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Cage Dynamics in the Third-Order Off-Resonant Response of Liquid Molecules: A Theoretical Realization

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It is generally believed that the ultrafast initial spectroscopic response from the molecules in the condensed phase originates from small amplitude inertial motions within the cage formed by the nearest-neighbor solvent molecules surrounding the probe, or the cage effect. However, no quantitative estimate of this dynamics has been available for the currently popular experiments which measure the third-order off-resonant response. In this work, we fill this gap by a microscopic approach and demonstrate that the cage dynamics alone can produce the initial rise in the subpicosecond (ca. 200 fs) range in the third-order response. A simple analytical expression for the initial Gaussian time constant relevant to various kinds of the third-order off-resonant experiments is presented, which is found to be rather strongly dependent on the temperature. Connection with the non-polar solvation dynamics is also discussed.

Many elementary chemical reactions of interest take place in the condensed phase with extreme rapidity. Accordingly, the ultrafast dynamics in the condensed phase has received considerable attention. Recent advent of the ultrafast laser technology has enabled us to probe such fast phenomena directly in the time domain. Many novel experimental techniques have been developed in recent years.[1] These include various kinds of the third-order off-resonant spectroscopy[2] [such as the optical Kerr effect (OKE)[3,4] and the impulsive stimulated scattering (ISS)[6]], photon echo,[7] Raman echo,[8] three-pulse photon-echo,[9,10] and also two-dimensional fifth-order Raman spectroscopy.[11—13] The results of these experiments have augmented our understanding of liquid dynamics, although much remains to be understood.

These new results seem to suggest that there is a rather universal ultrafast response from the molecules in the condensed phase irrespective of the spectroscopic method used to probe. When no ultrafast rotational responses exist, this phenomenon has been ascribed to the cage dynamics where a solute performs a translational vibration in a collective potential well formed by surrounding molecules.[4] The collective potential is also time dependent, making the understanding of cage dynamics difficult. The role of cage dynamics in friction or in solvation dynamics has been discussed recently.[5] However, the relation between currently popular third-order off-resonant experiments and the cage dynamics has never been explored at a molecular level. Here, we present a microscopic theory which allows the molecular-level description. We shall demonstrate below that, at short times, the dynamics can be determined primarily by the intermolecular potential and the static radial distribution function $g(r)$ of the system. To test our theory, we performed molecular dynamics simulations and compared the results with our theoretical results.

The third-order response reflects the dynamics of polarizability correlation. In this paper, we consider the case of isotropic polarizability with keeping the first-order term in the dipole-induced dipole (DID) expansion[2,12—16] of the polarizability.

To construct the theory, we combine three well-known approximations: (1) the Gaussian decaying correlation, (2) the lattice gas model, and (3) the Weeks–Chandler–Andersen (WCA) scheme.

The first one is to extend the theory for a short time dynamics to a longer-time scale.[17] Since our concern is in the ultrafast dynamics, this may be a reasonable choice.

The second one is to include the cancellation effect, which has been known in a slightly different context.[18,15,19] Since the polarizability correlation, which is related to the third-order response, contains multi(more than two)-particle collision effects, we encounter multi-particle distribution functions, which are known to make significant contributions to cause the cancellation. To deal with this problem for rather dense liquids, which are the main interest of the recent experiments, we employ the simplest approximation of the lattice gas model,[20,19] which we introduce below.

The third one, WCA,[21] is to calculate the pair distribution function $g(r)$ for a Lennard–Jones (LJ) liquid. Only from the above two approximations, we can propose the expression for the third-order optical response [see Eq. 29 with Eq. 27],

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which includes no more multi-particle distribution functions but a pair distribution function $g(r)$. For the demonstration of our theory, however, we shall employ the LJ potential for argon. To have a $g(r)$ which is reasonably precise for the present purpose from a simple calculation, we employ WCA, although there now exist better approximations of liquid state structure.

A motivation of the present work has been to understand the time scales involved in the decay of the polarization time-correlation function originating from purely translational motions. In the non-polar solvation dynamics (NPSD), translational motions should again play a dominant role, while, in the polar solvation dynamics, the main contribution is made by the rotational motions of the solvent molecules.[5] In this respect, NPSD and third-order off-resonant spectroscopy probe fundamentally the same dynamical process. There is, however, also a large difference between NPSD and third-order off-resonant response. While both probe collective response from many molecules, the latter involves a dynamical quantity which decreases slower with distance (as $1/r^3$) of the probe from the solvent molecules, as opposed to at least $1/r^6$ in the case of NPSD. In other words, the NPSD probes more local structural dynamics (mostly the solvation dynamics in the first shell region) than in the present case. The present study seems to indicate that although the two relaxations occur with basically the same time scale, NPSD is somewhat faster for argon-like liquids. This seems reasonable, since the third-order response involves the collective dynamics of more global structural origin.

To test the relevance of our theory thus constructed, we performed the molecular-dynamics (MD) simulation. We pay special attention to obtaining the correct normalization of the third-order response to offer severer tests on our theory, as we see below.

I. Simple Theory for the Cage Dynamics

In the present study, we consider an N-particle classical three-dimensional system subject to the pair potential the $v(\boldsymbol{r}, \boldsymbol{r}')$, whose Hamiltonian is given by

$$H_N\left(\boldsymbol{p}^N;\boldsymbol{q}^N\right) = \sum_{i=1}^{N} \frac{|\boldsymbol{p}_i|^2}{2m} + \frac{1}{2}\sum_{i,j}{}' v\left(\boldsymbol{q}_i,\boldsymbol{q}_j\right), \tag{1}$$

where $v(\boldsymbol{q}_i, \boldsymbol{q}_j)$ is symmetric under the interchange of position variables, $\boldsymbol{q}_i$, and the prime for the summation implies that the self interaction, or the (i,i) terms, are removed from the summation. Here, $\boldsymbol{p}^N = (\boldsymbol{p}_1, \cdots, \boldsymbol{p}_N)$ and $\boldsymbol{q}^N = (\boldsymbol{q}_1, \cdots, \boldsymbol{q}_N)$, while $|\cdots|$ denotes the absolute value. Although our formalism is quite general, we shall employ the LJ potential for argon, $v(\boldsymbol{q}_i, \boldsymbol{q}_j) \equiv v_{\mathrm{LJ}}(|\boldsymbol{q}_i - \boldsymbol{q}_j|)$, in the numerical calculations, where

$$v_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right].$$

Here, $\sigma = 3.405$ Å and $\varepsilon/k_{\mathrm{B}} = 119.8$ K, where k_{B} is the Boltzmann's constant. The mass of argon employed below is $m = 6.63 \times 10^{-26}$ kg.

When constructing theory, we use the canonical ensemble where the phase space averaging is given by

$$\left\langle O\left(\boldsymbol{p}^N;\boldsymbol{q}^N\right)\right\rangle \equiv \frac{1}{N!h^{3N}Z}\int \mathrm{d}\boldsymbol{p}^N \int \mathrm{d}\boldsymbol{q}^N O_N\left(\boldsymbol{p}^N;\boldsymbol{q}^N\right) \mathrm{e}^{-\beta H_N\left(\boldsymbol{p}^N;\boldsymbol{q}^N\right)}, \tag{2}$$

where the partition function Z is given by

$$Z = \frac{1}{N!h^{3N}}\int \mathrm{d}\boldsymbol{p}^N \int \mathrm{d}\boldsymbol{q}^N \mathrm{e}^{-\beta H_N\left(\boldsymbol{p}^N;\boldsymbol{q}^N\right)}.$$

Here, β is the inverse temperature, i.e., $\beta = 1/(k_{\mathrm{B}}T)$, where T is temperature.

