Characteristics of instantaneous resonant modes in simple dense fluids with short-ranged repulsive interactions

Ten-Ming Wu, Wen-Jong Ma, and S. L. Chang

Citation: The Journal of Chemical Physics **113**, 274 (2000); doi: 10.1063/1.481793
View online: http://dx.doi.org/10.1063/1.481793
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/113/1?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF CHEMICAL PHYSICS VOLUME 113, NUMBER 1 1 JULY 2000

Characteristics of instantaneous resonant modes in simple dense fluids with short-ranged repulsive interactions

Ten-Ming Wu
Institute of Physics, National Chiao-Tung University, HsinChu, Taiwan, Republic of China

Wen-Jong Ma
Institute of Mathematics, Academia Sinica, Nankang, Taipei, Taiwan, Republic of China

S. L. Chang
Institute of Physics, National Chiao-Tung University, HsinChu, Taiwan, Republic of China

(Received 2 November 1999; accepted 3 April 2000)

We manifest the characteristics of the low-frequency, quasilocalized instantaneous normal modes, named as the instantaneous resonant modes (IRMs), in simple dense fluids with short-ranged repulsive interactions. The analyses include the potential energy profiles of the IRMs, and the local geometric structures and the number of the interacting neighbors of the particles at which the centers of the quasilocalization are located. We conclude that an IRM is created due to fluctuations in the local density, and has a barely-isolated center, which slightly interacts with one or two nearest neighbors, and the potential energy profile of an IRM is basically single-well with strong anharmonicity. The differences in character between the IRMs and the high-frequency localized instantaneous normal modes are also examined. Based on the barely isolated center picture, a necessary criterion for the occurrence of the IRMs is proposed. While only the imaginary-frequency IRMs are found in dense fluids with purely repulsive interactions satisfying the criterion, a tiny attractive well in the pair potential allows the occurrence of the real-frequency IRMs. The physical systems to detect the presence of the IRMs are discussed. © *2000 American Institute of Physics.* [S0021-9606(00)50225-6]

I. INTRODUCTION

Resonant modes, low-frequency quasilocalized vibrational excitations, occur in various kinds of solids and have been one of the most interesting subjects in solid-state physics.[1] Properties of resonant modes in harmonic lattices with heavy mass or weakly coupled impurities[2] or in anharmonic lattices[3,4] have been well studied analytically. In the former case, the vibrational motion of a resonant mode is sharply localized to an impurity and its nearby particles, and the decay of the quasilocalized vibration from the impurity is generally not exponential, but is much more extensive in space. In glassy systems, resonant modes have been observed by experiments[5] and computer simulation[6–8] and are proposed to be the physical origin of many anomalous thermal properties, including the specific heat and the thermal conductivity, of glasses at temperatures above 1 K.[9] The potential energy profiles of the resonant modes in glasses can be described by the soft-potential model,[10–12] which occurs in the single-well potentials with strong enough anharmonicity.

Materials in the fluid phases have many different dynamic properties from those in the solid phases, for their constituents moving more rapidly and irregularly as compared with the molecular motions in solids. Energy landscape paradigms are usually used to describe qualitatively the dynamic behavior of fluids.[13] In the configuration space, the potential energy hypersurface of a many-particle system has been proposed to possess many local minima, which correspond to the inherent structures of the system.[14] The motions of the system at high temperatures can be visualized as vibrational motions around an inherent structure in the short-time scales, and making transitions between the inherent structures through barrier crossings in the long-time scales. Thus, the overall landscape is anharmonic in general, and the dynamics of a fluid at high temperatures should experience the anharmonicity of the landscape.[15] Similar in concept to the phonon modes in the crystalline solids, which give a good description of lattice dynamics, the instantaneous normal modes (INMs), which describe well the fluid dynamics in the short-time scales,[16,17] are the harmonic analysis for the local curvatures of the landscape through such a way that the INM frequencies at a configuration are given by the square roots of the eigenvalues of the Hessian matrix, the matrix of second derivatives of the potential energy hypersurface with respect to particle coordinates. Unlike the phonon density of states (DOS) for a crystal, the configuration-averaged DOS of INMs for a fluid is composed of two lobes: one for the real frequencies and the other for the imaginary frequencies, which are associated with the positive and the negative local curvatures of the landscape, respectively. According to the potential energy profile of an INM, which is the potential energy hypersurface along the eigenvector direction of this mode, an imaginary-frequency INM occurs at either the barrier top of a double-well (DW) potential or the convex region of a shoulder (SH) potential, which has only single well in the whole profile; the former case is mostly found in the high-frequency end of the lobe and the latter case in the low-frequency end.[18–20] Except for a very small amount of the small-frequency SH modes, the real-frequency INMs arise from the single-well (SW) potentials, which have always positive curvatures in the potential energy profile. There is indication that for INMs in the high-frequency end of the real-frequency lobe the SW potential becomes more and more anharmonic.[20] For many fluid systems,[16–18,21–24] the INMs in the high-frequency end of both lobes are localized modes, defined as having participation ratios inversely scaling with the system size. The localization of these high-frequency INMs can be understood, since the anharmonicity in the potential energy profiles of these INMs becomes dominant.

Recently, in terms of the standard instantaneous normal mode analysis and a newly defined quantity, the reduced participation ratio, Wu and Ma have presented the evidence for the existence of quasilocalized, low- frequency INMs in a model simple dense fluid, in which the pair interaction is merely the repulsive portion of the Lennard-Jones (LJ) potential.[25] This pair potential is named as the truncated LJ (TLJ) potential, and the fluid, the TLJ fluid. Since the TLJ potential is purely repulsive, these low-frequency INMs are found only in the imaginary-frequency lobe. Many characteristics of these INMs are quite similar as those of the resonant modes in solids. In a large scale beyond the INM approximation, the potential energy profiles of these quasilocalized INMs are strongly anharmonic, single-well potentials, with small variations near the bottom to cause the INM frequencies to be imaginary. At a fixed low frequency, the more quasilocalized the INM is, the stronger the anharmonicity in its potential energy profile. One of the major differences between these INMs and the resonant modes in solids is that their lifetimes are extremely short. Therefore, these quasilocalized, low-frequency INMs are named as instantaneous resonant modes[25] (IRMs). The short-ranged nature of the TLJ potential is essential for the occurrence of IRMs in the TLJ fluid; the IRMs are never present in the LJ fluid at the same density and temperature. It is the interplay between the interaction range and the mean nearest- neighbor separation in the TLJ fluid that leads to the presence of barely isolated particles, where the centers of these quasilocalized IRMs are located.

