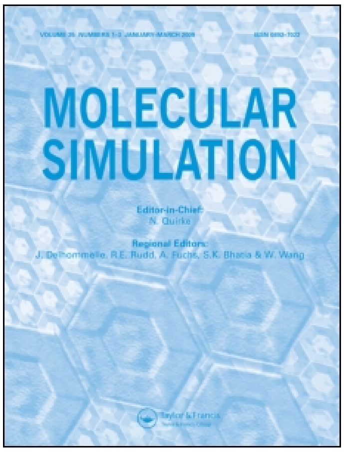

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Numerical Calculation of the Bridge Function for Soft-Sphere Supercooled Fluids via Molecular Dynamics Simulations

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NUMERICAL CALCULATION OF THE BRIDGE FUNCTION FOR SOFT-SPHERE SUPERCOOLED FLUIDS VIA MOLECULAR DYNAMICS SIMULATIONS

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Isokinetic molecular dynamics simulations have been performed for 13,500 soft-spheres interacting through the inverse-power potential, $\varepsilon(\sigma/r)^n$, near and below the freezing temperature. The bridge function for the integral equation of the theory of liquids is extracted from the pair distribution function (PDF) obtained by the computer simulations for $n = 6$ and 12. The result is compared with that of approximate theories, i.e., the Rogers-Young (RY) approximation and a modified hypernetted-chain approximation for supercooled soft-sphere fluids (MHNCS approximation). Below the freezing temperature, the bridge function obtained by the computer simulation begins to oscillate around zero at intermediate distances where the second peak of the PDF appears. Such oscillatory behavior of the bridge function is well reproduced by the MHNCS approximation which includes correlations given by the leading elementary diagram, in remarkable contrast to that of the RY approximation. The present result suggests that the split second peak of the PDF for highly supercooled liquids is essentially dominated by the intermediate-distance-range correlation of the leading elementary diagram.

KEY WORDS: Bridge Function, Pair Distribution Function, Supercooled Liquids, Soft-Sphere Fluids, Molecular Dynamics Simulation, Integral Equation

INTRODUCTION

In principle, the pair distribution function (PDF) of an isotropic and uniform system in which particles interact through a spherically symmetric pair potential $u(r)$ is uniquely determined from the solution of the integral equation of the theory of liquids [1], i.e., the Ornstein-Zernike relation

$$h(r) - c(r) = \rho\int h(r')c(|\mathbf{r} - \mathbf{r}'|)d\mathbf{r}' \qquad (1)$$

coupled with the closure relation

$$g(r) = \exp[-\beta u(r) + h(r) - c(r) + B(r)], \tag{2}$$

where $g(r)$ is the PDF, $h(r) = g(r) - 1$ the pair correlation function, $c(r)$ the direct correlation function, $B(r)$ the bridge function, ρ the number density, and β the inverse temperature $(k_B T)^{-1}$. In calculations of the PDF using the integral equation for given potential and thermodynamic parameters, one needs detailed knowledge of the bridge function $B(r)$. It is well known that $B(r)$ can be expanded in terms of h-bond elementary diagrams as [1]

$$B(r) = \sum_{n=4}^{\infty} \{\varepsilon_n(r)\}, \tag{3}$$

where $\{\varepsilon_n(r)\}$ represents a set of n-point elementary diagrams. The convergence of Equation (3) is, however, generally too slow to be applicable to practical calculations for a highly dense liquid state. Because of such a difficulty in the calculation of $B(r)$, various approximations have been proposed to obtain a self-consistent solution of the integral equation. For example, well-known hypernetted-chain (HNC) and Percus-Yevick (PY) approximations [1] are equivalent to substituting in Equation (2) $B(r) = 0$ and $c(r) - h(r) + \ln[1 + h(r) - c(r)]$, respectively.

The reliability of an approximate integral equation can be tested by comparing its solution, i.e., a set of $g(r)$, $c(r)$, and $B(r)$ with the "exact" result obtained by computer simulations for a wide range of density and temperature. It has been shown that both the HNC and PY approximations break down when the density or temperature approaches the freezing point [1]. Since the approximation for $B(r)$ is tightly related to details of the PDF through Equation (2), a more reliable approximation could be obtained by modifying $B(r)$ in some manner. During last decade, several thermodynamically consistent approximations [2, 3, 4] with some parametrized bridge function have been proposed and found to yield a better approximation up to the freezing point over the HNC or PY approximation. Among these approximations, the reference HNC (RHNC) (Reference [3]) and Rogers-Young (RY) (Reference [4]) equations have most extensively been studied for various potentials, including one-component plasmas (OCP), hard-sphere, soft-sphere, and 12–6 Lennard-Jones fluids.

