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# Density expansion for particle-particle correlations in time-dependent physical clusters

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We present a theory for the particle-particle correlations in physical clusters for which bonding between particles is determined by a connectivity distance and a permanency time. A generalized Mayer density expansion for the cluster pair correlation function is found, as well as an Ornstein-Zernike like relation. We can rely on this formalism to study clustering in realistic models by applying techniques of liquid state theory.

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The relevance of physical clusters in condensed matter physics, particularly in relation with transition phenomena, has been recognized since more than sixty years ago when Bijl, Band, and Frenkel [1] (among others) introduced the concept of physical (or real) clusters, in place of the mathematical ones that Mayer had considered in the virial expansion of imperfect gases [2].

The application of statistical mechanics formalism to describe clustering in equilibrium classical systems is mainly due to Hill [3]. In Hill theory the concept of cluster is directly related to that of connectivity: two particles belong to the same cluster if they are connected trough a path of directly connected particles. Therefore, a crucial point in the identification of the physical clusters is the definition of directly connected particles (a bonded pair). Whereas thermodynamic properties are not affected whatever the particular definition used to identify the clusters is, clustering and percolation properties are very sensitive to this choice instead [3].

To our knowledge all previous works on clustering theory used connectivity criteria which are based on just ‘‘present time’’ configurations in phase space [3,4]. More elaborated criteria must include some information on the ‘‘previous’’ (or ‘‘subsequent’’) configurations. For example, two particles could be close enough as to form a bond, but if their relative velocity is quite large then they can move far away one from the other in a very short time. In this case we cannot say that a true bond was formed in a physical sense, even if the particles satisfy the criterion for direct connectivity at a given ‘‘instant.’’

In the past few years, several papers have renewed the interest on energetic and dynamic aspects of bonding, particularly in relation with the properties of water [5]. Hydrogen-bond lifetimes 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.

Hill theory separates Boltzmann factor $e(\mathbf{r}_1,\mathbf{r}_2)=\exp[-\beta v(\mathbf{r}_1,\mathbf{r}_2)]$ [we will consider only systems interacting via pairwise additive potentials throughout and will denote with $v(\mathbf{r}_1,\mathbf{r}_2)$ the pair potential] into bonded (†) and unbonded (*) terms: $e(\mathbf{r}_1,\mathbf{r}_2)=e^{\dagger}(\mathbf{r}_1,\mathbf{r}_2)+e^{*}(\mathbf{r}_1,\mathbf{r}_2)$. As usual $\beta=1/k_BT$ with $T$ the absolute temperature and $k_B$ the Boltzmann constant. Since $e^{\dagger}(\mathbf{r}_1,\mathbf{r}_2)$ represents the basic probability density that two particles at positions $\mathbf{r}_1$and $\mathbf{r}_2$, respectively, are directly connected (bonded), this separation allows us to get a diagrammatic expansion for the partition functions in terms of physical rather than mathematical (Mayer’s) clusters.

Fugacity and density expansions similar to those obtained by Mayer and Montroll [6] for the ordinary pair correlation function $g(\mathbf{r}_1,\mathbf{r}_2)$ have been found by Coniglio and collaborators for the pair connectedness function $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2)$, which is proportional to the joint probability density of finding two particles at positions $\mathbf{r}_1$ and $\mathbf{r}_2$ and belonging to the same cluster [4]. Moreover, by collecting nodal and non-nodal diagrams in these expansions, they also obtained an Ornstein-Zernike like relation from which integral equations for $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2)$ can be posed [7].

In this Rapid Communication we show how to generalize the Hill-Coniglio formalism in order to apply it to clusters for which bonding between particles is determined by a connectivity distance $d$ and a permanency time $\tau$. We give fugacity and density expansions for the pair connectedness function $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$, 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 $\mathbf{p}_2$ and belonging to the same cluster. An Ornstein-Zernike-like integral equation for $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ is presented together with an approximation of the Percus-Yevick type. Here we just present the main results; the details will be given elsewhere [8].