A. Gaussian Approximation for Longer-Time Behavior. The observable in any kind of third-order off-resonant experiments is given by a linear combination of some polarization components of the third-order response function and, in the classical limit, a component is given by[1,12]

$$R^{(3)}_{\varkappa\lambda\mu\nu}(t) = -\theta(t)\beta\frac{\partial}{\partial t}\overline{C}_{\varkappa\lambda\mu\nu}(t). \tag{3}$$

where $\theta(t)$ is the Heaviside's step function. This relation can be obtained from the corresponding quantum expression by replacing the commutator with the Poisson bracket and by using the explicit form of the canonical distribution, i.e., $\mathrm{e}^{-\beta H_N(\boldsymbol{p}^N;\boldsymbol{q}^N)}/Z$. We have introduced the correlation function of the polarizability defined as

$$\overline{C}_{\varkappa\lambda\mu\nu}(t) = \langle \Pi_{\varkappa\lambda}(t)\Pi_{\mu\nu}(0)\rangle,$$

where the average is the classical phase space averaging in the canonical ensemble defined in Eq. 2. Here, the Greek indices denotes the direction in the laboratory frame. In this study, the time-dependent total polarizability is considered up to the dipole-induced dipole term, namely, the macroscopic polarizability is approximated by[22,16]

$$\Pi_{\mu\nu}(t) = \Pi^{\mathrm{mol.}}_{\mu\nu}(t) + \Pi^{\mathrm{ind.}}_{\mu\nu}(t), \tag{4}$$

with

$$\begin{aligned}\Pi^{\mathrm{mol.}}_{\mu\nu}(t) &= \sum_i \alpha_i^{\mu\nu}(t),\\ \Pi^{\mathrm{ind.}}_{\mu\nu}(t) &= \sum_{i,j}{}' \sum_{\varkappa,\lambda} \alpha_i^{\mu\varkappa}(t) T_{\varkappa\lambda}\left(\boldsymbol{q}_{ij}(t)\right) \alpha_j^{\lambda\nu}(t),\end{aligned} \tag{5}$$

where the prime implies, as in Eq. 1, that the terms in which any pair of the summed indices (i,j) coincides are excluded from the sum. Here, each molecule is indexed by i or j and the distance vector between the molecules i and j at the time t is denoted as $\boldsymbol{q}_{ij}(t) = \boldsymbol{q}_i(t) - \boldsymbol{q}_j(t)$. The matrix $T_{\mu\nu}(\boldsymbol{r})$ is given by

$$T_{\mu\nu}(\boldsymbol{r}) = \frac{1}{r^3}\left(3\frac{r_\mu r_\nu}{r^2} - \delta_{\mu\nu}\right), \tag{6}$$

where r_μ is the μ-component of the vector $\boldsymbol{r}$, and r is its magnitude. Here, we have introduced the Kronecker delta by $\delta_{\mu\nu}$.

Since the cage effect is due to the *collective* hindered translational motion in a collective potential, essential features should emerge from a *classical* molecular liquid system with an *isotropic* polarizability and the result in the isotropic case should give a qualitative estimate for the general anisotropic case.

In the case of isotropic polarizability, the polarizability of a molecule in the laboratory frame, $\alpha_i^{\mu\nu}(t)$, is diagonal (in the indices μ,ν), and does not depend on time. In addition, we assume below that it is the same for all the molecules, i.e., $\alpha_i^{\mu\nu}(t) = \alpha$. Thus, the total polarizability in the present study is given by Eq. 4 with

$$\Pi_{\mu\nu}^{\text{mol.}}(t) = N\alpha^2\delta_{\mu\nu}, \tag{7}$$

$$\Pi_{\mu\nu}^{\text{ind.}}(t) = \alpha^2 \sum_{i,j}{}' T_{\mu\nu}(\boldsymbol{q}_{ij}(t)), \tag{8}$$

where N is the number of molecules in the system.

Since our aim is to calculate the response function given in Eq. 3, which is the time derivative of the correlation function $\overline{C}(t)$, we are interested in the time-dependent part of $\overline{C}(t)$. In the case of isotropic polarizability, the time-dependent part is given by

$$\begin{aligned} C_{\varkappa\lambda\mu\nu}(t) &= \langle \Pi_{\varkappa\lambda}^{\text{ind.}}(t)\Pi_{\mu\nu}^{\text{ind.}}(0)\rangle \\ &= \alpha^4 \sum_{i,j}{}' \sum_{k,l}{}' \langle T_{\varkappa\lambda}(\boldsymbol{q}_{ij}(t)) T_{\mu\nu}(\boldsymbol{q}_{kl}(0))\rangle, \end{aligned}$$

since the other terms are time independent.[23] It follows that $R^{(3)}$ is formed by $\Pi^{\text{ind.}}$ only, which represents the hindered translational motion. This implies that the third-order response from the liquid system with the isotropic polarizability is mostly from the hindered translational motion. This expression, proportional to α^4, suggests that even in the system with the isotropic polarizability we may have the birefringence response: the OKE response does not necessarily correspond to the relaxation of the *anisotropic* polarizability.

In the present case of a uniform, isotropic system, we can show,[24]

$$\langle T_{\varkappa\lambda}(\boldsymbol{r}) T_{\mu\nu}(\boldsymbol{r}')\rangle = \frac{A_{\varkappa\lambda\mu\nu}}{10} \sum_{\rho,\sigma} \langle T_{\sigma\rho}(\boldsymbol{r}) T_{\rho\sigma}(\boldsymbol{r}')\rangle.$$

where $A_{\varkappa\lambda\mu\nu} = \delta_{\varkappa\mu}\delta_{\lambda\nu} + \delta_{\varkappa\nu}\delta_{\lambda\mu} - (2/3)\delta_{\varkappa\lambda}\,\delta_{\mu\nu}$. In addition, introducing the auxiliary function,

$$F(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{(rr')^3}\left[(\bar{\boldsymbol{r}}\cdot\bar{\boldsymbol{r}}')^2 - \frac{1}{3}\right], \tag{9}$$

where $\bar{\boldsymbol{r}}$ and $\bar{\boldsymbol{r}}'$ are the unit vectors defined as $\bar{\boldsymbol{r}}^{(\prime)} = \boldsymbol{r}^{(\prime)}/r^{(\prime)}$, we can show

$$\sum_{\mu,\nu} T_{\nu\mu}(\boldsymbol{r}) T_{\mu\nu}(\mathbf{r}') = 9F\left(\boldsymbol{r},\boldsymbol{r}'\right).$$

Using these relations, we have

$$C_{\varkappa\lambda\mu\nu}(t) = \frac{9}{10} A_{\varkappa\lambda\mu\nu}\alpha^4 C(t),$$

where

$$C(t) = \sum_{i,j}{}' \sum_{k,l}{}' \langle F(\boldsymbol{q}_{ij}(t), \boldsymbol{q}_{kl}(0))\rangle, \tag{10}$$

Accordingly, we have

$$R_{\varkappa\lambda\mu\nu}^{(3)}(t) = \frac{9}{10}\theta(t) A_{\varkappa\lambda\mu\nu}\alpha^4 R(t), \tag{11}$$

where

$$R(t) = -\beta \frac{\partial}{\partial t} C(t).$$

From Eq. 11, we see that the time dependence of any kind of the third-order response is independent of the polarizations of the applied fields in the system with the isotropic polarizability, except for a constant factor. Thus, in the following, we mainly discuss $C(t)$ and $R(t)$ instead of $C_{\varkappa\lambda\mu\nu}(t)$ and $R_{\varkappa\lambda\mu\nu}^{(3)}(t)$.

Since our principal concern lines in the fast dynamics, we expand the correlation function $C(t)$ in terms of time t (up to the second order), which should be an even function of t due to the stationary property. This means that there is no expansion term proportional to t for a system with a continuous potential. In order to obtain a reasonable longer-time behavior from the short-time expansion, we simply exponentiate to have a Gaussian decaying correlation. This approximation has been known to work well numerically.[17] (A general reason for this observation is given by the idea of the stochastic frequency modulation.[25]) Accordingly, assuming the continuous potential, we need the expansion of the $C(t)$ in the form,

$$C(t) = C(0) + \frac{t^2}{2} \left.\frac{\partial^2 C(t)}{\partial t^2}\right|_{t=0}. \tag{12}$$

and then $C(t)$ in the Gaussian approximation is given by

$$C_{\text{Gauss}}^*(t) \equiv \frac{C(t)}{C(0)} = \exp\left(-\frac{t^2}{\tau^2}\right),$$

where

$$\tau^2 = -\frac{2C(0)}{\ddot{C}(0)}. \tag{13}$$

B. Lattice Gas Approximation for Three- and Four-Particle Contributions. For later convenience, we divide the correlation function into the two-, three-, and four-particle terms:

$$C(t) = 2C^{(2)}(t) + 4C^{(3)}(t) + C^{(4)}(t),$$

where

$$\begin{aligned} C^{(2)}(t) &= \sum_{i,j}{}' \langle F(\boldsymbol{q}_{ij}(t), \boldsymbol{q}_{ij}(0))\rangle, \\ C^{(3)}(t) &= \sum_{i,j,k}{}' \langle F(\boldsymbol{q}_{ij}(t), \boldsymbol{q}_{ik}(0))\rangle, \\ C^{(4)}(t) &= \sum_{i,j,k,l}{}' \langle F(\boldsymbol{q}_{ij}(t), \boldsymbol{q}_{kl}(0))\rangle. \end{aligned} \tag{14}$$

Here, the prime indicates that the terms in which any pair of the summed indices coincides are removed from the summation. For example, in the case of $\sum_{i,j,k}'$, the terms for $i = j$, $i = k$, or $j = k$ are all excluded from the sum.