In our previous paper [5], it has been shown that even in an equilibrium supercooled liquid regime, the thermodynamic properties predicted by the RY integral equation agree well with the computer simulation data for soft-sphere fluids. However, the PDF's obtained by these integral equations do not reproduce a correct behavior at both intermediate- and long-range distances where those calculated by computer simulations yield a clear splitting of the second peak neat and below the glass transition temperature [6] and a broader second peak in an equilibrium supercooled regime [7]. The PDF's calculated from the RY and RHNC equations for soft-sphere fluids yield no broadening of the second peak in an equilibrium supercooled state, nor splitting below the glass transition temperature [10], in disagreement with results of the computer simulations.

For further improvements on approximate theories of the integral equation, it is particularly interesting to extract $B(r)$ from a numerically exact PDF obtained by the computer simulation, and to provide a deeper insight on the behavior of the bridge function in a highly supercooled liquid state. Essentially, the bridge function is able to be calculated when complete data for $g(r)$ is available. Since the computer simulation provides only limited information for the PDF, i.e., $g(r)$ is available within the half of the side length L of the simulation cell, an extraction of the bridge function from results of usual computer simulations with a system size of $O(10^3)$ is applicable only for weakly coupled states (i.e. near and above the freezing temperature), in which $g(r)$ is damped rapidly at intermediate-range distances [8, 9].

The aim of this paper is to present the bridge function numerically obtained from results of the molecular dynamics (MD) simulations of 13,500 particles for supercooled soft-sphere fluids near the glass transition temperature, and to discuss theoretical interpretation for a split second peak of the PDF in terms of properties of the bridge function by comparing the present results with theoretical predictions. It is found that the bridge function below the freezing temperature begins to oscillate around zero at the intermediate distances, where the second peak of the PDF appears. This behavior is well reproduced by a modified hypernetted-chain approximation for supercooled soft-sphere fluids (MHNCS approximation) proposed by us [10], suggesting that the intermediate-distance-range correlation represented by the leading elementary diagram, i.e., $\varepsilon_4(r)$ in Equation (3) is essential for the splitting of the second peak of the PDF.

MODEL AND MOLECULAR DYNAMICS SIMULATION

We consider a simple model liquid of N atoms of mass m and diameter σ. They interact via the repulsive "soft-sphere" potential given by

$$u(r) = \varepsilon\left(\frac{\sigma}{r}\right)^n, \tag{4}$$

where n (≥ 3) is the softness parameter of the potential. Due to the scaling property of the inverse-power potential, all reduced equilibrium properties in excess of their ideal-gas counterparts depend only on single coupling parameter, not on the temperature and the number density of the system separately. This can easily be shown by taking the following units of length and time [11];

$$l = \rho^{-1/3}, \tag{5}$$

$$\tau = l(m\beta)^{\frac{1}{2}}. \tag{6}$$

We choose for a coupling parameter

$$\Gamma = \rho\sigma^3(\varepsilon\beta)^{3/n}. \tag{7}$$

The freezing point of the soft-sphere fluids for $n = 4$, 6, 9, and 12 was found to be $\Gamma = 5.54$, 2.18, 1.33, and 1.15, respectively [12, 13]. The glass transition point for $n = 12$ is situated around $\Gamma = 1.5$ to 1.6 [14]. The soft-sphere model has been found to work well for various real liquids, in which short-range repulsive forces are dominant, by choosing a suitable softness parameter n; for example, the case $n = 15$ works for liquefied inert gases and the case $n = 4 \sim 5$ for liquid alkali metals [11, 15].

