Equilibrium Clusters in Dense Lennard-Jones Gas: Molecular Dynamics Simulation

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We present molecular dynamics simulations of equilibrium clusters in two-dimensional Lennard-Jones (6–12) gas near the gas–liquid coexistence curve and in the overcritical region. Different cluster selection criteria are considered. The influence of cluster types on nonideal gas properties and the characteristics of relaxation to equilibrium for clusters are discussed. The radial distribution function near the critical point and the dependence of binding energy per cluster particle on number of particles in the cluster are calculated.

1. Introduction

The investigation of the structure and other properties of clusters of atoms and molecules is of great interest for many areas of study in physics and chemistry, such as nucleation in liquids and gases, the structure of amorphous materials, crystal growth, catalytic processes, and atmospheric physics. In addition the existence of clusters in condensed matter has a fundamental influence on processes in technical systems, such as MHD generators, rocket nozzles, and dynamical lasers. Although there is no direct experimental evidence for the existence of microclusters in dense media homogeneous on microscopic scales, empirical cluster models are successful in explaining certain properties of these media; thermodynamical properties of sodium and cesium vapor, for example. Macromolecular concepts, such as surface energy, are not applicable to clusters consisting of less than 100 particles, because the structure of such clusters is strongly dependent on the number of particles (see, e.g., ref 3). This may be understood as a manifestation of the fact that all particles in such clusters act as surface particles. It is therefore desirable to develop microscopic descriptions of these clusters. To draw conclusions about the concentration and kinetics of clusters using microscopic theory, it is necessary to know the cluster structure; however, the mathematical calculation of properties of clusters is in general a difficult task. The mathematical simulation of micromolecular models in dense media by molecular dynamics and Monte Carlo techniques is therefore fruitful.

The main difficulty of such simulations is uncertainty of the concept of "a cluster in a dense medium" and so of a definition suitable for use in simulation. For example, the geometrical cluster selection criterion is based on the location of cluster particles. Binding energies of cluster particles may be analyzed using energy criteria. Zurec and Schievelb discussed both geometrical and energy criteria for clusters in dense media in terms of chemical bonds between two particles. They proposed a dynamical definition of bound particles for a hard-core square-well system and used it for dimers and trimers concentration calculations in a 2D system.

In this paper, we propose a new energy criterion for cluster selection and present an analysis of various energy and geometrical criteria (section 3). We present molecular dynamics simulation results for clusters near the gas–liquid coexistence curve and in the overcritical region. We find that clusters selected by different criteria are fundamentally different physical objects and that they influence on different experimental properties of a nonideal gas. We propose a classification scheme for clusters in a dense nonideal gas and show the relation between this classification scheme and our cluster selection criteria. We present calculations of the radial distribution function (RDF) near the critical point, which allows us to draw qualitative conclusions about the structure of the fluid near the critical point (section 4). The relaxation from the initial simulation conditions to an equilibrium state is discussed.

2. Simulated Nonideal Gas Model

We used a square cell containing 144 particles to simulate a nonideal gas using molecular dynamics. The simulation was also carried out for 100 and 256 particles to study the influence of the number of particles on the physical properties of the system. The equations of motion were solved using the simple first-order algorithm (see, e.g., ref 12). The length of the cell was determined from the density of particles. Periodic boundary conditions and a truncated Lennard-Jones (6–12) potential were used:

\[ U(r) = \begin{cases} 4\alpha((\sigma/r) - (\sigma/r)^6), & r < r_0 \\ 0, & r > r_0 \end{cases} \]

where \( r_0 = 2.6 \), \( \sigma \) and \( \epsilon \) are Lennard-Jones (6–12) potential coefficients. For the Lennard-Jones system simulation we used units \( \sigma = \epsilon = m = 1 \), where \( m \) is the mass of gas particle. The integration step was \( \tau = 2.5 \times 10^{-3} \) in this unit system.