More recently, using the same technique of analysis, Wu and Tsay[26] have found by molecular dynamics simulation that the IRMs exist in the high-temperature Ga liquids and have frequencies very close to those of short- wavelength, nonacoustic excitations observed by means of inelastic neutron scattering in a recent experiment.[27] Therefore, it will be interesting to further investigate the nature and characterization of the IRMs in simple dense fluids and the thermodynamic criterion on the fluids for their occurrence. To find the conditions on a simple dense fluid in which the real-frequency IRMs may exist is also one aim of this paper.

In this paper, the TLJ fluid is still our basic model fluid for studying the characteristics of IRMs. In Sec. II, we show the difference in characteristics between the quasilocalized IRMs and the high-frequency localized INMs, and present the evidence from the geometric analyses on the local structures that the occurrence of an IRM in the TLJ fluid is indeed associated with a barely isolated center, which has only one or two interacting neighbors. In Sec. III, by studying the density of states of IRMs in various thermodynamic states of the TLJ fluid and in fluids with different interaction ranges of pair potentials, we propose a necessary criterion for the occurrence of IRMs in the simple dense fluids. Furthermore, choosing a pair interaction, which is still short-ranged but has a tiny attractive well, and a proper thermodynamic state, which satisfies the necessary occurrence criterion for IRMs, we indeed find the real-frequency IRMs in this simple model fluid. Our conclusions are given in Sec. IV.

II. QUASILOCALIZATION OF IRMS

In computer simulation, a finite-range pair potential based on the LJ interaction is usually given by

$$\phi(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]+A\left(\frac{r}{\sigma}\right)+B, \tag{1}$$

where A and B are chosen so that both the potential and the force vanish at some cutoff r_c, and beyond the cutoff the potential is truncated. This potential is close to the original LJ potential as the value of r_c is large enough. The reflection point in the attractive part of the original LJ potential, which is at $(26/7)^{1/6}\sigma\approx 1.244\sigma$, is a critical value of r_c. As r_c is less than this critical value, the potential given in Eq. (1) becomes purely repulsive; otherwise, the potential has an attractive well. The TLJ potential can be described by Eq. (1) by setting $r_c=2^{1/6}\sigma\approx 1.122\sigma$, the distance corresponding to the minimum of the original LJ potential, and by $A=0$ and $B=\epsilon$. We have carried out a series of molecular dynamics simulations for a system of 750 particles interacting via the pair potential given in Eq. (1) with several cutoffs varying from $2^{1/6}\sigma$ to 3.5σ, so that the pair-interaction range of the simulated fluids varies from short-ranged to long-ranged. The reduced densities $\rho^*=\rho\sigma^3$ in our simulations are from 0.7 to 0.972 and the reduced temperatures $T^*=k_BT/\epsilon$ from 0.5 to 1.3. The details of the simulations and the calculation of the INM DOS are found in Refs. 22 and 25.

In an N-particle system, the reduced participation ratio[25] s_α of each INM α is defined as the ratio, R_N^α/Q_N^α, where R_N^α is the number of particles involved in this INM, and is given by

$$R_N^\alpha=\left(\sum_{j=1}^{N}|\mathbf{e}_j^\alpha|^4\right)^{-1} \tag{2}$$

with $\mathbf{e}_j^\alpha$ the component of the normalized INM eigenvector on atom j, and Q_N^α similar to R_N^α given in Eq. (2), except that the term of the largest eigenvector component is excluded from the summation. Thus, the value of s_α is between 0 and 1. For an IRM, there is a quasilocalized center, in which a sharply peaked component on a particle is surrounded with a small-amplitude background, so that s_α will be close to zero. On the other hand, for an extended INM, in which the magnitudes of all eigenvector components are comparable, both R_N^α and Q_N^α scale with N and s_α is close to unity. Therefore, s_α acts as a measure for the quasilocalization of IRMs in a fluid.

For the TLJ fluid at $\rho^*=0.88$ and $T^*=0.836$, the $R_N(\omega)$ distribution,[22,25] which is the configuration average of

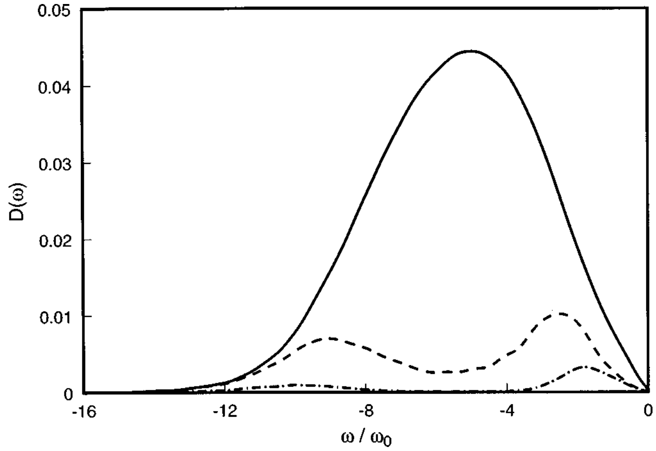

FIG. 1. The DOS of the imaginary-frequency INMs in a TLJ fluid ($\rho^*=0.88$ and $T^*=0.84$) with the reduced participation ratios less than 1 (solid line), 0.5 (dashed line), and 0.1 (dot-dashed line), respectively. As usual, the imaginary-frequency lobe is plotted along the negative frequency axis.