Our concern here is to obtain these functions at $t = 0$ and the second time-derivatives of them at $t = 0$, i.e., $C^{(n)}(0)$ and $\ddot{C}^{(n)}(0)$ [see Eq. 13]. Introducing the n-th order distribution function by

$$\begin{aligned} & g^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n) \\ &= \frac{1}{\rho^n} \sum_{i_1,i_2,\cdots,i_n}{}' \langle \delta(\boldsymbol{r}_1 - \boldsymbol{q}_{i_1})\delta(\boldsymbol{r}_2 - \boldsymbol{q}_{i_2})\cdots\delta(\boldsymbol{q}_n - \boldsymbol{q}_{i_n})\rangle, \end{aligned}$$

where ρ is the number density of the system, we obtain

$$C^{(2)}(0) = \rho^2 \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2\, g^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2) F(\boldsymbol{r}_{12},\boldsymbol{r}_{12}), \tag{15}$$

$$C^{(3)}(0) = \rho^3 \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \int \mathrm{d}\boldsymbol{r}_3 g^{(3)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) F(\boldsymbol{r}_{12},\boldsymbol{r}_{13}), \tag{16}$$

$$C^{(4)}(0) = \rho^4 \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \int \mathrm{d}\boldsymbol{r}_3 \int \mathrm{d}\boldsymbol{r}_4 g^{(4)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\boldsymbol{r}_4) F(\boldsymbol{r}_{12},\boldsymbol{r}_{34}), \tag{17}$$

with $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$. In the canonical ensemble, as shown in Appendix A, we have

$$\ddot{C}^{(2)}(0) = -2\rho^2 \frac{k_B T}{m} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 g^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2) F_2(\boldsymbol{r}_{12},\boldsymbol{r}_{12}), \tag{18}$$

$$\ddot{C}^{(3)}(0) = -\rho^3 \frac{k_B T}{m} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \int \mathrm{d}\boldsymbol{r}_3 g^{(3)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) F_2(\boldsymbol{r}_{12},\boldsymbol{r}_{13}), \tag{19}$$

$$\ddot{C}^{(4)}(0) = 0. \tag{20}$$

When the molecular system is at a high density ρ_0 $(\equiv 1/v_0)$ where v_0 is the volume occupied per molecule, it is nearly exact to assume that, by descretizing the coordinate space with a lattice constant $v_0^{1/3}$, all sites are occupied by a molecule with no doubly occupied sites (Assumption I). In this case, the probability that n particles are found at $\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n$, respectively, i.e., $\rho^n g^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n)$, should be 1 if $\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n$ are all different; otherwise $\rho^n g^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n)$ is zero.

When the system is at a lower density ρ, we assume that the double occupancy of a site is forbidden and all the other configurations are *equally probable* (Assumption II). In this case, since the probability for a site to be occupied is ρ/ρ_0, $\rho^n g^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n)$ should be $(\rho/\rho_0)^n$ if $\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n$ are all different; otherwise $\rho^n g^{(n)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n)$ is zero. Thus, Eqs. 15, 16, and 17 may be approximated by

$$\hat{C}^{(2)}(0) = (\rho/\rho_0)^2 \sum_{i,j} (1 - \delta_{\boldsymbol{r}_i,\boldsymbol{r}_j}) F(\boldsymbol{r}_{ij},\boldsymbol{r}_{ij}),$$

$$\hat{C}^{(3)}(0) = (\rho/\rho_0)^3 \sum_{i,j,k} (1 - \delta_{\boldsymbol{r}_i,\boldsymbol{r}_j})(1 - \delta_{\boldsymbol{r}_i,\boldsymbol{r}_k})(1 - \delta_{\boldsymbol{r}_j,\boldsymbol{r}_k}) F(\boldsymbol{r}_{ij},\boldsymbol{r}_{ik}),$$

$$\hat{C}^{(4)}(0) = (\rho/\rho_0)^4 \sum_{i,j,k,l} (1 - \delta_{\boldsymbol{r}_i,\boldsymbol{r}_j})(1 - \delta_{\boldsymbol{r}_i,\boldsymbol{r}_k})(1 - \delta_{\boldsymbol{r}_i,\boldsymbol{r}_l}) \times (1 - \delta_{\boldsymbol{r}_j,\boldsymbol{r}_k})(1 - \delta_{\boldsymbol{r}_j,\boldsymbol{r}_l})(1 - \delta_{\boldsymbol{r}_k,\boldsymbol{r}_l}) F(\boldsymbol{r}_{ij},\boldsymbol{r}_{kl}).$$

Here and hereafter, the hat implies that the quantity is evaluated with this approximation. From the inversion symmetry of the lattice, we have the relation

$$\sum_i (1 - \delta_{\boldsymbol{r}_i,\boldsymbol{r}_j}) F(\boldsymbol{r}_{ij},\boldsymbol{r}_{kl}) = 0,$$

where $i \neq j$, k, and l. Note here that the function $F(\boldsymbol{r}, \boldsymbol{r}')$ is an odd function of $\boldsymbol{r}$ or $\boldsymbol{r}'$. This relation enables us to reduce the three- and the four-particle contributions, namely, we have $\hat{C}^{(3)}(0) = -\rho/\rho_0 \hat{C}^{(2)}(0)$ and $\hat{C}^{(4)}(0) = 2(\rho/\rho_0)^2 \hat{C}^{(2)}(0)$. In this way, we obtain the total contributions in the approximation:

$$\hat{C}(0) = 2(1 - \rho/\rho_0)^2 \hat{C}^{(2)}(0), \tag{21}$$

$$\hat{\ddot{C}}(0) = 2(1 - \rho/\rho_0) \hat{\ddot{C}}^{(2)}(0). \tag{22}$$

In the present work, we assume that these expressions hold approximately, even if the system is away from the ideal lattice gas (Assumption III); the relaxation time is given by

$$\tau^2 = -\frac{2(1 - \rho/\rho_0) C^{(2)}(0)}{\ddot{C}^{(2)}(0)}. \tag{23}$$

It should be noted here that $C^{(2)}(0)$ and $\ddot{C}^{(2)}(0)$ are not those for the ideal lattice gas but those for the liquid at the density ρ.

In this approximation, we have employed three assumptions as discussed above. The first assumption concerns the existence of a reference density ρ_0. The second assumption is a very simplified liquid structure. The last one is that we invoke the relation, which holds in the ideal lattice gas, even in liquids. Although this model is known to describe the essential features of the multi-particle collision, there is no clear way to determine ρ_0. At the zero temperature, it is reasonable to assume that ρ_0 is the close-packed density. In general, ρ_0 should be regarded as a fitting parameter.

C. Evaluation of the Two-Particle Contribution by Theory of Simple Liquids. If we use the relation

$$F(\boldsymbol{r},\boldsymbol{r}) = \frac{2}{3}\frac{1}{r^6}, \tag{24}$$

which is seen from Eq. 9, Eq. 15 can be reduced to

$$C^{(2)}(0) = \frac{8\pi}{3}\rho N \int \mathrm{d}r \frac{g(r)}{r^4}, \tag{25}$$

where

$$g(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) \equiv g^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2).$$

If we use the relation, $F_2(\boldsymbol{r}, \boldsymbol{r}) = 10/r^8$, which is shown in Appendix B, Eq. 18 can be reduced to

$$\ddot{C}^{(2)}(0) = -80\pi\rho N \frac{k_B T}{m} \int \mathrm{d}r \frac{g(r)}{r^6}, \tag{26}$$

Substituting Eqs. 25 and 26 into Eq. 23, we obtain the relaxation time,

$$\tau^2 = (1 - \rho/\rho_0) \frac{m}{15 k_B T} \frac{\int \mathrm{d}r g(r) / r^4}{\int \mathrm{d}r g(r) / r^6}. \tag{27}$$

This expression has been known in a more specific context (for example, Ref. 35). In the present paper, we show that this expression is quite generally applicable to the currently popular third-order off-resonant experiments for the system with the isotropic polarizability. The normalized third-order response function defined by

$$R^*(t) \equiv -\frac{\partial}{\partial t}\frac{C(t)}{C(0)}, \tag{28}$$

is expressed as

$$R^*_{\mathrm{Gauss}}(t) = \frac{2t}{\tau^2} \exp\left(-\frac{t^2}{\tau^2}\right), \tag{29}$$

in the Gaussian decaying approximation. Here, τ is given in Eq. 27, or, in a dimensionless form, by

$$(\tau^*)^2 = (1 - \rho^*/\rho_0^*) \frac{1}{T^*} \frac{\int \mathrm{d}r^* g(\sigma r) / |r^*|^4}{\int \mathrm{d}r^* g(\sigma r) / |r^*|^6}, \tag{30}$$

where $t^* = t/\tau_0$, $\tau^* = \tau/\tau_0$, $r^* = r/\sigma$, $\rho^*_{(0)} = \rho_{(0)}/\sigma^3$, and $T^* = kT/\varepsilon$. Here, the unit of the time scale has been introduced as

$$\tau_0 = \sqrt{\frac{m\sigma^2}{15\varepsilon}}. \tag{31}$$

It should be noted that Eqs. 27, 28, 29, and 30 are not restricted to the LJ system, if we regard σ and ε as the characteristic range and energy of the potential, respectively.

