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# Dynamic structure factor of liquid Ga close to the melting point: spectral linewidth at high momentum transfer

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## Abstract

By simulating an interatomic pair potential obtained from the first-principles generalized energy-independent nonlocal model-pseudopotential (GEINMP) theory, we have reproduced the high-wavevector shoulder in the static structure factor and the recently observed anomaly in the linewidth of the dynamic structure factor of liquid Ga close to the melting point. Our results indicate that the two anomalies have the same physical origin, which is associated with the Friedel oscillations induced by conduction electrons. The anomaly in the dynamics can be well described by the revised Enskog theory for the hard-sphere (HS) system, with the effective HS diameter determined by the position at the first peak of the radial distribution function. We interpret the occurrence of the anomaly in the dynamics by the physical picture of cage diffusion.

(Some figures in this article are in colour only in the electronic version)

The collective dynamics of simple liquids in the kinetic regime, where the hydrodynamic theory is no longer valid, is still an interesting subject. As the wavelengths of the collective dynamics in a simple liquid are smaller than the average interparticle distance, the propagating sound mode is strongly damped and the dynamic structure factor has only a single Lorentzian-like central peak [1]. The linewidth  $Z(q)$  of the central peak as a function of the wavevector  $q$  of the collective dynamics shows a minimum, known as de Gennes narrowing, occurring near  $q_M$ , the first peak of the static structure factor of the liquid [2]. Theoretically, at such a short wavelength, it is only in the hard-sphere (HS) fluids that the microscopic dynamics can be described by the revised Enskog theory, which is a generalization of the kinetic theory by

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including the correlated collisions among particles [3, 4]. According to this theory, the central peak of the dynamic structure factor at a high wavevector is caused by the non-propagating heat mode, which essentially results from the thermal diffusion of particles [5, 6], and the linewidth of the peak is given as

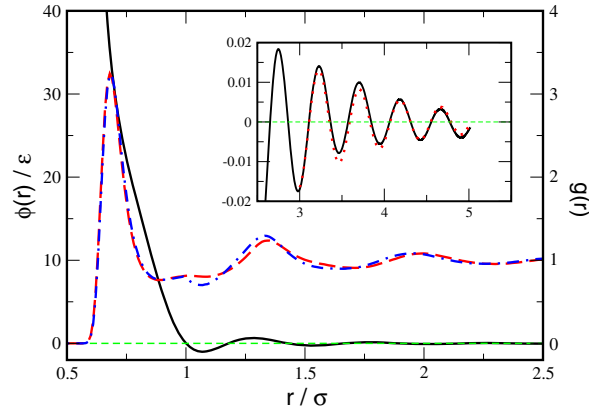
$$Z(q) = \frac{D_E q^2}{S_{\text{hs}}(q)} d(q) \quad (1)$$

where  $D_E$  and  $S_{\text{hs}}(q)$  are the Enskog diffusion coefficient and the static structure factor of the HS fluid, respectively.  $d(q)$  is a dynamic factor, which characterizes the diffusion of a particle out of the cage formed by its surrounding neighbours [7], and  $d(q) = (1 - j_0(q\sigma_{\text{hs}}) + 2j_2(q\sigma_{\text{hs}}))^{-1}$ , where  $\sigma_{\text{hs}}$  is the HS diameter and  $j_n(x)$  is the spherical Bessel function of order  $n$ . Tested for many realistic fluids, including rare-gas liquids and Rb, and model systems, like the Lennard-Jones (LJ) and repulsive LJ fluids, the  $Z(q)$  functions of these fluids around  $q_M$ , obtained from either experiments or computer simulations, are well fitted by this expression [5–7]. The parameter  $\sigma_{\text{hs}}$  is determined by the condition that the static structure factor of the HS fluid coincides in the first-peak position with that of the fitted system. This condition is achievable for those fluids mentioned above, which fall into the category I as classified by Waseda [8].

Liquid Ga close to the melting point ( $T_m = 302$  K) has a well-known peculiar static structure factor  $S(q)$ , which has an asymmetric first peak with a shoulder on the high- $q$  side. Not accommodated by an HS model [9], this peculiar static structure factor falls into the category III of Waseda's classification. The high- $q$  shoulder is interpreted as arising from the interplay between two characteristic length scales: the effective HS diameter  $\sigma_{\text{hs}}$  for the repulsive core to fulfil the structural requirements and the wavelength  $\lambda_F = \pi/k_F$  of the Friedel oscillations, where  $k_F$  is the Fermi wavenumber of the conduction electrons [10, 11]. With these two length scales, the principal peak of  $S(q)$  is expected to appear near  $2\pi/\sigma_{\text{hs}}$  and the high- $q$  shoulder near  $2k_F$ , which is the diameter of the Fermi sphere.