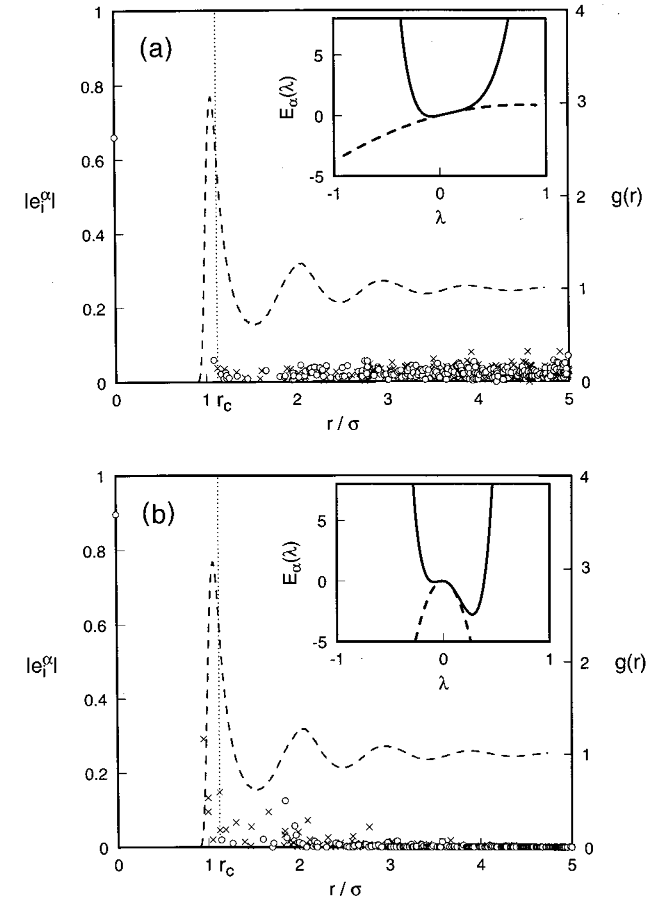

FIG. 2. The magnitudes of the eigenvector components $\mathbf{e}_j^\alpha$ as a function of the distance from the largest component particle for a low-frequency quasilocalized IRM with imaginary frequency $1.71\omega_0$ and $s=6\times10^{-3}$ (a), and a high-frequency localized INM with imaginary frequency $12.08\omega_0$ and $s=1.3\times10^{-2}$ (b) in a TLJ fluid. The open circles and the crosses represent particles with $\mathbf{e}_j^\alpha\cdot\mathbf{e}_1^\alpha$ greater and less than zero, respectively. In each plot, the left-hand and right-hand vertical scales are for $|\mathbf{e}_j^\alpha|$ and the radial distribution function, $g(r)$, which is indicated by the dashed line. The dotted line indicates the cutoff of the TLJ potential. In the inset of each part, the potential energy profile of the corresponding INM is given by the solid line, and the profile calculated with the INM approximation by the dashed line.

R_N^α within a small frequency width, has a sharp dip in the imaginary-frequency lobe at a region of frequency less than $5\omega_0$,[25] where $\omega_0=(\epsilon/m\sigma^2)^{-1/2}$ and m is the mass of each particle. Near the depth, the value of $R_N(\omega)$ depends on N, but does not scale with N. This implies that quite a portion of INMs in this region are quasilocalized in space. No corresponding dip is found in the $R_N(\omega)$ distribution of the LJ fluid at the same density and temperature. By comparing the INMs in these two fluids with pair interactions in different ranges, the small-imaginary-frequency INMs in this TLJ fluid can be roughly classified into three groups: the IRMs for s less than 0.1, the interacting IRMs for s between 0.1 and 0.5, and the extended INMs for s larger than 0.5 (our qualitative results given later are insensitive to the exact values of s for dividing these three groups). In Fig. 1, we show the DOS of the imaginary-frequency INMs with the reduced participation ratios less than 1, 0.5, and 0.1, respectively, in this TLJ fluid.

The magnitudes of $\mathbf{e}_j^\alpha$, which are plotted as a function of the distance from the largest eigenvector component particle, and the potential energy profiles of three INMs from each group, have been presented in Fig. 4 of Ref. 25. With the classification given above, a small-frequency INM with $s<0.1$ indeed has a quasilocalized center with the characteristic we described above for an IRM. While the potential energy profile of an IRM, in a local scale, may be a DW potential with a very small barrier, or a SH potential with the shoulder region very close to the minimum of the single well, the profile is actually part of a single well with strong anharmonicity, if it is examined in a global scale beyond the scale for the INM approximation. We believe that it is this strong anharmonicity that plays an important role in making the INM quasilocalized. With the same presentation for those three INMs, we illustrate in Fig. 2 the difference in character between a quasilocalized IRM and a high-frequency localized INM. In the latter case, the decay of the eigenvector components away from the particle with the largest component is more like an exponential decay.[23] For an interacting IRM, there are more quasilocalized centers, with some interactions between them.[7] The larger the value of s, the more the magnitudes of the peaked components on those central particles in an interacting IRM are reduced as compared with those of IRMs. On the other hand, for an extended INM, one can hardly identify a localized center, although the magnitudes of the eigenvector components fluctuate from particle to particle.

In order to manifest further the quasilocalization character of an IRM, we define three quantities for each INM α,

$$\tilde{n}_\alpha=\sum_{j\neq1}^{N}\Theta(r_c-r_{j1}),\tag{3}$$

$$\tilde{e}_\alpha=\sum_{j\neq1}^{N}|\mathbf{e}_j^\alpha|\Theta(r_c-r_{j1}),\tag{4}$$

$$\tilde{\phi}_\alpha=\sum_{j\neq1}^{N}\phi(r_{j1})\Theta(r_c-r_{j1}),\tag{5}$$

where the largest eigenvector component particle has been taken as the center, and indexed as 1. $\Theta(r)$ is a Heaviside step function.

$$\Theta(r_c-r_{j1})=\begin{cases}1 & \text{for } r_{j1}<r_c,\\ 0 & \text{for } r_{j1}>r_c,\end{cases} \tag{6}$$

where r_{j1} is the distance between particle j and particle 1. We define the interacting neighbors of a particle in the TLJ fluid as those particles having distances from the particle less than the cutoff r_c. Thus, $\tilde{n}_\alpha$ is the number of the interacting neighbor of particle 1, $\tilde{e}_\alpha$ is the magnitude sum of the eigenvector components on those interacting neighbors, and $\tilde{\phi}_\alpha$ is the total interaction between the particle 1 and its interacting neighbors.