For a system of $N$ classical particles interacting via a pair potential $v(\mathbf{r}_i,\mathbf{r}_j)$ we define a density correlation function $\rho(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ which is $N(N-1)$ times the probability density of finding two particles at phase space points $(\mathbf{r}_1,\mathbf{p}_1)$ and $(\mathbf{r}_2,\mathbf{p}_2)$, respectively:

$$\rho(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)=\frac{N(N-1)}{h^{3N}N!Q_N(V,T)}\times\int\prod_{i=1}^{N}\exp\left[-\beta\frac{\mathbf{p}_i^2}{2m}\right]\prod_{i=1}^{N}\prod_{j>i}^{N}\times\exp[-\beta v(\mathbf{r}_i,\mathbf{r}_j)]d\mathbf{r}^{N-2}d\mathbf{p}^{N-2}. \quad (1)$$

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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 $\exp[-\beta v(\mathbf{r}_i,\mathbf{r}_j)]$ into connecting and blocking parts

$$\exp[-\beta v(\mathbf{r}_i,\mathbf{r}_j)]=f^{\dagger}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{p}_i,\mathbf{p}_j)+f^{*}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{p}_i,\mathbf{p}_j)+1. \tag{2}$$

Here $f^{\dagger}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{p}_i,\mathbf{p}_j)$ represent the basic probability density that two particles at configuration $(\mathbf{r}_i,\mathbf{r}_j,\mathbf{p}_i,\mathbf{p}_j)$, are directly connected. The shorthand notation $f^{\gamma}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{p}_i,\mathbf{p}_j)\equiv f^{\gamma}_{i,j}$ $(\gamma=\dagger,*)$ will be sometimes used.

Substitution of Eq. (2) in Eq. (1) yields

$$\rho(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)=\frac{N(N-1)}{h^{3N}N!Q_N(V,T)}\exp[-\beta v(\mathbf{r}_1,\mathbf{r}_2)]$$
$$\times\int\prod_{i=1}^{N}\exp\left[-\beta\frac{\mathbf{p}_i^2}{2m}\right]\sum\left\{\prod f^{\dagger}_{i,j}f^{*}_{k,l}\right\}$$
$$\times d\mathbf{r}^{N-2}d\mathbf{p}^{N-2}, \tag{3}$$

where the sum is carried out over all possible arranges 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. (2) 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 directly connected or bonded particles is achieved:

$$f^{\dagger}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{p}_i,\mathbf{p}_j)=\begin{cases}\exp[-\beta v(\mathbf{r}_i,\mathbf{r}_j)] & |\mathbf{r}_{i,j}(t)|<d\ \forall t\leqslant\tau\\ 0 & \text{otherwise,}\end{cases} \tag{4}$$

$$f^{*}(\mathbf{r}_i,\mathbf{r}_j,\mathbf{p}_i,\mathbf{p}_j)=\begin{cases}-1 & |\mathbf{r}_{i,j}(t)|<d\ \forall t\leqslant\tau\\ \exp[-\beta v(\mathbf{r}_i,\mathbf{r}_j)]-1 & \text{otherwise,}\end{cases} \tag{5}$$

where $\mathbf{r}_{i,j}(t)$ is the relative position of particles $i$ and $j$ at time $t$. We see that, in fact, Eq. (2) is satisfied by Eqs. (4) and (5). Explicitly, time is introduced here by taking the set $\{\mathbf{r}^N,\mathbf{p}^N\}$ as initial conditions in $t=0$ and solving the equation of motion of the particles under their mutual interaction. By considering as effective interaction the pair potential of mean force between particles $i$ and $j$: $v^{eff}(\mathbf{r}_i,\mathbf{r}_j)=-\ln[g(\mathbf{r}_i,\mathbf{r}_j)]/\beta$, we obtain a two body problem and $\mathbf{r}_{i,j}(t)$ will depend on $\mathbf{r}_i$, $\mathbf{r}_j$, $\mathbf{p}_i$ and $\mathbf{p}_j$ only.