The rough estimate of the decay time should be given by τ_0 in the above expression. If we assume the LJ potential for argon, the characteristic decay time τ_0 is given by

$$\tau_0 = 556.8\ \text{fs}. \tag{32}$$

To obtain the decay time τ quantitatively, we consider a molecular system governed by the LJ potential for argon. Here, the radial distribution function $g(r)$ for the LJ system is calculated by the Weeks–Chandler–Andersen (WCA) approximation:[21] the LJ system is once mapped to a hard sphere system with the effective hard-sphere diameter by the WCA scheme, and then $g(r)$ is calculated for the hard-sphere system from the Percus–Yevick (PY) exact solution,[17] which is finally transformed to the approximate $g(r)$ for the LJ system. The approximate $g(r)$ is used for the numerical integration by the Simpson rule to obtain τ. The numerical results are compared with molecular dynamics (MD) simulations in Section III.

II. Molecular Dynamics Simulation

To test our theory, we obtain *experimental* results from molecular dynamics (MD) simulations. The velocity-Verlet algorithm[26] is used for the numerical integration and the periodic boundary condition is implemented via the minimum image convention with the potential truncated at half the box length. We performed 4N-step MD calculation to obtain positions and velocities of the last N steps; (1) For the first N steps, we start from a randomly deviated fcc lattice and melt it by the velocity scaling with keeping the total momentum of the system to be zero in order to attain the desired temperature. (2) For the second N steps, we start from the final configuration of the previous run and scaled the velocity every two steps as before to keep the temperature. (3) For the third run, we started from the final configuration of the previous run while we do not make the velocity scaling (microcanonical MD). (4) The phase space dynamics obtained from the final run (without the velocity scaling) starting from the final configuration of the third run is used to calculate statistical quantities.

To calculate the polarizability correlation function, we avoid the numerical differentiation. Instead, we evaluate the analytically differentiated expressions (given in Appendix C) directly. To obtain the correct normalization, we calculate $C(t)$ given in Eq. C1 and its time derivative given in Eq. C2 at the same time from the last N-step MD data. Since the polarizability is a two-particle quantity decaying as $1/r_{ij}^3$ where r_{ij} is the distance between the two particles, some truncation of taking particle pairs is required. To deal with this, we employed the periodic boundary condition with the minimum image convention (just as the one used for the truncation of LJ force).

As clarified in the previous sections, our theory is constructed in the canonical ensemble while the molecular dynamics simulation we performed is the microcanonical one. To justify that we can use the microcanonical MD results to test our theory, we prepared Appendix D, where some novel results for higher order correlation function are also presented.

The calculated polarizability correlation function shows rather strong system-size dependence. To emphasize this we compared the system size (and time-step) dependence of (the time-derivative of) the polarizability correlation function in Fig. 1. This dependence is in contrast with the case of velocity auto-correlation function; we have checked that the MD results of the velocity correlation for 0.0—0.5 ps do not show any significant differences except for the first case ($N = 32$, 2000 steps). Based on this result, we can conclude that the system size with more than 256 particles is enough to produce significant results at least near the triple point. However, we show below, for all the other cases, the MD results for 256- and 500-particle systems with $N = 2000$, where a single MD step is 0.02 ps, to explicitly show the validity of our MD results at each point in the phase diagram.

Rather strong system-size dependence of the third-order response might be a manifestation of the collective nature of the response. In other words, it is because the calculation of two-particle contributions, which is necessary for the third-order response but not for the velocity correlation, requires the truncation for taking particle pairs for the quantity decaying as the inverse inter-particle distance cubed. Note here that this decay is slower than the case of the potential truncation since the potential decays as the inverse distance to the sixth. It will be interesting to study the system-size dependence of MD results also for non-polar solvation dynamics.

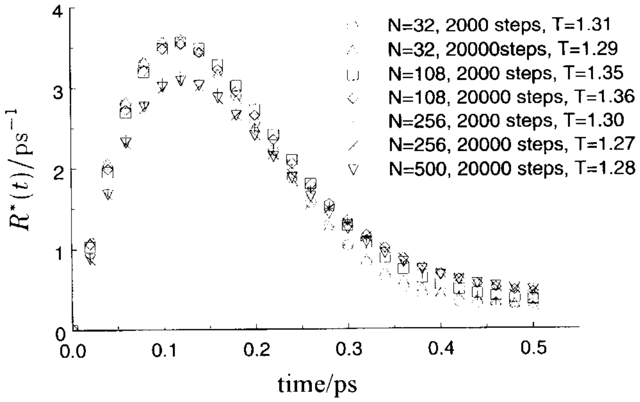

Fig. 1. Dependence on the system size and on the MD-step number of the response function near the triple point. The system size and the MD-step number are specified in the figure with temperature, by the number of the particle in the simulated system and by N (see the text for the detail), respectively. In all the cases the single MD time step is set to 0.02 ps. We see that the response function, which is the first time-derivative of the polarizability correlation function, shows rather strong system size dependence.

III. Numerical Results: Comparison between Our Theory and MD Results

We consider the nine points in the phase diagram as shown in Fig. 2 and also in Table 1, in order to study the relevance of our theory within a broad region of dense fluid in the phase diagram. The solid lines are from Ref. 27 (see also Ref. 28 for resent results for the phase diagram of LJ-argon). We note here that only the four points, denoted as ML (middle density and low temperature), LM, MM, and HM, are in the pure liquid region, while the three points, LH, MH, and HH, are in the dense supercritical region where the liquid theory is believed to apply well. The points LL and HL are in the phase in which the system may be separated into two states, i.e., liquids and gas and solid and liquid, respectively.

The result of the molecular simulations at low, medium, and high densities are given in Figs. 3, 4, and 5, respectively. In addition to the simulation results at the specified thermodynamic-state points for 500-particle system, we also show the MD results near the specified points for 256-particle system, in order to give a rough estimate of the precision of our calculations, as mentioned before. Overall, it seems that three digits of our results are significant except for the point HL: At this point, thermal equilibrium is not attained within the MD step number. Thus, we exclude this point from our discussion in the following. At the point LL the system should be in the liquid–gas coexistence phase (see Fig. 1). In our simulation, however, the behavior of the response function at this point LL seems fairly consistent with results at other thermodynamic-state points and we include this point in the following discussion, although there are some supports for the phase separation (a slightly inconsistent behavior at a time longer than 0.3 ps and a negative pressure).

As discussed in Section I-B, the parameter ρ_0 should be considered as a fitting parameter. In some previous papers, it is assumed to be the parameter determined by temperature but not by density. However, in this paper, we treat it as a mere parameter from the reason clear from our discussion in Section I-B. In the following, we present results by two ways of fitting; (1) maximum time fitting and (2) maximum height fitting. (The theoretical line by the maximum time fitting is

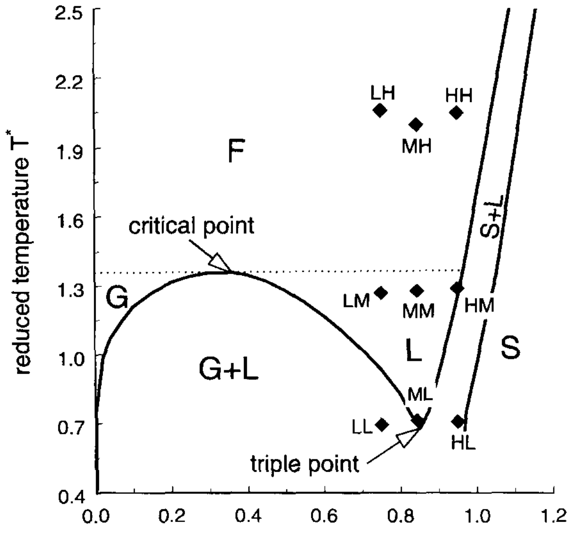

Fig. 2. Phase diagram of the LJ system with the argon parameter. The nine black diamonds indicate the points where we performed calculations. It covers a broad range of dense fluid.