MD simulations have been performed for 13,500 soft-spheres with the cubic periodic boundary conditions, where the softness parameter n is taken to be $n = 6$

Table 1 Parameters used in the present MD simulations for soft-sphere fluids, the equation-of-state $P\beta/\rho$, and interval time-steps N^{up} in average for updating the Verlet neighborhood table. r_c is the cut-off radius of the potential and Δ the "depth" of a shell covering the cut-off sphere for the bookkeeping method.

n	Γ	r_c/σ	Δ/σ	$P\beta/\rho$	N^{up}
6	1.4	5	1	18.60	42
6	1.8	5	1	28.43	43
6	2.2	5	1	40.44	45
6	2.6	5	1	54.66	49
6	3.0	3	1	71.04	52
6	3.4	5	1	89.83	62
6	3.6	5	1	100.1	66
12	0.8	3	1	8.413	42
12	1.2	3	1	21.90	47
12	1.3	3	1	27.35	50
12	1.4	3	1	33.90	54
12	1.5	3	1	42.13	63
12	1.6	3	1	52.36	77

and 12. In our simulations, the number density was kept constant and the temperature was scaled to achieve the desired Γ shown in Table 1. The side length L of the simulation cell is $L = 15\sqrt[3]{4}l$, which is corresponding to about 22 interatomic spacings. Throughout the present work, an isokinetic constraint by Hoover *et al.* [16] has been applied to the equations-of-motion to maintain the temperature. The equations-of-motion were integrated by a 5th-order differential algorithm [17] with the time increment $\Delta t = 0.0025\tau$ over 10,000 time-steps for each Γ, where the microscopic units of length and time were chosen to be Equation (5) and (6), respectively. The PDF has been obtained for each Γ with a sampling interval of 20 time-steps, discarding the configurations of initial 4,000 time-steps.

For an efficient computation of the inter-particle force, the so-called bookkeeping method introduced by Verlet [18] was used with a modification [19]; the neighborhood table is automatically updated, when the displacement of a particle from the previous update exceeds a certain fraction of the "depth" of a shell which covers the cut-off sphere. Table 1 shows values of the parameters used in our MD simulation, the equation-of-state $P\beta/\rho$ obtained, and average interval for updating the neighborhood table. The simulations were carried out on a vector processor VP2600/10 at Computing and Information Systems Center of Japan Atomic Energy Research Institute. The computational time required for 1,000 time-steps was about 20 minutes including the sampling of the PDF.

EXTRACTION OF BRIDGE FUNCTION

The procedure used in the present work to extract the bridge function from the PDF calculated by MD simulations is based on the extrapolation technique of the PDF for $r \geq L/2$ proposed by Verlet [20]. Verlet's extrapolation scheme assumes a hypothetical closure relation which includes numerical data of the PDF obtained from the MD simulation as follows;

$$g(r) = \begin{cases} g_{\mathrm{MD}}(r) & (r < R) \\ \exp[-\beta u(r)]\,(1 + h(r) - c(r)) & (r \geq R) \end{cases}. \tag{8}$$

Here, $g_{\mathrm{MD}}(r)$ is the PDF obtained from the MD simulation and $R = L/2$. Note that the right-hand-side of Equation (8) for $r \geq R$ is equivalent to the PY approximation. Coupled with the Ornstein-Zernike relation Equation (1), Equation (8) can be solved to yield $g(r)$ for $r \geq R$ and $c(r)$ for $r < R$. Verlet has applied this scheme for the Lennard-Jones fluids near the triple point by performing the MD simulation with 864 particles ($L/2 \simeq 4.8l$) [20]. Different models for the hypothetical closure relation have been proposed in Reference [8, 9], where the right-hand-side of Equation (8) for $r \geq R$ is replaced by a better approximation such as the modified HNC and mean-spherical approximations.

The above extrapolation scheme is indispensable to calculate the bridge function for supercooled fluids because the PDF tends to be far away from its asymptotic behavior, i.e. $g(r) = 1$, as the temperature decreases. In the present work, utilizing the fact that L is long enough to assume $B(r) = 0$ for $r \geq L/2$ ($\simeq 11.9l$), we first calculate $c(r)$ by solving the Ornstein-Zernike relation Equation (1) coupled with

$$g(r) = \begin{cases} g_{\mathrm{MD}}(r) & (r < R) \\ \exp[-\beta u(r) + h(r) - c(r)] & (r \geq R) \end{cases}. \tag{9}$$