We divide the imaginary-frequency INM DOS shown in Fig. 1 into two sections at $5\omega_0$ so that the IRMs and the high-frequency localized INMs apparently fall in different sections. In each section, we make a configuration average for $\tilde{n}_\alpha$, $\tilde{e}_\alpha$, and $\tilde{\phi}_\alpha$ with respect to the INMs having reduced participation ratios within a small width. After these averages, we obtain, respectively, $\tilde{n}_<(s)$, $\tilde{e}_<(s)$, and $\tilde{\phi}_<(s)$ for imaginary frequencies less than $5\omega_0$, and $\tilde{n}_>(s)$, $\tilde{e}_>(s)$, and $\tilde{\phi}_>(s)$ for imaginary frequencies larger than $5\omega_0$. The results of these averaged functions are shown in Fig. 3. In the TLJ fluid discussed above, the average number of interacting neighbors is about 4.75. Figure 3(a) clearly shows that both $\tilde{n}_<(s)$ and $\tilde{n}_>(s)$ are below this average value. However, $\tilde{n}_>(s)$ does not vary much with s, but $\tilde{n}_<(s)$ decays with the decreasing of s in general, and is less than two for $s<0.1$. So, on average, the IRMs have two interacting neighbors at most.

The trend of $\tilde{e}_<(s)$, shown in Fig. 3(b), decays, in general, with the decreasing of s; however, the function has two peaks at $s=0.5$ and $s=0.465$. These two peaks are not completely due to the statistical fluctuation in the configuration average, but resulted from some special INMs. According to the definition of the reduced participation ratio, an INM with $s=0.5$ has two large eigenvector components with exactly equal magnitudes; a little bias on the magnitudes of these two large components will cause the value of s to be a little less than half. We have found two kinds of INMs with $s=0.5$ and their characters are shown in Fig. 4. The magnitudes of the two large eigenvector components shown in Fig. 4(a) are exactly equal to $1/\sqrt{2}$, and the two corresponding particles, having a separation less than $2^{1/6}\sigma$, form a dimer isolated from the rest of the particles in the fluid. The INM on this isolated dimer is clearly proven to be optical-like. In Fig. 4(b), the separation between the two large-component particles is about half of the simulation box length. In the TLJ fluid, the probabilities of finding INMs with s near 0.5 are rather small. It is these small probabilities that make the function of $\tilde{e}_<(s)$ near $s=0.5$ split into two peaks.

From Figs. 3(b) and 3(c), both the functions of $\tilde{e}_<(s)$ and $\tilde{\phi}_<(s)$ in the IRM region decrease with decreasing s. This fact indicates that the central particle of an IRM interacts less and less with its interacting neighbors as the IRM becomes more and more quasilocalized. Combined with the result analyzed from $\tilde{n}_<(s)$ in the small-s region, we propose a barely isolated center picture for the local structure around the central particle of an IRM in the TLJ fluid, in which the local structure is constructed with the slight interactions between the central particle and only one or two of its nearest neighbors. According to the differences in behavior of the

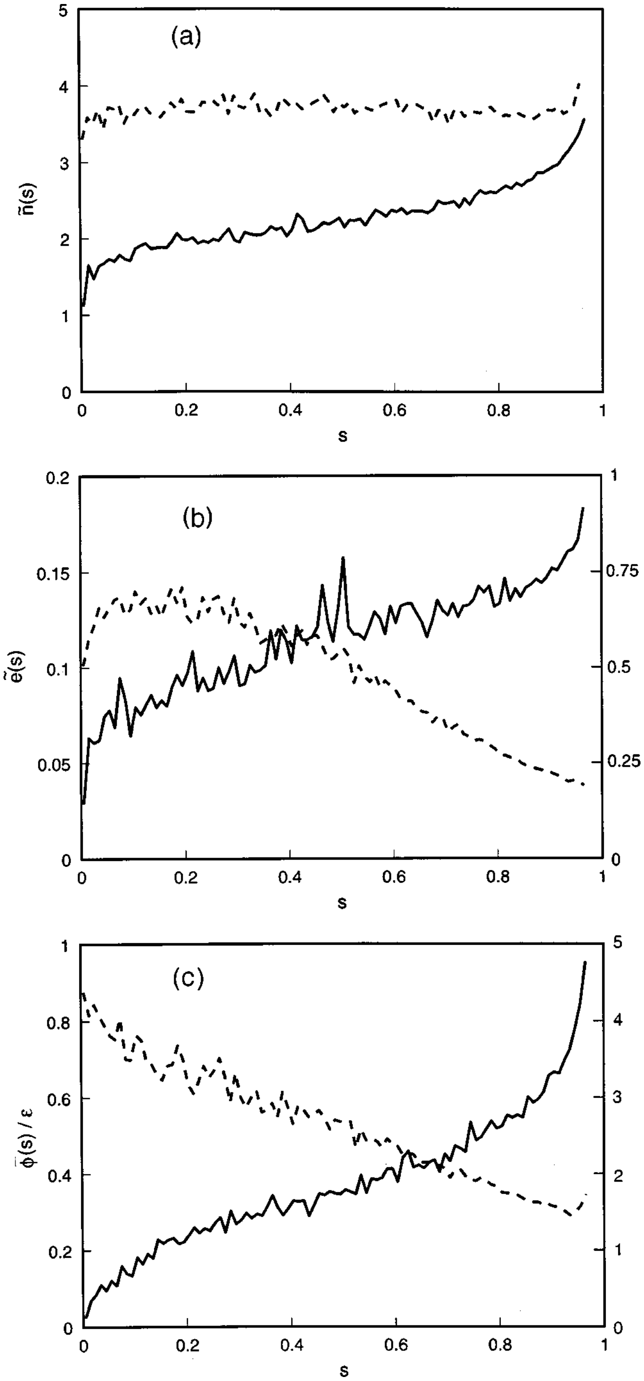

FIG. 3. Three functions of the reduced participation ratio s about the interacting neighbors of the particle with the largest eigenvector component of an imaginary-frequency INM in a TLJ fluid: The averaged number of the interacting neighbor (a), the sum of the magnitudes of the eigenvector components on those interacting neighbors (b), and the total interaction between the central particle and its interacting neighbors (c). The solid lines and the dashed are averaged for the INMs of imaginary frequencies below and above $5\omega_0$, respectively. Note that in (b) and (c) the right-hand and left-hand vertical scales are for the dashed and solid curves, respectively.