The initial locations of particles were near square lattice nodes with a random deviation amplitude less than 0.05. The initial velocities were assigned by a random number generator. The system relaxed to an equilibrium state during the first \( 10^4 \) integration steps. To derive the equilibrium state, at a different temperature from that of the given equilibrium state, we scaled all velocities at each step during the next \( 10^4 \) steps. To study the quantitative properties of the system such as the mole fractions \( C_n \) of clusters of various sizes we used a longer relaxation time of \( 8 \times 10^4 \) steps. This relaxation time was sufficient to allow the system to reach an equilibrium in which the fraction of clusters containing less than 10 particles was approximately constant. After this relaxation time we averaged cluster properties during an additional \( 10^4 \) steps. The total energy of the system was conserved to within \( 5 \times 10^{-3}U \), where \( U \) is the mean potential energy of the system.

3. Cluster Selection Criteria

According to the Stilinger criterion, if the distance between any two particles is smaller than the critical distance \( R_c \), the two particles are said to belong to the same cluster. We used the Stilinger criterion with \( R_c \) equal to \( R_c \), the distance between a given particle and particles belonging to the first coordination sphere of that particle. The radius of the first coordination sphere was taken to be equal to the radius of the first minimum in the radial distribution function. The value of distance \( R_c \) was found for five densities ranging from 0.04 to

using the following relation:
\[
R_c = R_{0c} + A\rho + B(T - T_0)
\]
(2)

where \( T_0 = 0.7 \), and \( R_{0c}, A, \) and \( B \) are extrapolation coefficients.

This adaptation of the geometrical criterion allows the study of denser clusters in denser media than others which have been used in past works (see also ref 9). For example, Stilinger used \( R_c \) equal to the interaction radius \( r_0 \) and in the modification of the Stilinger criterion used by Polimeropoulos and Briman, \( R_c \) was taken to be equal to 2.0. We used \( R_c \) equal to the interparticle distance in a liquid. In addition, to exclude random density fluctuations Polimeropoulos and Briman did not take into account rapidly disintegrating clusters with a lifetimeless than the mean period of particle oscillation in the gas; our approach allows us to take account of such fluctuations. Our approach is also more convenient for numerical simulation than that of Reiss et al., since in that work clusters in a dense media are considered only in terms of groups of particles within a given sphere, i.e., individual distance between particles is not taken into account.

Now we consider various energy criteria for cluster selection, which we shall call A, B, C, and D. Energy criteria A and B both consider cluster decay by the escape of a single particle. Energy criterion A is that proposed by Voroncov-Velyaminov and Pavlov and used by Zheludkov and Insepov, according to which an escaping particle is considered to belong to the cluster if the sum of relative kinetic and interaction potential energies between this particle and any other nearby particle of the cluster is positive. We improve this criterion by taking into account the interactions between the escaping particle and all other particles of the cluster using the following relation:

\[
\frac{2N_m}{(N + 1)} \left( \frac{1}{N} - \frac{1}{N - 1} \sum_{j \neq 1} \frac{u_j}{\mu_j} \right)^2 + \sum_{j \neq 1}^N \frac{u_j}{\mu_j} < 0
\]
(3)

where \( N \) is the number of cluster particles; this constitutes criterion B. Let \( C_N \) be the ratio of the number of clusters containing \( N \) particles to the total number of clusters, including monomers (note that this definition differs from the one used by Polimeropoulos and Briman and by Zheludkov and Insepov). The fractions \( C_N \) for \( N \geq 2 \) selected according to criterion A are found to be 2–10 times less than \( C_N \) selected according to criterion B. We therefore identify B as the more effective cluster selection criterion and use it instead of criterion A.

In some cases, a cluster defined by criterion B may be unstable, i.e., it may have total energy \( E_{tot} \) greater than zero. Such a cluster may be subject to decay into smaller fragments for with \( E_{tot} \) is less than zero. Our energy criterion C selects precisely those clusters with \( E_{tot} \) less than zero. The following algorithm was used for cluster search using the criterion C. First we found a cluster according to the Stilinger geometrical criterion; all particles with separation less than the first coordination sphere radius \( R_c \) were included in such a cluster. When each new particle was identified, the total energy of the configuration was calculated. If \( E_{tot} \) was less than zero, the current number of identified cluster particles \( N_c \) was said to satisfy energy criterion C. We repeated this procedure until we found all the cluster particles satisfying energy criterion C. All particles included in a cluster with negative total energy are than neglected in further cluster searches. Other particles included in the cluster according to the geometrical criterion but excluded from the configuration with negative total energy remain suitable to be included in another cluster.