Recently, in terms of inelastic neutron and x-ray scattering for liquid Ga at  $T = 315$  K, besides the minimum at  $q_M$ , the  $Z(q)$  function shows an anomaly appearing around the wavevectors coincident with the position of the shoulder in the static structure factor [12, 13]. This anomaly is similar as the one observed in a previous study for liquid Bi by the inelastic neutron scattering (INS) method [14]. However, it is by no means obvious to fit the anomaly in  $Z(q)$  of liquid Ga by equation (1), and some debates arise because of the peculiar static structure factor of liquid Ga [15, 16]. One is how to determine the effective HS diameter for liquid Ga, and another is whether the HS-like dynamics is a proper way to describe the microscopic dynamics in liquid Ga even though the spectral linewidth of the dynamic structure factor can be successfully described by the expression derived from the HS model. Actually, these debates are related to the more fundamental questions: what is the physical origin that causes the anomaly in  $Z(q)$  of liquid Ga, and is this origin the same one for the shoulder in  $S(q)$ ?

In this paper, by simulating an interatomic pair potential generated from the first-principles GEINMP theory [9], we reproduce the peculiar features observed in the static structure factor and the linewidth of the dynamic structure factor of liquid Ga, with reasonable agreements between the simulated results and the experimental data. In order to examine the effects due to Friedel oscillations in the interatomic pair potential on  $S(q)$  and  $Z(q)$ , we have done another simulation at the same  $NVT$  conditions as for liquid Ga with the interactions between particles being only the repulsive core of the pair potential. We refer to this simulated liquid as the liquid of repulsive Ga. We find that the anomalies in both  $S(q)$  and  $Z(q)$  of liquid Ga disappear as the Friedel oscillations are truncated. Thus, this result strongly indicates that both the structural and



**Figure 1.** The interatomic pair potential of liquid Ga (solid line) obtained from a first-principles pseudopotential theory [9]. The energy is scaled with  $\epsilon$ , the depth of the main attractive well, and the distance scaled with  $\sigma$ , the shortest distance where the potential is zero. The inset shows the result (dotted line) fitted with equation (2) for the pair potential at distances larger than  $3\sigma$ . With a scale referred to the right axis, the dashed and dot-dashed lines are the radial distribution functions  $g(r)$  of the liquids simulated at  $T = 323$  K with the full range of the pair potential and the repulsive core obtained by truncating the pair potential at  $\sigma$ , respectively.

dynamic anomalies of liquid Ga result from the same physical origin, which is associated with the Friedel oscillations. Also, we conclude that the  $Z(q)$  of liquid Ga at wavevectors around the de Gennes narrowing and the anomaly can be described by the revised Enskog theory, with  $\sigma_{\text{hs}}$  determined by the distance at the first peak of the radial distribution function  $g(r)$  and  $D_E$  calculated for the corresponding HS fluid.

We have carried out molecular dynamics simulations of 3500 particles in the equilibrium state of liquid Ga at  $T = 323$  K, pressure of about 1 bar and number density  $\rho = 0.05 \text{ \AA}^{-3}$  [9]. Shown in figure 1 is the simulated interatomic pair potential, which has two parameters:  $\sigma = 4.04 \text{ \AA}$ , the shortest distance where the potential is zero, and  $\epsilon$ , the depth of the main attractive well, corresponding to an effective temperature of about 47 K. The repulsive core, where the interatomic pair potential is truncated at  $\sigma$ , has a ledge shape with a curvature change around  $0.8\sigma$  [17]. At distances larger than  $3\sigma$ , the pair potential can be fitted by the equation of the shifted Friedel oscillations [10, 18],

$$\phi(r) = V \frac{\cos(2k_F r + \alpha)}{(2k_F r)^3}, \quad (2)$$

where  $k_F$ ,  $V$  and  $\alpha$  are treated as the fitting parameters. The fitting value of  $k_F$  is  $16.24 \text{ nm}^{-1}$ . Correspondingly, the wavelength  $\lambda_F$  of the Friedel oscillations is  $1.93 \text{ \AA}$ , and the effective valence charge per Ga ion in the simulated liquid is estimated to be  $2.9e$ , where  $e$  is the charge of a proton.

As shown in figure 1, the radial distribution functions of the two simulated liquids are almost identical in the first shell, with a peak position located at  $2.77 \text{ \AA}$ , which is well inside the repulsive core. Thus, for liquid Ga,  $g(r)$  at distances less than  $\sigma$  is almost unaffected by the Friedel oscillations. However, the Friedel oscillations cause the shell structures in  $g(r)$  beyond  $\sigma$  to have an outward shift by a small amount. At distances longer than  $\sigma$ ,  $g(r)$  of liquid Ga is determined by not only the repulsive core but also the oscillatory interactions between two Ga ions. This is quite different from the case of the dense LJ fluids, whose  $g(r)$  are completely determined by the repulsive core [19].