Then, the bridge function is determined for distances where $g_{\mathrm{MD}}(r) \neq 0$ by substituting $c(r)$ and $g_{\mathrm{MD}}(r)$ to Equation (2). To solve above integral equation, we have used an iterative procedure introduce by Ng [21]. Using $c(r)$ obtained by the RY approximation as an initial input function, it took about 5,000 iterations to achieve

$$\left(\int |c_{\mathrm{in}}(r) - c_{\mathrm{out}}(r)|^2 r^2 dr\right)^{1/2} < 10^{-6}, \tag{10}$$

where the subscripts "in" and "out" are attached for the input and output functions, respectively. The number of grid points and step size used in numerical integrations were chosen to be 2048 points and $\Delta r = 0.01l$, respectively. Note that we have used the truncated potential during the calculation of $B(r)$ as in the case of the MD simulations (see Table 1). The computational time required for the iterative procedure was about 0.4 ms per one iteration on a vector processor VP2600/10 with the vectorized fast-Fourier-transformation routine. We have tested our procedure by changing the "switching" radius R in Equation (9) and confirmed that results obtained little depend on the choice of R.

Figure 1 shows the extracted bridge function for the soft-sphere fluid of $n = 12$ above the freezing temperature, and Figure 2 and 3 show those for the supercooled soft-sphere fluids, together with approximate bridge functions of the RY approximation [4]

$$B(r) = c(r) - h(r) + \ln\left[1 + \frac{\exp[f(r)\{h(r) - c(r)\}] - 1}{f(r)}\right], \tag{11}$$

$$f(r) = 1 - \exp(-\alpha r), \tag{12}$$

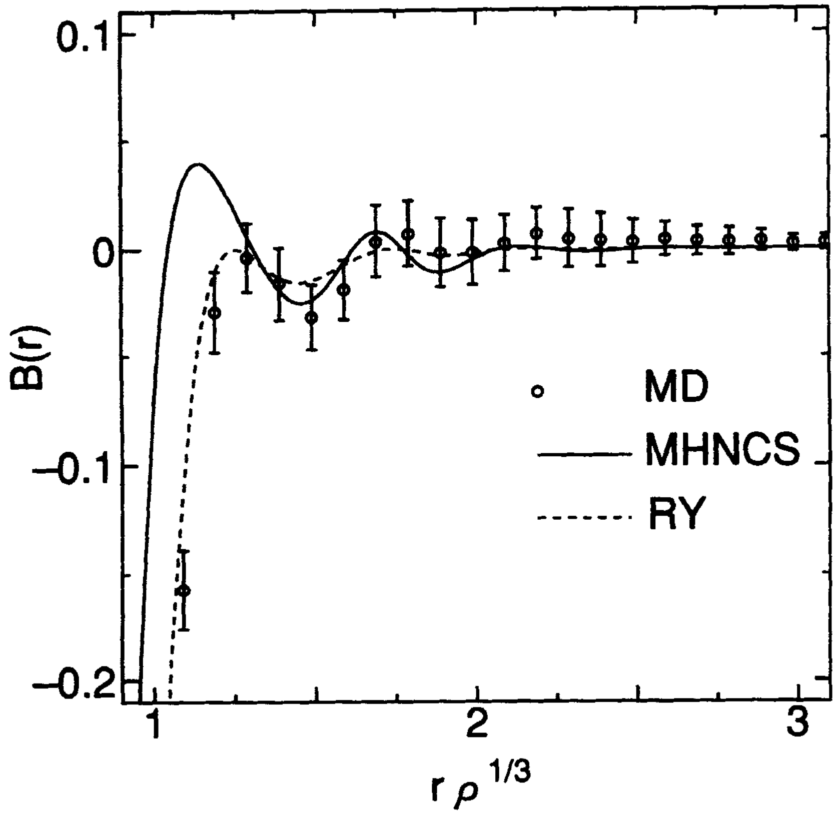

Figure 1 The bridge function obtained by the MD simulation (O), the RY approximation (dotted curve), and the MHNCS approximation (solid curve) for the soft-sphere fluid ($n = 12$) at $\Gamma = 0.8$. The error bar attached to the MD data represents the standard deviation of four different samples along the trajectory.

and the MHNCS approximation [10]

$$B(r) = [1 - f(r,d)]B_{PY}(r,d) + f(r,d)\varepsilon_4(r), \tag{13}$$

$$f(r,d) = \frac{1}{2}\left[1 + \tanh\left[\frac{r-d}{W}\right]\right]. \tag{14}$$