To find all possible clusters according to the energy criterion C, all possible combinations of particles included in the cluster according to the geometrical criterion should be tested. Particular attention should be paid to the case when there are two or more particles which have not yet been tested in the neighborhood of a particle which has already been identified as a cluster particle. In this case we can test these particles in several different orders: this may lead to different clusters being defined in each case, i.e., different clusters can be formed during cluster "growth". Thus, to sort out all possible combinations of particles selected in a cluster, we keep the number of particles in it constant but change the order of particle testing. This improvement of the basic algorithm is effective only for selection of clusters which are not very branched and does not help in accurate selection of highly branched clusters. We suppose that the number of large branchy clusters is much less than the number of less branchy clusters, and so an inability to accurately select branchy clusters is a negligible effect.

We also propose one more energy criterion which we call D. According to this criterion, a particle belongs to a cluster if both inequality 3 holds and the total energy of the cluster is less than zero, both criterion B and criterion C are satisfied. Through this criterion, both cluster decay due to escape of a single particle and cluster decay due to fragmentation into parts are considered.

4. Results and Discussion

The radial density function (RDF) of nonideal gas was found for several temperatures and densities by averaging during 104 integration steps for 100 discrete values of radius. The fluctuations of the RDF were less than 1%.

We find that the maxima of the RDF of the first, second, and third coordination spheres at \( T = 0.47, \rho = 0.32 \), which is a critical point for 2D Lennard-Jones system, are greater than the same maxima for temperatures and densities close to these critical values. The reason for this is the increase in correlation length near the critical point. Our simulations indicate that the RDF at the critical point is greater than the RDF for a denser fluid at the same temperature at all radii, due to large density fluctuations near the critical point. This is analogous to the result obtained by Koch et al. for spinodal decomposition at density \( \rho = 0.32 \) and temperature \( T = 0.45 \) near the critical point.

From diagrams of the instantaneous particle and velocity vector configurations for different values of temperature \( T \) and density \( \rho \), we determined that at the critical point almost all particles are connected in one large cluster (see also ref 17). At the critical point, the size of fluctuations is at least equal to and likely greater than the length of a cell \( L \), but these large density fluctuations are absent from the simulated system at the critical density \( \rho = 0.32 \) and temperature \( T = 0.94 \) (twice the critical temperature). The size of our cell is, of course, insufficient for a quantitative study of properties of systems at the critical point.

A cluster in a dense medium is considered by Reiss et al. as a configuration of particles within a sphere if the distance between this sphere and any other particle is larger than the interaction radius. All particles of our simulated system with temperature \( T = 0.564 \) and density \( \rho = 0.1 \) were included in a single cluster according to this criterion.

No groups of particles moving together were found in gas with density \( \rho = 0.1 \). Such groups were present in the system at the critical density \( \rho = 0.32 \) and temperature \( T = 1.88 \) (compare also ref 18).

In Figure 1a the fraction of clusters with \( N \) particles \( C_N(N) \) in systems under the same conditions but containing different total numbers of particles are compared. The change of the total sum of fractions of all clusters at a fixed distribution of clusters vs \( N \) according to definition 4 only shifts the curve \( C_N(N) \) along the Y coordinate (in the logarithmical scale). We can thus study the concentration of clusters. Note that this would be impossible using definition 5.