Equation (4) states that two particles $i$ and $j$ are directly connected if they are separated a distance shorter than $d$ during a time interval longer than $\tau$. Of course, more elaborated criteria (e.g., involving angular restrictions), as well as simpler ones (that consider, for example, configurations at just the extremes of the given time interval), can be posed [5,8].

Each term in the integrand of Eq. (3) can be represented as a diagram consisting of two white $e_1$- and $e_2$-points, $N-2$ black $e_i$-points and some $f^{\dagger}_{i,j}$ and $f^{*}_{i,j}$ connections except between the white points. Here we take $e_i\equiv\exp[-\beta(\mathbf{p}_i^2/2m)]$. White points 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 [9] can be now extended to treat these new kind of diagrams. We first reduce the disconnected diagrams in Eq. (3) into connected diagrams by integrating over those black points which are disconnected from any white point. So we get a fugacity expansion for $\rho(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$. Then, by eliminating diagrams with articulation points (i.e., black points such that upon their removal the diagram separates into two or more pieces of which at least one contains no white points) we transform (topological reduction [10]) the fugacity expansion into a density expansion for the function $g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ defined by $\rho(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)=g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)\rho(\mathbf{r}_1,\mathbf{p}_1)\rho(\mathbf{r}_2,\mathbf{p}_2)$ with

$$\rho(\mathbf{r}_1,\mathbf{p}_1)=\frac{1}{N-1}\int\rho(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)d\mathbf{r}_2d\mathbf{p}_2.$$

The final result is

$$g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)=1+\left\{\begin{array}{c}\text{The sum of all distinct connected diagrams consisting}\\ \text{of two white 1-points labeled 1 and 2 respectively,}\\ \text{black } \rho(\mathbf{r}_1,\mathbf{p}_1)\text{-points and } f^{\dagger}_{i,j} \text{ and } f^{*}_{i,j}\text{-bonds, and}\\ \text{which are free of articulations points}\end{array}\right\}. \tag{6}$$

We now separate $g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ in the form $g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)=g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)+g^{*}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$, where $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ is the sum of all the diagrams in $g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ that contain a path of $f^{\dagger}_{i,j}$ connections linking the white particles 1 and 2 and $g^{*}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)-1$ denotes the sum of the remaining diagrams. Then

$$g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)=\left\{\begin{array}{c}\text{The sum of all distinct connected diagrams consisting}\\ \text{of two white 1-points labeled 1 and 2 respectively,}\\ \text{black } \rho(\mathbf{r}_1,\mathbf{p}_1)\text{-points and } f^{\dagger}_{i,j} \text{ and } f^{*}_{i,j}\text{-bonds, and}\\ \text{which are free of articulations points and white}\\ \text{points are linked by a path of } f^{\dagger}_{i,j}\text{-bonds}\end{array}\right\}. \tag{7}$$

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Figure 1 shows the first graphs in the diagrammatic expansion (6). Graphs which are enclosed by a box belong to the expansion (7) and the remaining ones to the expansion of $g^{*}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$.

From the interpretation of all the operations carried out over the diagrams, we see that $\rho(\mathbf{r}_1,\mathbf{p}_1)\rho(\mathbf{r}_2,\mathbf{p}_2)g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ is $N(N-1)$ times 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 cluster, where the bonding criterion is given by Eqs. (4) and (5).