Here, α is a self-consistent parameter, $B_{PY}(r,d)$ the bridge function of the Percus-Yevick hard-sphere model with hard-sphere diameter d, $\varepsilon_4(r)$ the leading elementary diagram

$$\varepsilon_4(r) = \frac{1}{2}\rho^2\int\int d\mathbf{r}'d\mathbf{r}''h(r')h(r'')h(|\mathbf{r}'-\mathbf{r}''|)h(|\mathbf{r}-\mathbf{r}'|)h(|\mathbf{r}-\mathbf{r}''|), \tag{15}$$

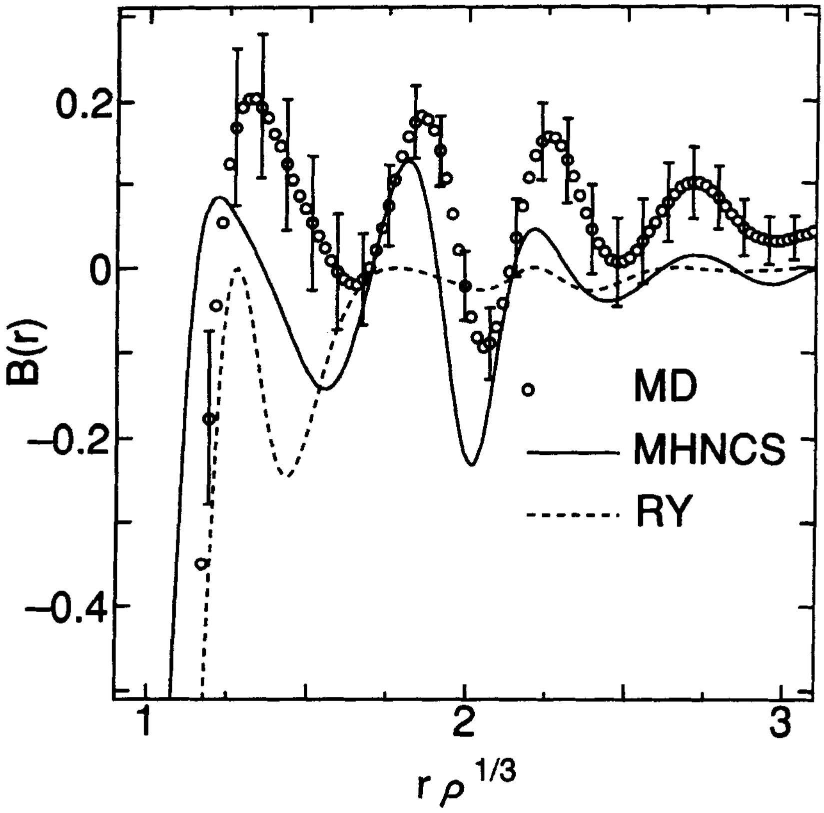

Figure 2 The bridge function obtained by the MD simulation (○), the RY approximation (dotted curve), and the MHNCS approximation (solid curve) for the supercooled soft-sphere fluid ($n = 12$) at $\Gamma = 1.5$. The error bar attached to the MD data represents the standard deviation of four different samples along the trajectory.

and W a dumping parameter [10]. Note that the bridge function obtained from MD simulations for short inter-particle distances ($r \leq 1$) is less reliable due to the statistical uncertainty in $g_{\mathrm{MD}}(r)$.

It is easily seen from Figures 2 and 3 that the bridge function obtained from MD simulations yields a significant oscillatory behavior around zero at intermediate distances where the second peak of the PDF appears, in contrast to the result above the freezing temperature shown in Figure 1. Taking into account the statistical error of $B(r)$ extracted, this behavior is well reproduced by the MHNCS approximation except for the very short-distance-range, in remarkable contrast to that of the RY approximation. The essential difference between the RY and MHNCS approximations is the description of the correlation at intermediate distances; the former shares the same class of correlations contained in the PY approximation, on the other hand, the latter includes correlations given by the leading elementary diagram appeared in the definition of the bridge function (see Equation (3)). Thus, the leading elementary diagram $\varepsilon_4(r)$ is responsible for the oscillatory behavior of