In general, our system containing 144 particles is insufficient for the determination of \( C_N \) for all \( N \), but it is adequate for studying fractions of clusters containing less than nine particles. The
properties of systems with finite numbers of particles is a subject of interest for other studies, as well.\textsuperscript{19}

The relaxation time $\tau_{\text{rel}} = 8 \times 10^4 \tau$ ($\tau = 2.5 \times 10^{-3}$) used for the majority of calculations is 2 orders of magnitude greater than the time necessary to achieve a Maxwellian velocity distribution. We note that this relaxation time is 10 times greater than the one used by Zheludkov and Insepov,\textsuperscript{7} 200 times greater than the value used by Rao et al.\textsuperscript{19} and 400 times greater than the relaxation time used by Polimeropoulos and Briman.\textsuperscript{6} In Figure 1b fractions of clusters $C(N)$ for different relaxation times $\tau_{\text{rel}}$ near the coexistence curve are compared, where a critical slow down probably takes place. The fractions of clusters for all $N$ significantly increase up to $\tau_{\text{rel}} = 8 \times 10^4 \tau$; then, up to $\tau_{\text{rel}} = 2.8 \times 10^5 \tau$ (the maximum time we considered) the fractions of clusters containing fewer than 10 particles change only slightly, while larger clusters continue to form. The same effect was also found far away from the coexistence curve. For example, at temperature $0.564$, density $0.06$, and an increase of $\tau_{\text{rel}}$ from $10^4 \tau$ to $8 \times 10^5 \tau$, the percent of clusters with total energy less than zero among clusters containing 3–5 particles increased from 60% to 90%, the percent of particles not belonging to clusters decreased from 66% to 50%, and the maximum size of clusters increased from 7 to 19 particles. Thus, at density 5 times less than the critical density in the overcritical region half of all the particles belong to clusters. Figure 1b shows that our relaxation time is insufficient to obtain an equilibrium cluster distribution for $N$ larger than 10. Of course, the evolution to a Maxwellian velocity distribution is not sufficient to achieve total thermal equilibrium in the system, which is necessary for multiparticle distribution function study. From Figure 1b we estimate the relaxation time required to reach equilibrium values for fractions of clusters containing less than 10 particles to be $\tau_{\text{rel}} = 8 \times 10^4 \tau$. Such large relaxation times for nonideal-gas-containing clusters is also a result of the macroscopical theory of homogeneous nucleation. For example, the time necessary to approach an equilibrium concentration of clusters containing 20 water molecules in supersaturated water is about $10^5 \tau$.\textsuperscript{20} Thus, although the relaxation time used and the number of particles in the systems considered here are insufficient for study of all quantitative properties of an infinite Lennard-Jones gas in equilibrium, they do allow estimation of equilibrium fractions of clusters containing less than 10 particles. In addition, the relaxation time and the number of particles in the systems studied are probably sufficient to consider cluster structure and energy properties.

Figure 2 demonstrates the dependence of $C_N$ on the number of particles $N$ for different temperatures and densities in the overcritical region. It can be seen that the fractions of clusters $C_N$ selected by different criteria differ from 2 to 10 times (compare refs 6 and 7 for a 3D system). We therefore conclude that clusters found by different criteria are fundamentally different physical objects. In the review by Kulik et al.\textsuperscript{21} a division into "physical" and "chemical" clusters is proposed. According to the proposed
definition, a cluster is chemical if it can exist in vacuum for an infinitely long time. In this paper we propose a more detailed cluster classification scheme, which is described below.

Clusters selected by the geometrical criterion we propose to call “fluctuational clusters.” They are essentially droplets of dense phase in a nonideal gas for which the interparticle distance is as small as in liquids. These dense groups of particles determine the difference between the electron states in an atom in a cluster existing in a nonideal gas from the electron states in a free atom. This difference can markedly affect the optical properties of a nonideal gas. We do not confine the lifetime of a fluctuational cluster to the time of particle oscillation in a gas, as did Polimeropoulos and Briman since this time may be several orders of magnitude greater than the time for electron levels to form in a cluster.

Figure 2 shows that the number of clusters identified using energy criterion C is several times greater than the number of clusters identified using energy criterion B. Clusters satisfying energy criterion D, i.e., simultaneously satisfying both criterion B (total energy of cluster below zero) and criterion C (validity of inequality 3) are “chemical clusters” (see Kulik et al.21). Clusters stable to decay by single particle escape but unstable to decay into multiple parts we proposed to call “metastable clusters” (see also ref 10 for dimers). Clusters selected according to energy criterion B are primarily chemical and metastable clusters, with the fraction of metastable clusters among them increasing with increasing density. The existence of stable and metastable clusters corresponding to criterion B is related to the appearance of the infrared vibrational spectrum. The kinetics of these clusters determine the chemical properties of a nonideal gas.