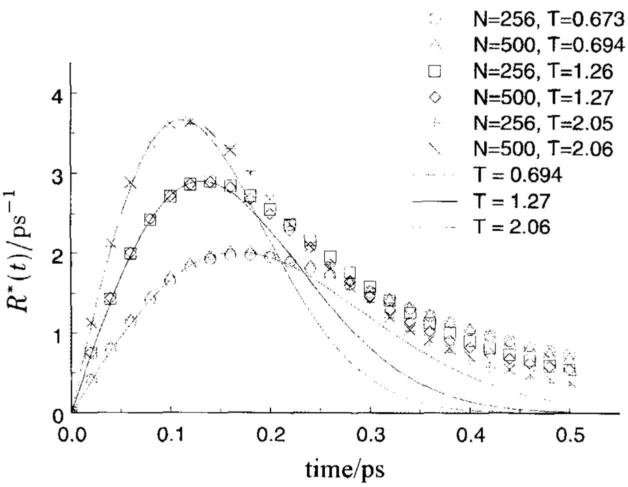

Fig. 3. Comparison between the results from MD simulation and our theory at low density ($\rho = 0.75$). The lines and points are from the theory with maximum time fitting and MD simulation, respectively. The system sizes and temperatures are specified for MD.

Table 1. The Reference Density ρ_0^*, Relaxation Time τ, and the Scale Factor ϕ at Each Thermodynamic State Points of Our Calculation

(1) and (2) refer to the maximum time fitting and maximum height fitting, respectively.

Label	ρ^*	T^*	(1) ρ_0^*	(2) ρ_0^*	(1) τ_{th}/ps	(2) τ_{th}/ps	(1) ϕ
LL	0.75	0.694	0.822	1.05	0.237	0.427	0.556
LM	0.75	1.27	0.836	1.02	0.186	0.298	0.629
LH	0.75	2.06	0.855	1.04	0.157	0.236	0.671
ML	0.844	0.714	0.911	1.10	0.210	0.374	0.565
MM	0.844	1.28	0.927	1.11	0.171	0.278	0.617
MH	0.844	2.00	0.937	1.14	0.143	0.229	0.629
HL	0.95	0.708	—	—	—	—	—
HM	0.95	1.29	1.02	1.25	0.146	0.273	0.543
HH	0.95	2.05	1.04	1.25	0.128	0.213	0.604

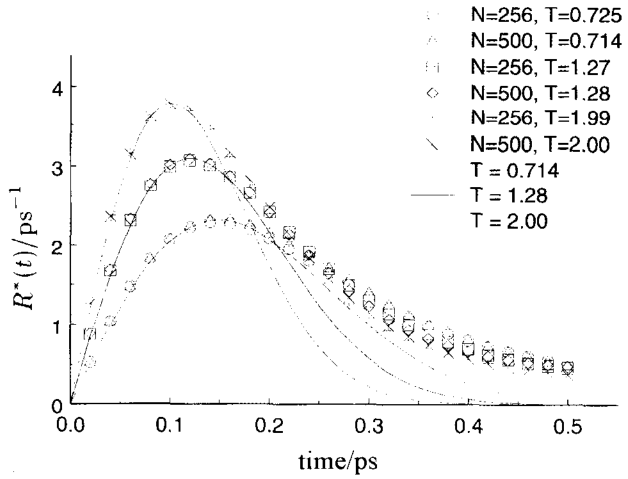

Fig. 4. Comparison between the MD-simulation results and our simple theory at medium density ($\rho = 0.844$).

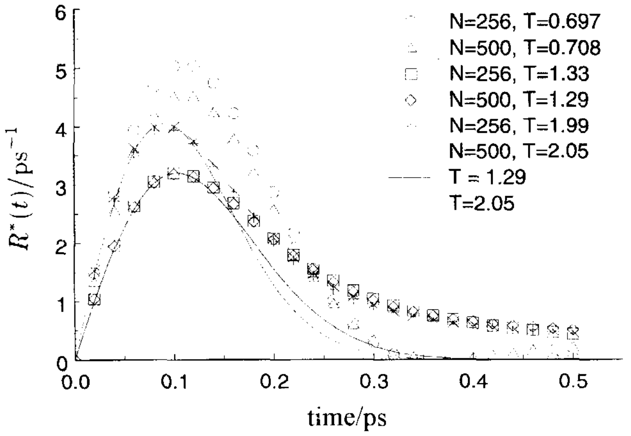

Fig. 5. Comparison between the MD-simulation results and our simple theory at high density ($\rho = 0.95$).

shown in Figs. 3, 4, and 5 with those on MD. In Table 1, results obtained by both ways of fitting are summarized.)

In the maximum time fitting, we optimized the parameter ρ_0 so that the peak delay time of the theoretical line given by Eq. 29 coincides with that of MD line; the decay time τ in Eq. 29 is calculated from Eq. 27 by using the optimized value of ρ_0. The theoretical lines thus obtained are superposed on those of MD in Figs. 3, 4, and 5. Note that the theoretical curves are scaled by the scale factor ϕ (see below) in order to show how the maximum time fitting works well for the short dynamics. At the longer time scale, however, our theoretical results deviate from the MD results rather significantly, which is anticipated since we employed the Gaussian short-time approximation.

In the maximum height fitting, we adjusted the parameter ρ_0 so that the peak height of the theory agrees with that of MD. With this maximum height fitting, we are not free to adjust the time scale of initial rises, since the peak height is properly normalized in both MD and theory; the decay time τ is calculated from Eq. 27 by using the adjusted value of ρ_0.

The values of the reference density ρ_0, the decay time τ, and the scale factor ϕ obtained by the maximum time fitting are given in Table 1, together with those obtained by the maximum height fitting. We see that ρ_0 takes about the same value at the same density, especially in the maximum height fitting; ρ_0 seems to be a density-dependent parameter, rather than a temperature-dependent one. We see that the decay time obtained by the maximum height fitting, which is inadjustable in the above sense, reflects that by MD (or that by the maximum time fitting) fairly well. Especially, temperature dependence of the decay time is well reproduced (see Fig. 6).

This figure demonstrates the validity of the approximate relation,

$$\tau \propto T^{-1/2}.$$

The reasons for the emergence of this simple law from our theory are as follows: (1) the last factor in Eq. 27 is dependent on temperature only weakly. (2) ρ_0 is a density-dependent parameter, rather than a temperature-dependent one.

The first reason, which is in turn supported by Fig. 6, leads to an important physical picture of the collision-induced cage dynamics. The temperature insensitivity of the last factor in Eq. 27 indicates that this factor is also insensitive to the LJ-energy parameter ε, since $g(r)$ contains temperature always as in the combination form $\beta\varepsilon$, as is clear from the definition of $g(r)$. Then, from Eq. 27, we expect the approximate relation

$$\tau \propto \sqrt{\frac{m\sigma^2}{k_B T}}. \tag{33}$$

This time scale corresponds to the collision time for particles separated by the LJ-distance parameter σ at the

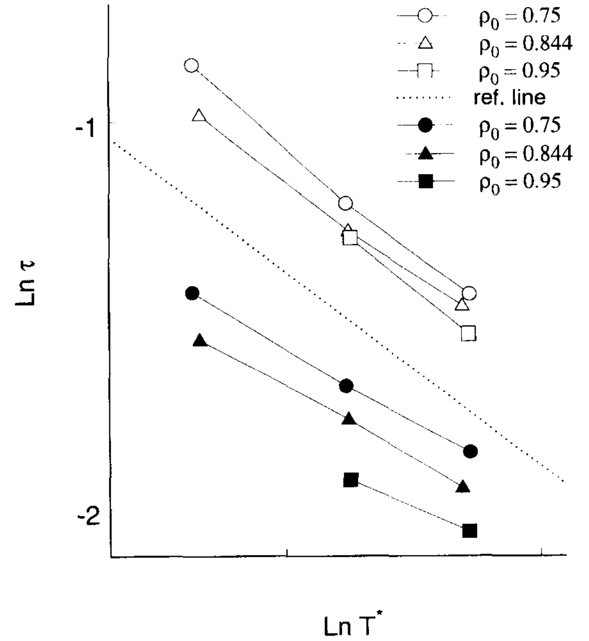

Fig. 6. Simple relation between the decay time and temperature. The reference line is the one with which the line connecting the MD data at each density should be parallel if the relation $\tau - 1/\sqrt{T}$ holds. Open and solid symbols refer to the maximum height fitting and the maximum time fitting, respectively.

Maxwell–Boltzmann's velocity at the temperature T. Since we are concerned with dense liquids, we conclude that the present cage dynamics are dominated by the collective motion associated with collisions.

On the contrary, if it were the case where the approximate relation

$$\tau \propto \sqrt{\frac{m\sigma^2}{\varepsilon}}, \tag{34}$$

holds, which is another fundamental time scale we can think of from the parameters of our theory, the dynamics would be dominated by the collective motion associated with the harmonic bound to other particles. Note here that the above time scale corresponds to the vibrational period for a particle of the mass m with the energy ε. However, Fig. 6 suggests that the present cage dynamics is mainly of collisional origin, which seems in contrast with the NPSD.