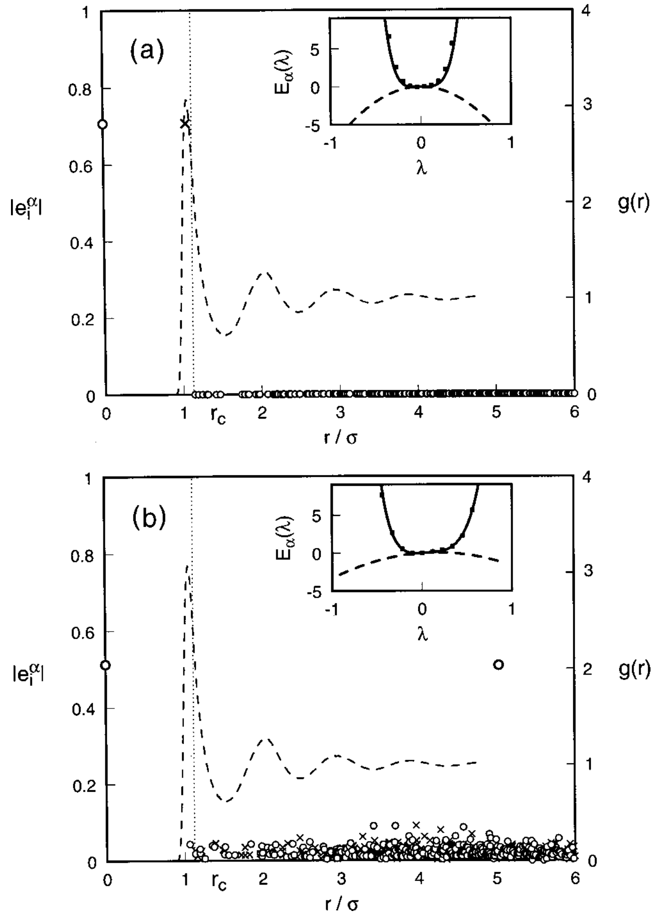

FIG. 4. As in Fig. 2 for two imaginary-frequency INMs with $s=0.5$ in a TLJ fluid. The two equal-magnitude large components in each INM are indicated by larger symbols. Their frequencies are $4.0\omega_0$ (a) and $2.23\omega_0$ (b). The separations of the two large-component particles in cases of (a) and (b) are less than the cutoff of the TLJ potential, and about half of the simulation box, respectively. In the inset of each plot, the dotted points are fit for the potential energy profile with a quartic polynomial.

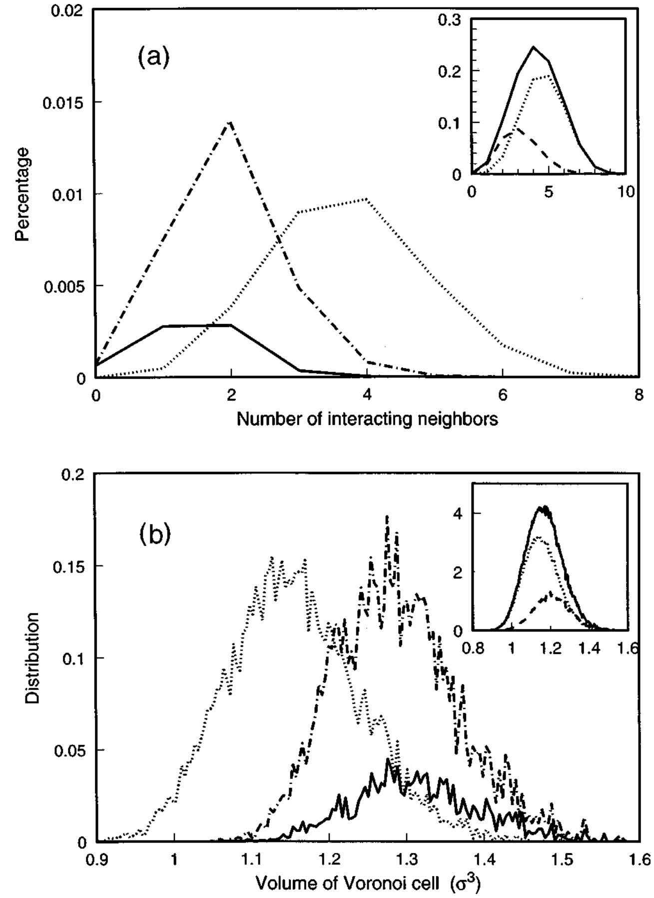

FIG. 5. The geometric analyses of the fluid structures associated with the imaginary-frequency INMs in the TLJ fluid, the DOS of which are shown in Fig. 1: The distributions for the number of the interacting neighbor (a), and the cell volume (b) of the particles with the largest eigenvector component of each INM. In each part, the solid line is for the INMs with imaginary $\omega<5\omega_0$ and $s<0.1$; the dot-dash line for the INMs with imaginary $\omega<5\omega_0$ and $s<0.5$, and the dotted line for the INMs with imaginary $\omega>5\omega_0$ and $s<0.5$. In the inset of each part, the solid, the dotted, and the dashed lines are for the total, the real-frequency, and the imaginary-frequency INMs, respectively.

$\tilde{e}_>(s)$ and $\tilde{\phi}_>(s)$ functions from those of $\tilde{e}_<(s)$ and $\tilde{\phi}_<(s)$, respectively, the topology of the local structure around the center of an IRM is expected to be quite different from that of a high-frequency localized INM, which has a central particle strongly interacting with its interacting neighbors.

Our picture of the local structure of an IRM can be verified through the geometrical analysis on the microstructure of the TLJ fluid. We have carried out two different structural analyses for the TLJ fluid at $\rho^*=0.88$: the statistical distributions for the number of the interacting neighbor and the Voronoi-cell[28] volume of each particle in the fluid, in which the Voronoi cell of a particle is defined as the polyhedral whose interior contains all points which are closer to the particle than to any other particles. The average Voronoi volume of each particle in a fluid can be obtained from the inverse of the fluid density, which is about 1.136 in reduced units for this TLJ fluid. To characterize the local structure of each INM, we focus on the number of interacting neighbors and the Voronoi volume of the central particle in each INM, which has the largest eigenvector component. This local structure characterization of a normal mode is significant for the localized or quasilocalized INMs, but not for the extended INMs. The statistical distributions of these two analyses for various kinds of INMs are shown in Fig. 5 for comparison. The results can be summarized as the following observations:

(a) The average Voronoi volume of the imaginary-frequency INMs is larger than that of the real-frequency INMs, and the situation for the average number of the interacting neighbor is reversed.