An Ornstein-Zernike like integral equation for $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ can be written if we separate nodal and non-nodal diagrams in Eq. (7). We find

$$\begin{aligned}g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)={}&c^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)\\&+\int\rho(\mathbf{r}_3,\mathbf{p}_3)c^{\dagger}(\mathbf{r}_1,\mathbf{r}_3,\mathbf{p}_1,\mathbf{p}_3)\\&\times g^{\dagger}(\mathbf{r}_3,\mathbf{r}_2,\mathbf{p}_3,\mathbf{p}_2)d\mathbf{r}_3d\mathbf{p}_3,\end{aligned}\tag{8}$$

where the function $c^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ denotes the sum of all the non-nodal diagrams in Eq. (7). We remember that a nodal diagram contain at least a black point through which all paths between the two white points pass (see the last three graphs in Fig. 1). For homogeneous systems we have

$$\begin{aligned}g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)={}&c^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)+\frac{\rho}{(2\pi mk_BT)^{3/2}}\\&\times\int\exp\left[-\beta\frac{\mathbf{p}_3^2}{2m}\right]c^{\dagger}(\mathbf{r}_1,\mathbf{r}_3,\mathbf{p}_1,\mathbf{p}_3)\\&\times g^{\dagger}(\mathbf{r}_3,\mathbf{r}_2,\mathbf{p}_3,\mathbf{p}_2)d\mathbf{r}_3d\mathbf{p}_3,\end{aligned}\tag{9}$$

with $\rho=N/V$ the particles number density.

To get an integral equation from Eq. (8) is necessary a closure relation between $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ and $c^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$. We take the Percus-Yevick-like approximation $g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)\exp[\beta v(\mathbf{r}_1,\mathbf{r}_2)]=1+N(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$, where the function $N(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ is the sum of the nodal diagrams in the expansion given by Eq. (6). Separation into connecting and blocking parts yields

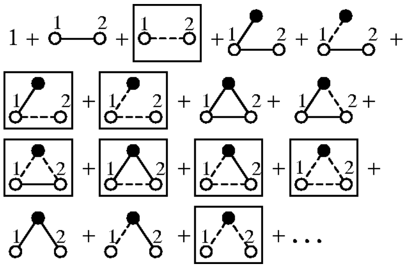

FIG. 1. Diagrammatic expansion for $g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$. Full and dotted lines represent unbonded and bonded particles respectively. Boxed diagrams belong to the expansion of $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$.

$$\begin{aligned}g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)={}&[h^{*}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)+1][g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)\\&-c^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)]\\&+\exp[\beta v(\mathbf{r}_1,\mathbf{r}_2)]g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)\\&\times f^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2).\end{aligned}\tag{10}$$

Equation (8) closed by Eq. (10) gives an integral equation for $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$.

From the function $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$ we define the cluster pair correlation function

$$g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2)=\int\rho(\mathbf{r}_1,\mathbf{p}_1)\rho(\mathbf{r}_2,\mathbf{p}_2)g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)d\mathbf{p}_1d\mathbf{p}_2.$$

It is the joint probability density of finding two particles that belong to the same cluster at positions $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively.

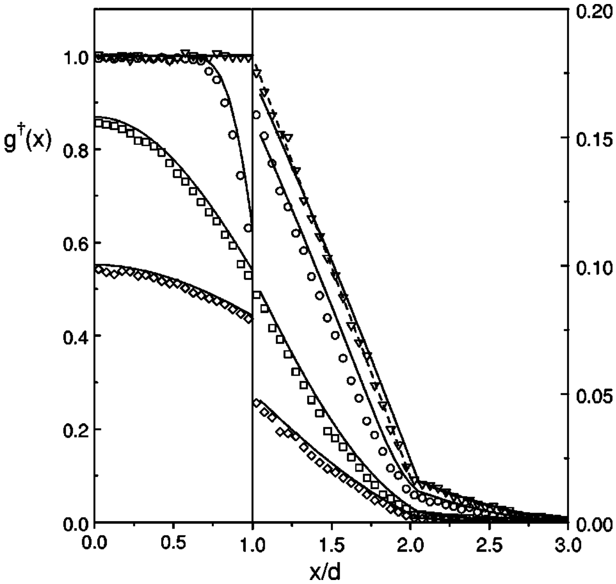

FIG. 2. Cluster pair correlation function $g^{\dagger}(x)$ vs $x$ for $\rho^{*}=0.2$ as calculated from the present theory (solid lines) and from molecular dynamics simulation (symbols). Triangles are for $\tau^{*}=0$ (standard connectivity criterion); circles, squares, and diamonds are for $\tau^{*}=0.1$, 0.5, and 1, respectively. Dashed line (for $\tau^{*}=0$) is calculated from the exact expression of Ref. [11]. Note the scale change at $x/d=1$.