It should be noted here that the above statements do not contradict with the successful results by the normal mode analysis.[12] The harmonics or normal mode in the analysis are collective and are not directly related to the harmonic approximation of the two-body LJ potential. The physical origin of the dominant collective harmonic modes can be collisions.

At a fixed density the decay time may decrease with temperature increase, while at a fixed temperature it may decrease with density increase. This is because at higher temperatures the coherence is lost faster, while at higher densities the frequency of the cage is higher. This fact is reflected in our theoretical results.

IV. Discussion

We have demonstrated here that, in the third-order response, the cage dynamics is reflected in the initial rise usually observed in the subpicosecond range. Our approach is simple and transparent and, at the same time, provides a molecular-level description which is missing in the Brownian oscillator model.[1] For example, our relaxation time τ depends significantly on temperature and density, which can be calculated explicitly starting from the knowledge of the intermolecular potential $v(r)$. This dipole-induced dipole mechanism of the cage dynamics is expected to be very general and inherent in most of the ultrafast responses, though we did not include the orientation effect (for anisotropic molecules) explicitly and we discussed only in the context of the third-order experiment.

The orientational relaxation can be taken into account by the molecular hydrodynamic approach,[29] and other spectroscopic observables, including the fifth-order 2D Raman response, may be treated in a similar manner to the present treatment if we start from the response function formalism.[1] For example, the ultrafast component observed by Joo et al.[9] may be understood from the nonpolar solvation dynamics[30,31] which can be addressed through the approach presented here. In this case, a heavy probe molecule (1) is surrounded by the solvent molecules (2), so that we may define $g_{12}(r)$ instead of $g(r)$ function here, and then the short dynamics can be described by the solute–solvent intermolecular potential $v_{12}(r)$ and the static information $g_{12}(r)$. The rate of decay becomes faster as $v_{12}(r)$ increases[32] and one may observe sub-hundred femtosecond response from the cage dynamics alone.

In this paper, we have employed the lattice-gas model. This model has the parameter of the reference density and we have employed two reasonable ways of fitting to determine the parameter. By the maximum time fitting, the short-time dynamics is almost perfectly reproduced while the theoretical maximum height is 1.5 to 1.8 times of the MD one. By the maximum height fitting, the theoretical decay time is 1.6 to 1.9 times of the MD one. Especially, the temperature dependence of the decay time observed in MD is reproduced well irrespective of the ways of fitting. These findings suggest that our simple theory offers a solid starting point for the future development. Note here that, at the current state of the research, there has been no analytical theory to describe the third-order off-resonant response on the molecular level.

The improvement of the inclusion of the multi-particle collision from the lattice-gas model is a challenging problem. Several workers have been studying this important issue in a somewhat different context,[33,19] for example, by the viral expansion[34] or by Kirkwood's superposition approximation.[35] We will work on this problem under the novel framework proposed by one of the authors.[36]

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Appendix A: Derivation of Eqs. 18—20

From the definition, $\ddot{C}^{(2)}(0)$ can be expressed as

$$\ddot{C}^{(2)}(0) = -\sum_{i,j}{}' \left\langle \sum_{\mu,\nu} \frac{\mathrm{d}r_\mu}{\mathrm{d}t} \frac{\mathrm{d}r'_\nu}{\mathrm{d}t} \frac{\mathrm{d}}{\mathrm{d}r_\mu} \frac{\mathrm{d}}{\mathrm{d}r'_\nu} F(\boldsymbol{r},\boldsymbol{r}') \right\rangle_{\boldsymbol{r}=\boldsymbol{r}'=\boldsymbol{q}_{ij}} . \tag{A1}$$

If we note that the averages for the momentum space and the coordinate space are independent, and that the weight function for the momentum space averaging is even function of the velocity, we have, for $i \neq j$,

$$\left\langle (v_{ij})_\mu (v_{ij})_\nu \right\rangle = \left[\left\langle \left[(v_i)_\mu \right]^2 \right\rangle + \left\langle \left[(v_j)_\mu \right]^2 \right\rangle \right] \delta_{\mu\nu},$$

where $(v_{ij})_\mu$ and $(v_j)_\mu$ are the μ-component of the velocities, $\boldsymbol{v}_{ij} \equiv \mathrm{d}\boldsymbol{q}_{ij}/\mathrm{d}t$ and $\boldsymbol{v}_i \equiv \mathrm{d}\boldsymbol{q}_i/\mathrm{d}t$, respectively. In addition, we can readily show the law of equipartition,

$$\left\langle \left[(v_i)_\mu \right]^2 \right\rangle = \frac{k_\mathrm{B} T}{m},$$

in the canonical ensemble.[37] Using these two relations, we can reduce the expression for $\ddot{C}^{(2)}(0)$ to

$$\ddot{C}^{(2)}(0) = -2\frac{k_{\mathrm{B}}T}{m}\sum_{i,j}{}'\left\langle F_2(\boldsymbol{r},\boldsymbol{r}')\right\rangle_{r=r'=q_{ij}}, \tag{A2}$$

where

$$F_2(\boldsymbol{r},\boldsymbol{r}') = \sum_{\mu}\frac{\mathrm{d}}{\mathrm{d}r_\mu}\frac{\mathrm{d}}{\mathrm{d}r'_\mu}F(\boldsymbol{r},\boldsymbol{r}'). \tag{A3}$$

From the definition of the distribution function, Eq. A2 reduces to Eq. 18.

The three-particle contribution, $\ddot{C}^{(3)}(0)$, is given by

$$\ddot{C}^{(3)}(0) = -\sum_{i,j,k}{}'\left\langle\sum_{\mu,\nu}\frac{\mathrm{d}r_\mu}{\mathrm{d}t}\frac{\mathrm{d}r'_\nu}{\mathrm{d}t}\frac{\mathrm{d}}{\mathrm{d}r_\mu}\frac{\mathrm{d}}{\mathrm{d}r'_\nu}F(\boldsymbol{r},\boldsymbol{r}')\right\rangle_{r=q_{ij},r'=q_{ik}}.$$

If we note the relation for $i\neq j$, $i\neq k$, and $j\neq k$,

$$\left\langle (v_{ij})_\mu (v_{ik})_\nu\right\rangle = \left\langle \left[(v_i)_\mu\right]^2\right\rangle \delta_{\mu\nu},$$

we have

$$\ddot{C}^{(3)}(0) = -\frac{k_{\mathrm{B}}T}{m}\sum_{i,j,k}{}'\left\langle F_2(\boldsymbol{r},\boldsymbol{r}')\right\rangle_{r=q_{ij},r'=q_{ik}},$$

which leads to Eq. 19.

The four-particle contribution, $\ddot{C}^{(4)}(0)$, becomes zero to give Eq. 20 because of the relation,

$$\left\langle (v_{ij})_\mu (v_{kl})_\nu\right\rangle = 0,$$

where i, j, k, and l are all different.

Appendix B: Expression with Regard to $F(\boldsymbol{r}, \boldsymbol{r}')$

As is clear from the definition, Eq. 9 can be re-expressed as

$$F(\boldsymbol{r},\boldsymbol{r}') = \sum_{\mu,\nu} b_{11}^{\mu\nu}(\boldsymbol{r})b_{11}^{\mu\nu}(\boldsymbol{r}') - \frac{1}{3}b(\boldsymbol{r})b(\boldsymbol{r}'), \tag{B1}$$

where

$$b_{11}^{\mu\nu}(\boldsymbol{r}) = \frac{r_\mu r_\nu}{r^5},$$
$$b(\boldsymbol{r}) = \frac{1}{r^3}.$$

As also clear from Eq. A3, $F_2(\boldsymbol{r}, \boldsymbol{r}')$ can be re-expressed as

$$F_2(\boldsymbol{r},\boldsymbol{r}') = \sum_{\mu,\nu,\rho}\frac{\mathrm{d}b_{11}^{\mu\nu}(\boldsymbol{r})}{\mathrm{d}r_\rho}\frac{\mathrm{d}b_{11}^{\mu\nu}(\boldsymbol{r}')}{\mathrm{d}r'_\rho} - \frac{1}{3}\sum_{\rho}\frac{\mathrm{d}b(\boldsymbol{r})}{\mathrm{d}r_\rho}\frac{\mathrm{d}b(\boldsymbol{r}')}{\mathrm{d}r_\rho}.$$