(b) For the imaginary-frequency INMs in the low-frequency section ($\omega<5\omega_0$) and with $s<0.5$, the Voronoi volumes of these INMs are almost above the average, and the numbers of their interacting neighbors are below the average value, 4.75, of this TLJ fluid.

(c) Within the region of the same frequency as in (b), but with s less than 0.1, which is the IRM region, the Voronoi-volume distribution covers almost the same range as that for $s<0.5$; however, the number distribution on the interacting neighbor shifts toward even smaller value, and does not have significant values above 3.

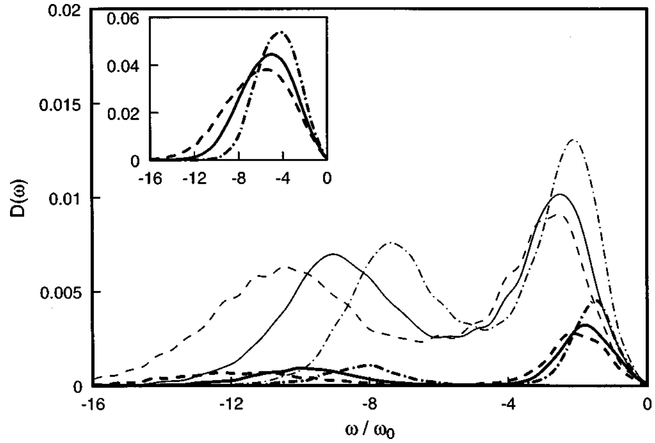

FIG. 6. Temperature dependence of the DOS of the imaginary-frequency INMs with reduced participation ratios less than 0.1 (the thicker lines), 0.5 (the thinner lines), and 1 (in the inset), respectively, for the TLJ fluids at $\rho\sigma^3=0.88$. The reduced temperature of the TLJ fluid is varied from 0.5 (dot-dash curves), to 0.84 (solid curves), to 1.3 (dashed curves).

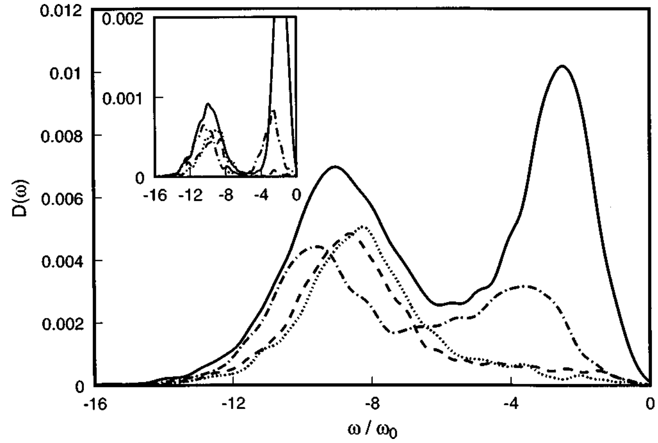

FIG. 7. The DOS of imaginary-frequency INMs with the reduced participation ratios less than either 0.5 or 0.1 (in the inset) for several dense fluids with the value of the ratio r_c/d varied from 0.87 (solid curves for $\rho^*=0.88$, $r_c=2^{1/6}\sigma$), to 0.90 (dot-dash curves for $\rho^*=0.972$, $r_c=2^{1/6}\sigma$), to 0.96 [dashed curves for $\rho^*=0.88$, $r_c=(26/7)^{1/6}\sigma$], to 2.70 (dotted curves for $\rho^*=0.88$, $r_c=3.5\sigma$). For all curves, $T^*=0.84$.

Thus, the results of these geometrical analyses are consistent with our picture of the local structure of the IRMs given above. In addition to this verification, our results also indicate that the local structures of the high-frequency localized INMs are more compact than those of the IRMs, with more interacting neighbors and smaller Voronoi volumes.

III. CRITERION FOR THE OCCURRENCE OF IRMS

Although we have presented the characteristics of the IRMs in the TLJ fluids, the criterion for the occurrence of IRMs in dense fluids is still an open question. In order to find the answer to this question, we have carried out two series of simulations: one for checking the density and temperature dependence of the IRMs in the TLJ fluid, the other for examining the effect of the shape of pair potential on the occurrence of IRMs by tuning the cutoff in Eq. (1) for systems at constant density and temperature. For these two series of simulations, we take the thermodynamic state ($\rho^*=0.88$ and $T^*=0.84$) of the TLJ fluid discussed in the last section as a reference one.

For the TLJ fluid at $\rho^*=0.88$ and three different temperatures, the DOS of the imaginary-frequency INMs with s less than 0.1, 0.5, and 1, respectively, are shown in Fig. 6. At the small imaginary frequency region, the temperature dependence of the DOS with s less than 0.1 follows that of the total DOS (with s less than 1) and the ratios of these two DOS are insensitive to temperature. Thus far, we conclude that the occurrence of IRMs in the equilibrium TLJ fluids is independent of temperature.[29]

Based on the barely isolated center picture on the local structures of IRMs given in the last section, the possibility for the IRMs occurring in a simple dense fluid essentially depends on two factors in competition: the density of the fluid and the interaction range of the pair potential. That is, the occurrence of the IRMs is actually determined by a competition in length between r_c, the cutoff of the pair potential, and d, the mean nearest-neighbor separation, which depends on density ρ through the definition

$$d=2\left(\frac{4\pi\rho}{3}\right)^{-1/3}. \tag{7}$$

How this competition determines the occurrence of IRMs in dense fluids can be understood from the following argument. Consider first fluids with finite short-range interactions, like the TLJ fluid. As $d>r_c$, the barely isolated centers are easily generated due to the local density fluctuation. In the other limit, as $d<r_c$, the fluid becomes packed, and each particle is not so easily detachable from its neighbors due to the local density fluctuation, even though the interaction range is short. Thus, in some thermodynamic states with the ratio r_c/d above some critical value, the barely isolated centers can not be generated so that the IRM DOS is expected to vanish. On the other hand, consider the case, like the second series of our simulations, in which the densities of the fluids are fixed, as are the values of d, but the interaction range r_c can be changed. As long as the fixed density is high enough, the structures of these systems should be similar, since the structure of a fluid is primarily determined by the short-range repulsive force. We expect that the IRM DOS of these constant-density fluids should decrease by increasing the interaction range of the pair potential, and disappear as the ratio r_c/d is above a critical value.