In Table 1 the fraction of dimers selected by energy and geometrical criteria are compared with the results obtained by Harrison and Schieff.23 Our fraction of dimers is greater than that found by these authors, probably due to the insufficient relaxation time used by them23 in their system.

Figure 3 shows the percent of bound clusters \( P(N) \) (those with total energy less than zero) among the clusters selected by the geometrical criterion. From 90% to 100% of fluctuational clusters containing more than five particles are bound at temperature \( T = 0.564 \). There is a peak near \( N = 10 \) which is a fluctuation due to the very small number of large clusters in the system. Of course, the percent of clusters which are bound dramatically decreases with increasing temperature. At \( T = 0.564 \) and \( \rho = 0.14 \) the fractions of clusters identified by the geometrical criterion and by energy criterion C nearly coincide (Figure 2b). This indicates that energy criterion C merely identifies those fluctuational clusters with negative total energy and does not select fundamentally new physical objects in comparison with other criteria. We therefore suggest that C is not the most useful criterion for cluster search. It is interesting, however, to compare the total, internal, or kinetic energy of selected groups of particles not only with zero but also with their mean value in the system. To this purpose modifications of criterion C can be used for the investigation of energy and temperature fluctuations.

The coexistence curve for a two-dimensional Lennard-Jones system was found by Singh et al. There is a nearly horizontal plateau on this curve from the point \( (T = 0.465, \rho = 0.047) \) to the critical point \( (T = 0.47, \rho = 0.32) \). We compared the changes in the fraction of clusters selected by the geometrical criterion with increasing density for \( T = 0.46 \) and \( T = 0.49 \). The system with \( \rho = 0.038 \) and \( T = 0.46 \) corresponds to the gas phase, while other systems with \( T = 0.46 \) and densities \( \rho \geq 0.04 \) correspond to a metastable region. Large clusters near the coexistence curve are absent. There is not a significant increase of cluster fraction \( C_N \) for \( N \leq 9 \) when the system moves from a saturated gas or the overcritical region to a metastable region. This confirms that for the 3D case the “liquid drop” macroscopical theory is invalid near the coexistence curve.

In the “liquid drop” model for clusters the binding energy is considered to be the sum of the volume and surface energies. The volume energy of the cluster is proportional to the square of the radius and hence to the number of particles in the cluster. The surface energy of the cluster is proportional to the radius and hence to the square root of the number of particles in the cluster. Therefore, in the framework of the “liquid drop” model, the cluster binding energy \( E_N \) and the cluster binding energy per particle \( \epsilon_N \) are

\[
E_N = cN + dN^{1/2}
\]

(4)

\[
\epsilon_N = c + dN^{-1/2}
\]

(5)

where \( N \) is the number of particles in the cluster, and \( c \) and \( d \) are
coefficients. Figure 4 shows the dependence of binding energy on number of particles in the cluster derived using energy criterion C. This figure clearly demonstrates the inappropriateness of the "liquid drop" model approach for microclusters, since the binding energy per cluster particle increases with the number of particles in the cluster, contrary to the behavior predicted by eq 5.

5. Conclusion

We have proposed several new concepts concerning clusters in a nonideal gas in thermal equilibrium. Our simulations indicate that clusters found by different criteria are fundamentally different physical objects. We proposed a classification scheme for these objects and have suggested links between different classes of clusters and the different cluster selection criteria discussed here. We recommend use of the geometrical criterion for the selection of fluctuational clusters and use of our energy criterion D for selection of metastable and stable clusters. In our simulations, a significant fraction of clusters was found in the overcritical region.

In future we intend to use our criteria for cluster selection in a nonideal gas to investigate the energy and structural properties of clusters in a nonideal gas; the kinetics of clusters, the calculation of rate constants of reactions; nonequilibrium properties of systems containing clusters, e.g., spinodal decomposition and homogeneous nucleation; and fluctuations of density and energy in a nonideal gas.

References and Notes

(22) Skowronek, M.; Rous, J.; Larour, J. Physica 1986, 139, 547.