\left(\mathbf{r},\mathbf{r}';d,\hat{\tau}\right) = {}& \hat{h}_0^{\sim\dagger}\left(\mathbf{r},\mathbf{r}';\hat{\tau}\right)\\ & -\beta\int_0^{\hat{\tau}}d\hat{\tau}'\int d\mathbf{s}\hat{h}_0^{\sim\dagger}\left(\mathbf{r},\mathbf{s};\hat{\tau}-\hat{\tau}'\right)W(\mathbf{s};d)\hat{h}_0^{\sim\dagger}\left(\mathbf{s},\mathbf{r}';\hat{\tau}'\right)\\ & +\beta\int_0^{\hat{\tau}}d\hat{\tau}'\int_0^{\hat{\tau}'}d\hat{\tau}''\int d\mathbf{s}\int d\mathbf{s}'\hat{h}_0^{\sim\dagger}\left(\mathbf{r},\mathbf{s};\hat{\tau}-\hat{\tau}'\right)W(\mathbf{s};d)\\ & \times\hat{h}_0^{\sim\dagger}\left(\mathbf{s},\mathbf{s}';\hat{\tau}'-\hat{\tau}''\right)W(\mathbf{s}';d)\hat{h}_0^{\sim\dagger}\left(\mathbf{s}',\mathbf{r}';\hat{\tau}''\right)+\cdots\end{aligned} \quad (48)$$

The function $h^{\dagger\sim\dagger}\left(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau\right)$ is then calculated

$$h^{\dagger\sim\dagger}\left(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau\right) = \left[\frac{g_{Still}(r_{1,2},d)}{g(r_{1,2})}\right]\times\hat{h}^{\sim\dagger}\left(\mathbf{r}_{12},\mathbf{r}'_{12};d,\hat{\tau}=\tau^2\right), \quad (49)$$

and the cluster pair correlation function $g_{Phys}(r_{1,2};d,\tau)$ is given by

$$g_{Phys}(r_{1,2};d,\tau) = \int h^{\dagger\sim\dagger}\left(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau\right)d\mathbf{r}'_{12}, \quad (50)$$

from where the mean cluster size is obtained:

$$S(\rho) = 1+4\pi\rho\int_0^{\infty} g_{Phys}(r_{1,2};d,\tau)r_{12}^2 dr_{12}. \quad (51)$$

It should be remarked that, although they were deduced starting from the expression of $G\left(\mathbf{r}_{12},\mathbf{r}'_{12};t\right)$ in the CAA which works well just for short times, the previous path-integral formulas are valid for any time if an adequate form of $G\left(\mathbf{r}_{12},\mathbf{r}'_{12};t\right)$ is considered.

4.2. Molecular dynamics

Next we reproduce the algorithm to identify the physical clusters in the strong sense [44] from the MD trajectories obtained as indicated in Subsection 2.2.

1) All initial conditions are set for the MD ($t=t_0$).
2) Stillinger clusters are tabulated by standard routines [56]. The positions of the particles at $t=t_0$ are used in that operation.
3) The MD is carried out one time step ($t_1=t_0+\Delta t$). The clusters obtained at step 2 are updated deleting those particles that do not belong to them.
4) If $t_1-t_0<\tau$ go back to step **3**, else go to step **5**.
5) Save the interesting information. The cluster table contains all the set of particles which met the physical cluster definition introduced in the beginning of Section 4.
6) Initial conditions are set from the last configuration and go back to step **2**.

Steps **1** to **6** are the loop to identify the physical clusters for the final configuration at time $t=t_1$.

In step **3** 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.

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4.3. Results

Fig. 4 shows the cluster pair correlation function for the strong version of the physical clusters $g_{Phys}(r_{1,2};d,\tau)$ given by Eq. (50) with $h^{\dagger\sim\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau)$ calculated from the two first terms of Eq. (48) for residence times (in reduced units) $\tau^* = 0.047$ and 0.141. The corresponding curves obtained from MD trajectories following the recipe of the previous subsection are also displayed for comparison as well as the PY and MD curves for Stillinger clusters. We note that when the integration in Eq. (50) is performed the reference term in Eq. (48) gives, according to Eqs. (49), (47) and (3), just $g_{Still}(r_{1,2},d)$. The second term perturbs it lowering its value along the whole range of $r_{1,2}$. For the shortest time considered ($\tau = 0.047$) both curves $g_{Phys}(r_{1,2};d,\tau)$ and $g_{Still}(r_{1,2},d)$ practically fix together. For $\tau^* = 0.141$ (panel **b**) the curves start to differ, the difference being more notable at distances $r_{1,2} < d$. However for times even larger the curves obtained for $g_{Phys}(r_{1,2};d,\tau)$ become unphysical. For example, for $\tau^* = 0.47$ the curve we obtained takes negative values at some points. We believe that the main reason for this behavior is that the CAA is not a good approximation at that times (see Fig. 1**d**). We need expressions for $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ that be valid at larger times. Unfortunately there is no such an analytical expression available at the moment. So, to roughly check our path integral formula, we improvise an expression for it such that, at $\tau^* = 0.47$, the resulting curve of $g_2(r_{12},t)$ compares with MD 's better than that shown in Fig. 1**d**. The proposed expression is a simple modification of CAA Eq. (15):

$$G(\mathbf{r}_{12},\mathbf{r}'_{12};t) = g(r_{12})\left(\frac{m\beta}{c_0 4\pi t^2}\right)^{3/2} \times \exp\left\{-\frac{\beta m}{c_0 4t^2}\left[\mathbf{r}'_{12}-\mathbf{r}_{12} + \left[\sum_{n=1}^{n_{\max}} c_n\left(\frac{t^2}{m\sigma}\frac{dV(r_{12})}{dr_{12}}\right)^n\right]\frac{\mathbf{r}_{12}}{r_{12}}\right]^2\right\}, \tag{52}$$