In order to test our argument, we have calculated the imaginary-frequency INM DOS with s less than 0.5, which includes both the IRMs and the interacting IRMs, for systems with several different values of the ratio r_c/d, and the results are illustrated in Fig. 7. In the TLJ fluids at a constant temperature, as the value of r_c/d increases from 0.87 ($\rho^*=0.88$) to 0.9 ($\rho^*=0.972$), the low-frequency peak of the INM DOS with $s<0.5$ shrinks dramatically and its position shifts to a higher frequency. Quantitatively, for imaginary frequencies less than $5\omega_0$, the area under this DOS curve at $r_c/d=0.9$ is estimated to be one third of that at $r_c/d=0.87$. Next, consider the fluids in our second series of simulations. The densities of these fluids are fixed $\rho^*=0.88$, and the value of r_c/d is 0.96 for $r_c=(26/7)^{1/6}\sigma$, and

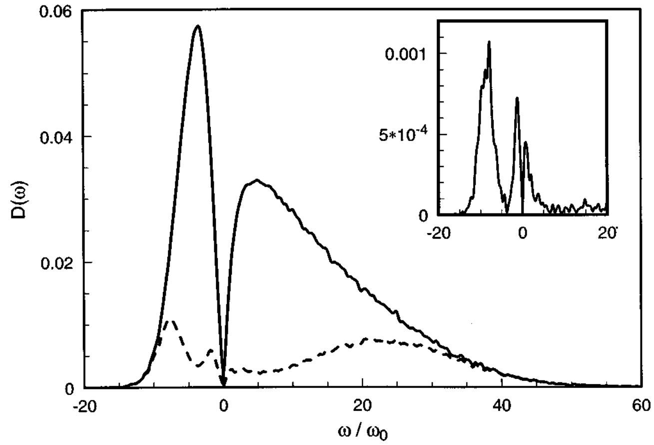

FIG. 8. The INM DOS of a system of particles interacting via the pair potential given in Eq. (1) with $r_c = 1.32\sigma$. The thermodynamic state of the system is $\rho^* = 0.7$ and $T^* = 1.0$. The DOS of INMs with s less than 1 and 0.5 are indicated with the solid and dashed lines, respectively; the DOS with s less than 0.1 are given in the inset.

2.7 for $r_c = 3.5\sigma$. We have checked the radial distribution functions, $g(r)$, of these two systems, and no significant differences are found. This result agrees with the theory of Chandle, Weeks, and Andersen,[30] and indicates that the static structures of these constant-density fluids are basically similar, which is a consequence of the same repulsive short-range interactions. As the value of r_c/d increases to 0.96, the INM DOS with $s < 0.5$ reduces further and there is no bump in the low-frequency section. However, by further increasing the value of r_c/d, the DOS with $s < 0.5$ does not change at all.

According to the above analyses, we conclude that the DOS of the IRMs in a dense fluid is sensitive to the ratio r_c/d, and propose that the ratio less than a critical value about 0.95 be the necessary criterion for the occurrence of the IRMs. The exact value of this critical ratio needs to be further determined, but, does not affect our qualitative conclusion. So far, the IRMs in the dense fluids with short-ranged repulsive pair interactions are only found to be in the imaginary-frequency lobe. Practically, the real-frequency IRMs, even in some model fluids, are more interesting. Our proposed necessary occurrence criterion serves as a guideline for finding the fluids having the real-frequency IRMs.

We suggest two conditions for a dense fluid to have the real-frequency IRMs: (1) a short-range pair interaction with a attractive well, and (2) the density of the system satisfied with the necessary IRM occurrence criterion. In order to satisfy these two conditions, we consider a system of particles interacting via the pair potential given in Eq. (1) with $r_c = 1.32\sigma$ and choose the reduced density of the system to be 0.7. For this chosen model fluid, the pair potential is still short-ranged, but has an attractive well with a depth about 0.02ϵ at $r \cong 1.19\sigma$. The value of r_c/d of this model fluid is about 0.945, and the calculated INM DOS of this fluid at $T^* = 1.0$ are shown in Fig. 8. We found that, in addition to the imaginary-frequency IRMs, the DOS of the IRMs extends into the low-frequency part of the real-frequency lobe. Therefore, this result justifies the two conditions for the occurring of the real- frequency IRMs.

IV. CONCLUDING REMARKS

In this paper, we have presented the general characteristics of IRMs, which are the low-frequency, quasilocalized INMs, in the dense fluids with short- ranged pair interactions. For the TLJ fluid, in which the short-ranged pair interaction is purely repulsive, the IRMs are only found in the imaginary-frequency lobe, which is associated with the negative local curvatures of the potential energy landscape. Through examining the potential energy profiles of these IRMs, the potential energy hypersurface along the IRM eigenvector directions, we found that in a large scale beyond the INM approximation the IRMs basically occur in strongly anharmonic, single-well potentials with small variations near the bottom of these wells producing the negative local curvatures. Combined with the geometric analysis on the structure of the fluid, the quasilocalization of the IRMs is found to be centered at the barely isolated particles in the fluid, which slightly interact with one or two of their neighbors. We also examined the differences in character between the IRMs and the high-frequency localized INMs in the TLJ fluid through comparing the interacting neighbors of the largest eigenvector component particles of these two kinds of INMs, and the interactions between this particle and its interacting neighbors. Our results indicate that the characteristics of these two kinds of localization are quite different. The more quasilocalized an IRM is, the less are the interactions between the central particle and its nearest neighbors. On the contrary, a high-frequency localized INM has a central particle strongly coupled with its neighbors, with stronger interactions for more localization.

The occurrence of the IRMs in a simple dense fluid is sensitive to the ratio of r_c/d, where r_c is the pair interaction range and d the mean nearest-neighbor separation of the fluid. The necessary criterion for the IRM occurrence is simply that the value of r_c/d of the dense fluid is lower than a critical value, which is found to be about 0.95. In a dense fluid with r_c/d less than this critical value, the IRMs are generated due to the local density fluctuation. The picture is consistent with that of the soft vibrational modes in metallic glasses due to the fluctuation of the density and the force constants.[39]

According to the necessary occurrence criterion for the IRMs, some consequences have been given, and some suggestions are proposed. Choosing a proper model fluid, in which the pair interaction is still short-ranged but has a tiny attractive well, and the density of the fluid is fulfilled with the necessary occurrence criterion for the IRMs, we have found the real-frequency IRMs in this model fluid. This result makes the IRMs in dense fluids more significant. It will be interesting to further study the characteristics of these real-frequency IRMs and how they are related to the physical quantities of a fluid.