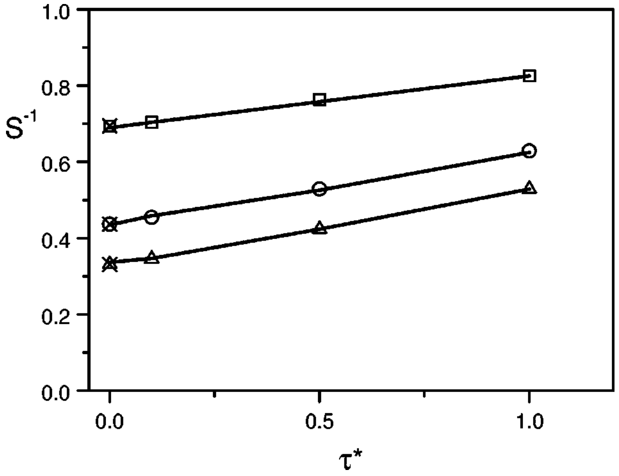

FIG. 3. Inverse of the mean cluster size as calculated from the present theory (lines) and from molecular dynamics simulation (symbols). Squares, $\rho^*=0.2$; circles, $\rho^*=0.5$; triangles, $\rho^*=1.0$. Crosses are from the exact theory (Ref. [11]).

Moreover, the mean cluster size $S$ is calculated as

$$S=1+\frac{1}{(N-1)}\int g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \tag{11}$$

so that a percolation critical density $\rho_c$ can be obtained from the equation $\lim_{\rho\to\rho_c} S(\rho)=\infty$. The meaning of $\rho_c$ is clear: the minimum density at which a macroscopic cluster is formed. Many interesting phenomena, which are characterized by qualitative changes in the macroscopic behavior of the involved systems, can be explained in terms of a percolation transition at a critical density.

To quickly check the previous formalism, we have numerically solved the Percus-Yevick-like integral equation [Eqs. (9) and (10)] for the simplest imaginable system and compared the results with those obtained from molecular dynamics simulations. We consider a one-dimensional ideal gas [$v(\mathbf{r}_i,\mathbf{r}_j)\equiv 0$; $v^{eff}(\mathbf{r}_i,\mathbf{r}_j)=0$] in which two particles are considered directly connected if they are separated a distance smaller than $d$ in a time interval longer than $\tau$.

Figure 2 shows $g^{\dagger}(x)$ [the one-dimensional version of $g^{\dagger}(\mathbf{r}_1,\mathbf{r}_2)$] as calculated for $\rho^*\equiv\rho d=0.2$ and several values of $\tau^*\equiv\tau\sqrt{\beta m}/d$. We compare the theoretical results with molecular dynamics simulations of the same system and for the same clusters definition. For $\tau^*=0$ (standard connectivity criterion) we have also compared the numerical approximate result of this work with the analytical exact one of Ref. [11]. In Fig. 3 a comparison is made of the mean value of cluster's size as a function of $\tau^*$ for several densities as calculated from Eq. (11) and from simulations. As we can see, mean cluster size is temperature-dependent even in this ideal case in contrast with the standard connectivity criterion.

Although we have applied our generalized Orstein-Zernike relation with Percus-Yevick-like closure to a very simple case, the present formalism can be also considered to account for the clustering in realistic systems [8] and approximations other than Percus-Yevick's can be used as well. So, a theoretical tool to study clustering in systems for which dynamical aspects of bonding are very important is available.

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