Especially, when $\boldsymbol{r} = \boldsymbol{r}'$, from the relations,

$$\frac{\mathrm{d}b(\boldsymbol{r})}{\mathrm{d}r_\rho} = -3\frac{1}{r^4}\frac{r_\rho}{r},$$
$$\frac{\mathrm{d}b_{11}^{\mu\nu}(\boldsymbol{r})}{\mathrm{d}r_\rho} = \frac{r_\mu}{r^5}\delta_{\nu\rho} + \frac{r_\nu}{r^5}\delta_{\mu\rho} - 5\frac{r_\mu r_\nu}{r^6}\frac{r_\rho}{r},$$

we can show

$$F_2(\boldsymbol{r},\boldsymbol{r}) = \frac{10}{r^8}.$$

Appendix C: Analytical Expressions Calculated in the Simulation

The correlation function is defined by Eq. 10 with Eq. B1. Thus, introducing the macroscopic quantities,

$$B_{11}^{\mu\nu}(t) = \sum_{i,j}{}'\frac{q_{ij}^{\mu}(t)\,q_{ij}^{\nu}(t)}{q_{ij}^{5}(t)},$$

$$B(t) = \sum_{i,j}{}'\frac{1}{q_{ij}^{3}(t)},$$

we have

$$C(t) = \left\langle\sum_{\mu,\nu}B_{11}^{\mu\nu}(t)B_{11}^{\mu\nu}(0) - \frac{B(t)B(0)}{3}\right\rangle. \tag{C1}$$

Here we have used the notation where $q_{ij}^{\mu}(t)$ and $q_{ij}(t)$ are the μ-component and the magnitude of the vector $\boldsymbol{q}_{ij}(t)$. Since the third-order response function is given by $R(t) = -\beta\mathrm{d}C(t)/\mathrm{d}t$, we calculate $\mathrm{d}B_{11}^{\mu\nu}(t)/\mathrm{d}t$ and $\mathrm{d}B(t)/\mathrm{d}t$ (see Eq. C1). Introducing the auxiliary functions

$$B_{12}(t) \equiv \sum_{i,j}{}'\sum_{\rho}\frac{v_{ij}^{\rho}(t)q_{ij}^{\rho}(t)}{q_{ij}^{5}(t)},$$
$$B_{1}^{\mu\nu}(t) \equiv \sum_{i,j}{}'\frac{v_{ij}^{\mu}(t)q_{ij}^{\nu}(t)}{q_{ij}^{5}(t)},$$
$$B_{2}^{\mu\nu}(t) \equiv \sum_{i,j}{}'\frac{q_{ij}^{\mu}(t)\,q_{ij}^{\nu}(t)}{q_{ij}^{7}(t)}\sum_{\rho}v_{ij}^{\rho}(t)q_{ij}^{\rho}(t),$$

we can write the derivatives in a compact way:

$$\frac{\mathrm{d}B(t)}{\mathrm{d}t} \equiv -3B_{12}(t),$$
$$\frac{\mathrm{d}B_{11}^{\mu\nu}(t)}{\mathrm{d}t} = B_{1}^{\mu\nu}(t) + B_{1}^{\nu\mu}(t) - 5B_{2}^{\mu\nu}(t).$$

Then the response function is given, through the auxiliary functions, by

$$R(t) = -\beta\left\langle\sum_{\rho,\sigma}\left[2B_{1}^{\rho\sigma}(t) - 5B_{2}^{\rho\sigma}(t)\right]B_{11}^{\rho\sigma}(0) + B_{12}(t)B(0)\right\rangle. \tag{C2}$$

In the simulation, we calculate the brackets defined in the right hand-sides of Eqs. C1 and C2 at the same time by using the positions and velocities obtained from the final N-step MD run with the periodic boundary condition (the minimum image convention) and obtained $R^*(t)$ by taking the ratio of the brackets thus calculated.

Appendix D: Ensemble Dependence

In this appendix, we justify that we can use the microcanonical MD simulation to test our theory, which is constructed for the canonical ensemble, for the time correlation function of polarizability. The main issue here is the ensemble dependence of correlation functions. We basically follow the original article by Lebowitz et al.,[38] but emphasize somewhat subtle points which are not clearly stated in the original article and standard textbooks (e.g. Ref. 26). Some results with regard to higher-order correlation function might have not been presented before, since they have become experimentally available only recently.

We first show in a simple and novel way that the fluctuation of extensive quantities scale as $\sqrt{N}$ where N is the total number of the particles in the system. Another simple treatment can be found in Section II of Ref. 39. Although we work in the quantum canonical ensemble, it shall be clear that the result does not depend on the choice of ensembles and on whether the system is a quantum or classical one.

Extensive quantities O is of the order N, i.e., $O(N)$: they may be expressed as

$$O = \sum_{i=1}^{N} o_i, \tag{D1}$$

where o_i is the operator independent of N, i.e., of the order $O(1)$. In some case, o_i may be expressed as

$$o_i = \sum_{j=1}^{N} v(\boldsymbol{q}_i, \boldsymbol{q}_j),$$

when $v(\boldsymbol{q}_i, \boldsymbol{q}_j)$ approaches zero as $|\boldsymbol{q}_i - \boldsymbol{q}_j| \to \infty$ sufficiently fast so that the integral over $\boldsymbol{q}_j$ exists. The generating function W_J is introduced as

$$\mathrm{e}^{W_J} = Tr\mathrm{e}^{-\beta H + JO}. \tag{D2}$$

The expectation value and the variance of O are given by

$$\langle O \rangle \equiv \left(\frac{\mathrm{d}W_J}{\mathrm{d}J} \right)_0, \tag{D3}$$

$$\left\langle \delta O^2 \right\rangle \equiv \left\langle (O - \langle O \rangle)^2 \right\rangle = \left(\frac{\mathrm{d}^2 W_J}{\mathrm{d}J^2} \right)_0, \tag{D4}$$

where the subscript 0 implies that the quantity is evaluated at $J = 0$. (Here, the definition of the average $\langle \cdots \rangle$ reduces to that in Eq. 2 or Eq. D6 below in the classical limit.)

The N-dependence of the quantities is as follows: H, O, and W_J are of the order N, or $O(N)$, while β and J are independent of N, or $O(1)$. Then, from Eq. D4, it is clear that $\langle \delta O^2 \rangle$ is of the order N and the fluctuation scales as $\sqrt{\langle \delta O^2 \rangle} / \langle O \rangle \propto 1/\sqrt{N}$. Along with the same line, we can show

$$\frac{\langle \delta O_i \delta O_j \rangle}{\langle O_i O_j \rangle} \propto \frac{1}{N},$$

where O_i is $O(N)$-variable which may be expressed as Eq. D1.

In general, n-th order cumulant or connected Green function can be generated by

$$\langle O_{i_1} O_{i_2} \cdots O_{i_n} \rangle^c = \left(\frac{\mathrm{d}^2 W_{J^n}}{\mathrm{d}J_{i_1} J_{i_2} \cdots J_{i_n}} \right)_0,$$

where W_{Jn} is given by Eq. D2 but with JO replaced by $\sum_{i=i_1}^{i_n} J_i O_i$. Eqs. D3 and D4 are the examples of $n = 1$ and $n = 2$, respectively. By following the same line as above, we conclude that

$$\langle O_{i_1} O_{i_2} \cdots O_{i_n} \rangle^c \propto N,$$

that is, *the cumulant of O(N)-variable generally scales as N.*

Next, we consider the ensemble dependence of expectation value. Although we work in the classical system, it shall be clear that the treatment is almost the same in the quantum system. In the microcanonical and canonical ensembles, expectations are given, respectively, as follows,

$$\langle A_\Gamma \rangle_E = \frac{\int A_\Gamma \delta(H_\Gamma - E) \mathrm{d}\Gamma}{\int \delta(H_\Gamma - E) \mathrm{d}\Gamma}, \tag{D5}$$

$$\langle A_\Gamma \rangle_T = \frac{\int A_\Gamma \mathrm{e}^{-\beta H_\Gamma} \mathrm{d}\Gamma}{\int \mathrm{e}^{-\beta H_\Gamma} \mathrm{d}\Gamma}, \tag{D6}$$

where Γ stands for the phase space of $6N$ degrees of freedom. If we expand $\langle A_\Gamma \rangle_E$ around

$$E_0 \equiv E_0(T) = \langle H_\Gamma \rangle_T,$$

we have

$$\langle A_\Gamma \rangle_E = \langle A_\Gamma \rangle_{E_0} + \delta E \left(\frac{\mathrm{d} \langle A_\Gamma \rangle_E}{\mathrm{d}E} \right)_0 + \frac{1}{2} \delta E^2 \left(\frac{\mathrm{d}^2 \langle A_\Gamma \rangle_E}{\mathrm{d}E^2} \right)_0 + \cdots, \tag{D7}$$

where

$$\delta E = H_\Gamma - E_0,$$

Here, the subscript 0 implies that the quantity is evaluated at $E = E_0$. We emphasize here that we have to interpret the derivative terms such as $(\frac{\mathrm{d}\langle A_\Gamma \rangle_E}{\mathrm{d}E})_0$ with great care when A_Γ depends on E_0 or T.