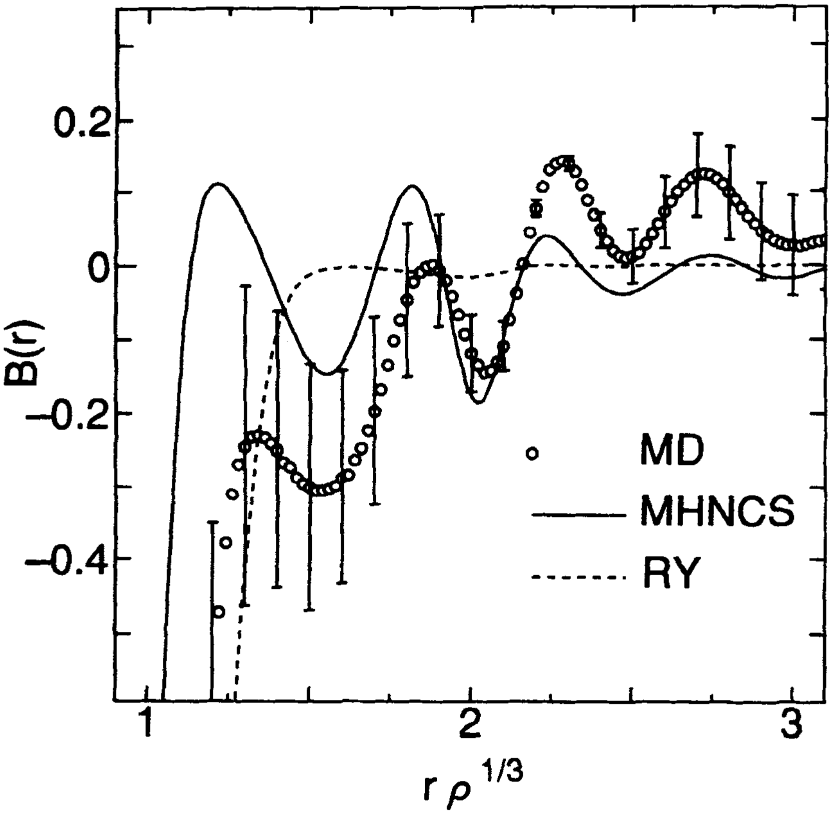

Figure 3 The bridge function obtained by the MD simulation (O), the RY approximation (dotted curve), and the MHNCS approximation (solid curve) for the supercooled soft-sphere fluid ($n = 6$) at $\Gamma = 3.6$. The error bar attached to the MD data represents the standard deviation of four different samples along the trajectory.

$B(r)$. As we have shown in our previous paper [10], the PDF obtained by the MHNCS approximation yields a clear splitting of its second peak for highly supercooled regime, while that of the RY approximation yields no splitting of the second peak. We thus conclude that $\varepsilon_4(r)$ included in the exact definition of $B(r)$ is essential for the characteristic feature (split second peak) of the PDF at intermediate distances for highly supercooled liquids.

DISCUSSIONS

We have performed isokinetic molecular dynamics simulations for highly supercooled soft-sphere fluids. The bridge function, whose properties are important for a practical application of the integral equation theory, has been extracted from the PDF obtained by the MD simulation. The bridge function extracted shows a significant oscillatory behavior at intermediate distances for highly supercooled regime, in contrast to its behavior above the freezing temperature, i.e., $B(r)$ is nearly equal to zero except for the core region. From comparisons of present results with predictions via approximate integral equations, this oscillatory behavior is found to be dominated by spatial correlations of the form of leading elementary diagram $\varepsilon_4(r)$ contained in the exact integral equation. It is also found that $\varepsilon_4(r)$ is responsible for a split second peak of the PDF for highly supercooled states, which is typically observed for a variety of glass forming materials near the glass transition temperature. We note that widely used RY and RHNC approximations could be capable for stable liquids, since $\varepsilon_4(r)$ has almost no contribution to a feature of the PDF at the intermediate-distance-range for such weakly coupled states. In order to apply approximate integral equations for highly supercooled liquids, however, it is important to take into account intermediate-distance-range correlations given by the elementary diagrams, which is obscure for stable liquids above the freezing temperature. Finally, we note that calculations of the bridge function for realistic materials are being undertaken.

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