where c_n ($n = 0,1,\cdots,n_{\max}$) are parameters to be determined. We remark that the conditions given by Eqs. (2) and (3) follow being verified. Also we note that for $c_0 = 1, c_1 = 2$ and $c_2 = c_3 = \cdots = c_{\max} = 0$ the CAA is recovered. By trial and error we find coefficients c_n that give a $g_2(r_{12},t)$ that improves that of Fig. 1**d**. In Fig. 5**a** we show the curve obtained for $c_0 = 0.5$, $c_1 = 0.05$ and

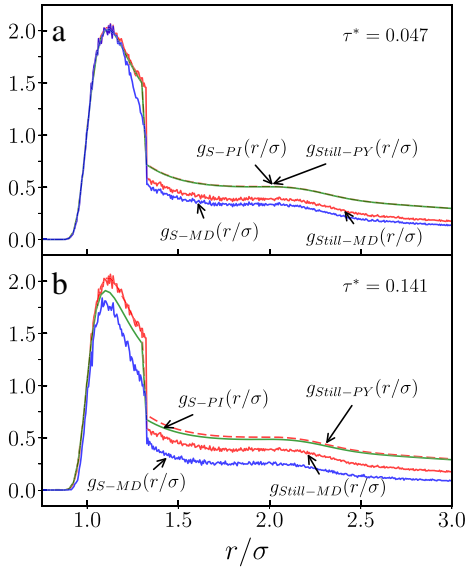

Fig. 4. Clusters pair correlation functions for physical clusters in the strong version $g_{Phys}(r;d,\tau)$ calculated using up to the first order in the perturbation formula (Eq. (48)) with $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ given in the CAA and from MD simulations.

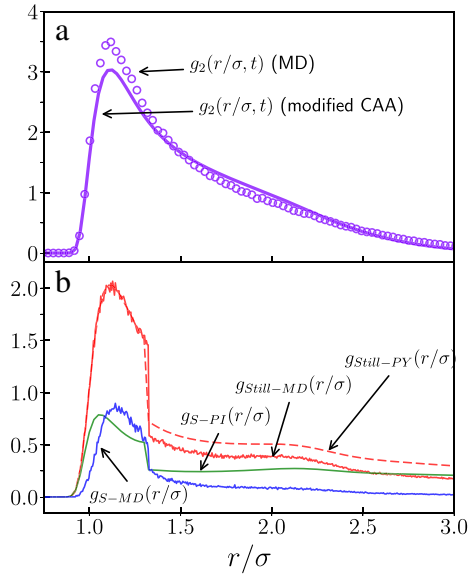

Fig. 5. Modified CAA for $\tau^* = 0.47$. Panel **a**: function $g_2(r_{12},t)$ (see Subsection 2.3). Panel **b**: clusters pair correlation function for physical clusters in the strong version $g_{Phys}(r;d,\tau)$ calculated using up to the first order in the perturbation expansion (Eq. (48)) with $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ given by the modified CAA (Eq. (52)) and from MD simulations.

$c_2 = c_3 = \cdots = c_{\max} = 0$. It should be pointed out that our search for these parameters was not exhaustive nor systematic.

The curve for $g_{Phys}(r_{1,2};d,\tau)$ given by the two first terms in the perturbation expansion of the path integral when we use this expression for $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ is shown in Fig. 5**b**. We observe the notable lowering of it with respect to the curve for Stillinger clusters. When analyzing this curve we may not forget that we are ignoring higher terms in the perturbation expansion as well as the rather approximate character of the expression given by Eq. (52) and the deficiencies already mentioned about $g_{Still-PY}(r_{1,2},d)$.

5. Conclusions

In this article we have developed a theory for the physical clusters previously introduced in our group. The main ingredients in the theory are the functions $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$, $g_{Still}(r_{1,2},d)$ and the approximation given by Eqs. (29), (30) for the connectedness function for physical clusters in the weak sense $\left(h_W^{\dagger\dagger}(\mathbf{r}_{12},\mathbf{r}'_{12};d,\tau)\right)$ at short times. Although the available expressions for these functions behave reasonably well at short times at larger times they start to fail. On the other hand, our expression for $g_{Phys}(r_{1,2};d,\tau)$ (Eqs. (50), (49) and (48)) is of real usefulness just at these larger times, since for the shorter ones the clusters pair correlations for the strong and also for the weak versions of the physical clusters do differ little of $g_{Still}(r_{1,2},d)$ as the MD simulations show. At this respect the main conclusion is that an expression for $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ which has been adequate for larger values of t is essential. In this vein, some possible ways to improve the results include: i) To make a more rigorous fitting of the parameters in Eq. (52) against simulations data; ii) To look for a better $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ from physical grounds. One way is to extend the deduction of Subsection 2.1 to larger times by considering higher terms in the action expansion (Eq. (9)). Another way is to consider $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ as solution of adequate diffusion like equations; iii) Search for better approximations of $g_{Still}(r_{1,2},d)$; iv) Study of higher terms in the perturbation expansion of $g_{Phys}(r_{1,2};d,\tau)$; v) To take for $G(\mathbf{r}_{12},\mathbf{r}'_{12};t)$ and $g_{Still}(r_{1,2},d)$ directly those calculated from MD simulations; etc. But this is a matter of future work.

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