Multiplying $\langle A_\Gamma \rangle_E$ and B_Γ by $\mathrm{e}^{-\beta E} \int \delta(H_\Gamma - \mathrm{E}) \mathrm{d}\Gamma / \int \mathrm{e}^{-\beta H_\Gamma} \mathrm{d}\Gamma$ and then integrating them over E, we obtain $\langle A_\Gamma \rangle_T$ and $\langle B_\Gamma \rangle_T$, respectively. Here, B_Γ is a mechanical quantity dependent on Γ. Thus, applying this operation to Eq. D7, we have

$$\langle A_\Gamma \rangle_T = \langle A_\Gamma \rangle_{E_0} + \frac{1}{2} \left\langle \delta E^2 \right\rangle_T \left(\frac{\mathrm{d}^2 \langle A_\Gamma \rangle_E}{\mathrm{d}E^2} \right)_0 + \cdots. \tag{D8}$$

It is convenient to invert Eq. D8 to express $\langle A_\Gamma \rangle_{E_0}$ in terms of $\langle A_\Gamma \rangle_T$ for the following discussion: we can replace $\langle A_\Gamma \rangle_E$ in the correction term, i.e., the second term on the right hand-side, by the leading term, $\langle A_\Gamma \rangle_T$ to have

$$\langle A_\Gamma \rangle_{E_0} = \langle A_\Gamma \rangle_T - \frac{1}{2} \left\langle \delta E^2 \right\rangle_T \frac{\mathrm{d}^2 \langle A_\Gamma \rangle_T}{\mathrm{d}E_0^2} + \cdots. \tag{D9}$$

We emphasize here that, if A_Γ is dependent on E_0, the derivative term in this equation is rather formal: it should be interpreted carefully. From this relation, we see that, if the operator A_Γ is of the order N, the difference of the two ensemble averages, i.e., the second term in the right hand-side, is of the order N^0, since E_0 and $\langle \delta E^2 \rangle_T$ are both the order of N: the difference becomes negligible in the thermodynamic limit. Note, however, that this type of argument on the order of terms becomes impossible to be justified when A_Γ depends on E_0.[40]

As we have emphasized, we have to use the above formula Eq. D9 with great care when $A_\Gamma = \delta_{E_0} O_i \delta_{E_0} O_j$ where $\delta_{E_0} O_i = O_i - \langle O_i \rangle_{E_0}$. (We note here that, none the less, we can derive the following equation directly form Eq. D9, if we pay careful attention.) Instead, we decompose the left hand-side, $\langle \delta_{E_0} O_i \delta_{E_0} O_j \rangle_{E_0}$, as $\langle O_i O_j \rangle_{E_0} - \langle O_i \rangle_{E_0} \langle O_j \rangle_{E_0}$, and then we can use the formula with no special care to have

$$\begin{aligned} \langle \delta_{E_0} O_i \ \delta_{E_0} O_j \rangle_{E_0} &= \langle O_i \ O_j \rangle_T - \langle O_i \rangle_T \langle O_j \rangle_T - \frac{1}{2} \left\langle \delta E^2 \right\rangle_T \\ &\times \left(\frac{\mathrm{d}^2 \langle O_i O_j \rangle_T}{\mathrm{d}E_0^2} - \langle O_i \rangle_T \frac{\mathrm{d}^2 \langle O_j \rangle_T}{\mathrm{d}E_0^2} - \langle O_j \rangle_T \frac{\mathrm{d}^2 \langle O_i \rangle_T}{\mathrm{d}E_0^2} \right) + \cdots. \end{aligned}$$

We can replace the second $\langle O_i O_j \rangle_T$ by $\langle O_i \rangle_T \langle O_j \rangle_T$, since the difference $\langle \delta_T O_i \delta_T O_j \rangle_T$ is smaller by the one order (in terms of N). Here, $\delta_T O_i = O_i - \langle O_i \rangle_T$. Thus we obtain

$$\langle \delta_{E_0} O_i \ \delta_{E_0} O_j \rangle_{E_0} = \langle \delta_T O_i \ \delta_T O_j \rangle_T - \left\langle \delta E^2 \right\rangle_T \frac{\mathrm{d} \langle O_i \rangle_T}{\mathrm{d}E_0} \frac{\mathrm{d} \langle O_j \rangle_T}{\mathrm{d}E_0} + \cdots.$$

From this relation, we see that, if the operator O_i and O_j are of the order N the difference of the two ensemble average, i.e., the second term in the right hand-side, is of the same order, i.e., $O(N)$, since $\langle \delta_{E_0} O_i \delta_{E_0} O_j \rangle_{E_0}$, $\langle \delta_T O_i \delta_T O_j \rangle_T$, E_0, and $\langle \delta E^2 \rangle_T$ are all the order of N: the difference is not negligible even in the thermodynamic limit.

In the same way, for the third-order cumulant, we have

$$\begin{aligned} \langle O_i O_j O_k \rangle_{E_0}^c &= \langle O_i O_j O_k \rangle_T^c - \left\langle \delta E^2 \right\rangle_T \\ &\times \left(\frac{\mathrm{d} \langle O_i \rangle_T}{\mathrm{d}E_0} \frac{\mathrm{d} \langle O_j \rangle_T}{\mathrm{d}E_0} \langle O_k \rangle_T + \frac{\mathrm{d} \langle O_j \rangle_T}{\mathrm{d}E_0} \frac{\mathrm{d} \langle O_k \rangle_T}{\mathrm{d}E_0} \langle O_i \rangle_T \right. \\ &\left. + \frac{\mathrm{d} \langle O_k \rangle_T}{\mathrm{d}E_0} \frac{\mathrm{d} \langle O_i \rangle_T}{\mathrm{d}E_0} \langle O_j \rangle_T + O_r(1/N) \right) + \cdots. \end{aligned}$$

where $O_r(1/N)$ indicates the terms one order smaller than the other explicitly-written terms in the parentheses. This relation shows that the *correction term* is *larger* than the third-order cumulant by one order. Thus, the attempt to obtain a significant result from the microcanonical MD is hopeless. In the same way, we can generally show that we can not obtain the canonical cumulant of higher order than two from the microcanonical MD simulation.

Although we only prove here the case between the canonical and microcanonical ensembles, it shall be clear that the above statement holds in the case between general ensembles. In general, we can conclude that, if A_Γ is independent of state variables such as E,T,P,V,N, and μ (i.e., O_i is a *purely mechanical quantity*), the correlation function of O_i, such as $\langle O_i(t_i)O_j(t_i)\cdots O_k(t_i)\rangle$ (but not the cumulant $\langle O_i(t_i)O_j(t_i)\cdots O_k(t_i)\rangle^c$), does not show the ensemble dependence in the thermodynamic limit.

Finally, we comment on how to determine E_0 when we want to have the result at the temperature T. In the canonical ensemble, we can show $3NkT/2 = \langle K\rangle_T$, while we have seen that $\langle K\rangle_T$ reduces to $\langle K\rangle_{E_0}$ in the thermodynamic limit. Thus, we select E_0 and run MD so that the expectation of $2K/(3Nk_\mathrm{B})$ from the MD run gives the desired value, T, i.e.,

$$T_{E_0} = 2\langle K\rangle_{E_0} / (3Nk_\mathrm{B}). \tag{D10}$$

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$$E_0 = -\frac{\mathrm{d}}{\mathrm{d}\beta}\ln\left(\int \mathrm{e}^{-\beta H_\Gamma}\mathrm{d}\Gamma\right),$$

$$\left\langle \delta E^2 \right\rangle_T = \frac{\mathrm{d}^2}{\mathrm{d}\beta^2}\ln\left(\int \mathrm{e}^{-\beta H_\Gamma}\mathrm{d}\Gamma\right) = -\frac{\mathrm{d}E_0}{\mathrm{d}\beta},$$

we can rewrite Eq. D8 as

$$\langle A_\Gamma \rangle_{E_0} = \langle A_\Gamma \rangle_T + \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}\beta}\left(\frac{\mathrm{d}\langle A_\Gamma \rangle_{E_0}}{\mathrm{d}E_0}\right) + \cdots.$$

Note here that the term in the parenthesis can be regarded as a function of β. Up to the lowest correction terms, $\langle A_\Gamma \rangle_{E_0}$ in the right hand-side can be replaced by the leading term, $\langle A_\Gamma \rangle_T$ to give

$$\langle A_\Gamma \rangle_{E_0} = \langle A_\Gamma \rangle_T + \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}\beta}\left(\frac{\mathrm{d}\beta}{\mathrm{d}E_0}\frac{\mathrm{d}\langle A_\Gamma \rangle_T}{\mathrm{d}\beta}\right) + \cdots.$$