The next question one may ask is what real physical systems may be good candidates to detect the presence of the IRMs. As mentioned in Sec. I, the IRMs have been found in the high-temperature Ga liquids, which have a peculiar pair potential.[26] The short-range nature of the pair interaction is essential for the occurrence of the IRMs. Recently, there have been many studies[31–35] on the role of the interaction range in the phase behavior in the colloidal physics. Colloidal dispersions[36] are the physical systems in which the interaction range between colloids is controllable, from short-ranged to long-ranged, and from purely repulsive to that with a deeply attractive well.[37] Many realistic examples and references can be found in the related literature in colloidal science;[38] the details are beyond the scope of this paper. Thus, we suggest that the colloidal dispersions are also the suitable physical systems to study the IRMs.

ACKNOWLEDGMENT

T. M. Wu would like to acknowledge support from the National Science Council of Taiwan, R.O.C. under Grant No. NSC 89-2112-M009009.

[1] A. A. Maradudin, E. W. Montroll, G. W. Weiss, and I. P. Ipatova, *Theory of Lattice Dynamics in Harmonic Approximation* (Academic, New York, 1971).
[2] A. A. Maradudin and A. J. Sievers, in *Localized Excitation in Solids*, edited by R. F. Wallis (Plenum, New York, 1968).
[3] S. Takeno and A. J. Sievers, Solid State Commun. **67**, 1023 (1988).
[4] S. A. Kiselev, R. Lai, and A. J. Sievers, Phys. Rev. B **57**, 3402 (1998).
[5] U. Buchenau, H. M. Zhou, N. Nucker, K. S. Gilroy, and W. A. Phillips, Phys. Rev. Lett. **60**, 1318 (1988).
[6] R. Biswas, A. M. Bouchard, W. A. Kamitakahara, G. S. Grest, and C. M. Souloulis, Phys. Rev. Lett. **60**, 2280 (1988).
[7] B. B. Laird and H. R. Schober, Phys. Rev. Lett. **66**, 636 (1991); H. R. Schober and B. B. Laird, Phys. Rev. B **44**, 6746 (1991).
[8] H. R. Schober and C. Oligschleger, Phys. Rev. B **53**, 11469 (1996).
[9] W. A. Philips, *Amorphous Solids, Low Temperature Properties* (Springer-Verlag, Berlin, 1981).
[10] V. G. Karpov, M. I. Klinger, and F. N. Igtnatiev, Sov. Phys. JETP **57**, 439 (1983); M. A. Il'in, V. G. Karpov, and D. A. Parshin, *ibid.* **65**, 165 (1987).
[11] U. Buchenau, Y. M. Galperin, V. L. Gurevich, and H. R. Schober, Phys. Rev. B **43**, 5039 (1991).
[12] D. A. Pashin, Sov. Phys. Solid State **36**, 991 (1994).
[13] A. Angell, Nature (London) **393**, 521 (1998).
[14] F. H. Stillinger and T. A. Weber, Science **225**, 983 (1984); R. A. LaViolette and F. H. Stillinger, J. Chem. Phys. **83**, 4079 (1985); F. H. Stillinger, Science **267**, 1935 (1995).
[15] P. Jund and R. Jullien, Phys. Rev. Lett. **83**, 2210 (1999).
[16] R. M. Stratt, Acc. Chem. Res. **28**, 201 (1995), and references therein.
[17] T. Keyes, J. Phys. Chem. **101**, 2921 (1997).
[18] S. D. Bembenek and B. B. Laird, J. Chem. Phys. **104**, 5199 (1996).
[19] F. Sciortino and P. Tartaglia, Phys. Rev. Lett. **78**, 2385 (1997).
[20] W. X. Li, T. Keyes, and F. Sciortino, J. Chem. Phys. **108**, 252 (1998).
[21] M. Cho, G. R. Fleming, S. Saito, I. Ohmine, and R. M. Stratt, J. Chem. Phys. **100**, 6672 (1994).
[22] T. M. Wu and S. F. Tsay, J. Chem. Phys. **105**, 9281 (1996).
[23] T. M. Wu and S. F. Tsay, Prog. Theor. Phys. Suppl. **126**, 343 (1997).
[24] M. C. C. Ribeiro and P. A. Madden, J. Chem. Phys. **108**, 3256 (1998).
[25] T. M. Wu and W. J. Ma, J. Chem. Phys. **110**, 447 (1999).
[26] T. M. Wu and S. F. Tsay (unpublished).
[27] F. J. Bermejo, R. Fernández-Perea, M. Alvarez, B. Roessli, H. E. Fischer, and J. Bossy, Phys. Rev. E **56**, 3358 (1997).
[28] G. Voronoi, Z. Reine Angew. Math. **134**, 199 (1908).
[29] We have rapidly quenched the TLJ system under a constant density well below the temperature of the liquid-glass transition. The IRMs still occur in the imaginary-frequency lobe but the IRM DOS is strongly squeezed toward smaller frequency. The results have been published in Physica A **281**, 393 (2000).
[30] D. Chandler and J. D. Weeks, Phys. Rev. Lett. **24**, 149 (1970); J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).
[31] S. M. Ilett, A. Orrock, W. C. K. Poon, and P. N. Pusey, Phys. Rev. E **51**, 1344 (1995).
[32] F. Leal Calderon, J. Bibette, and J. Biais, Europhys. Lett. **23**, 653 (1995).
[33] H. Löwen, Physica A **235**, 129 (1997).
[34] M. Hasegawa, J. Chem. Phys. **108**, 208 (1998).
[35] G. A. Vliegenthart, J. F. M. Lorge, and H. N. W. Lekerkerker, Physica A **263**, 378 (1999).
[36] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, 1989).
[37] H. N. W. Lekerkerker, J. K. G. Dhont, H. Verduin, C. Smits, and J. S. van Duijneveldt, Physica A **213**, 18 (1995).
[38] For example, J. K. G. Dhont, *An Introduction to Dynamics of Colloids* (Elsevier Science, Amsterdam, 1996).
[39] V. M. Manichev and E. A. Guesv, Phys. Solid State **41**, 334 (1999).