The static structure factors of the two simulated liquids are displayed in figure 3. Apparently, our simulation with the full-range interatomic pair potential reproduces the peculiar static structure factor of liquid Ga observed in the laboratory, with  $q_M$  located at  $25.4 \text{ nm}^{-1}$  and the shoulder roughly at  $32.5 \text{ nm}^{-1}$ , which is exactly  $2k_F$ . Without strong distortion in the overall shape from the  $S(q)$  of liquid Ga, the static structure factor of the repulsive Ga liquid has a first peak at  $25.7 \text{ nm}^{-1}$  and with an increment in magnitude, but no shoulder appears on the high- $q$  side of the first peak. This confirms that the high- $q$  shoulder in the  $S(q)$  of liquid Ga results from the Friedel interactions between the ions [10, 11].

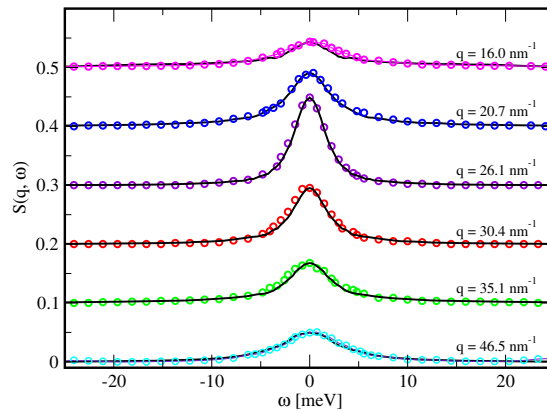
We give two ways to estimate the effective HS diameters  $\sigma_{\text{hs}}$  for the two simulated liquids. First, estimated through the position of the first peak of  $S(q)$ ,  $\sigma_{\text{hs}}$  is set to be  $2\pi/q_M$ ; the HS diameters are  $2.47 \text{ \AA}$  for liquid Ga and  $2.44 \text{ \AA}$  for the repulsive Ga liquid. With the HS diameter and the number density  $\rho$  in the simulations, the packing fractions  $\eta = \pi\rho\sigma_{\text{hs}}^3/6$  of the two corresponding HS fluids are 0.396 and 0.382, which are well in the fluid phase of the HS system. The Enskog diffusion coefficient  $D_E$  in equation (1) is given by

$$D_E = \frac{\sigma_{\text{hs}}}{8} \left( \frac{\pi k_B T}{m} \right)^{1/2} \frac{(1-\eta)^3}{\eta(2-\eta)}, \quad (3)$$

where  $k_B$  is the Boltzmann constant and  $m$  is the particle mass. With  $\sigma_{\text{hs}} = 2.47 \text{ \AA}$ ,  $D_E$  evaluated by equation (3) is  $3.74 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , which is roughly two times larger than the self-diffusion coefficient  $D_s = 1.77 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  obtained from integrating the velocity autocorrelation function. The other way to determine the HS diameter is to set  $\sigma_{\text{hs}}$  as the distance corresponding to the first peak of  $g(r)$ , so  $\sigma_{\text{hs}} = 2.77 \text{ \AA}$  for the two simulated liquids and  $\eta$  of the HS fluid is about 0.559, which is a little beyond the fluid–solid boundary for the HS system. With  $\sigma_{\text{hs}} = 2.77 \text{ \AA}$ ,  $D_E$  estimated by equation (3) is  $1.66 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , which is close to  $D_s$ .

To investigate the anomaly in the collective dynamics, we have calculated the dynamic structure factor  $S_{\text{MD}}(q, \omega)$ , which is a time Fourier transform of the intermediate scattering function of the Ga ions, obtained by simulations with wavevectors chosen to be the reciprocal lattice points of the simulation box, with box length  $41.25 \text{ \AA}$ , and averaged within a spherical shell with radii between  $q - \delta q$  and  $q + \delta q$ , where  $\delta q$  is set to be  $0.62 \text{ nm}^{-1}$ . After being weighted by the detailed balance factor and convoluted with the instrumental resolution used in the experiment of inelastic x-ray scattering (IXS) [12], the calculated dynamics structure factors are directly compared with the experimental data of IXS, and the results are shown in figure 2 for several  $q$  values, within a range covering the first peak and the shoulder in  $S(q)$ . For the wavevectors indicated in figure 2, the dynamic structure factors calculated by our simulation are in good agreement with the experimental data.

For large wavevectors,  $S_{\text{MD}}(q, \omega)$  can be fitted with a Lorentzian. We define  $Z(q)$  as the half width at half maximum (HWHM) of the fitting Lorentzian, and the  $Z(q)$  of the two simulated liquids are plotted in figure 3. Similar to the experimental results of inelastic scattering [12, 13], the  $Z(q)$  function of the simulated liquid Ga indeed shows a shoulder around  $32 \text{ nm}^{-1}$ , which is in coincidence with the position of the shoulder in  $S(q)$ . To predict the shoulder in  $Z(q)$  by the revised Enskog theory, the results with several different choices of  $\sigma_{\text{hs}}$  and  $D_E$  are presented in figure 3(a). We find that to get a good agreement with the simulation data for wavevectors between 30 and  $35 \text{ nm}^{-1}$ ,  $\sigma_{\text{hs}}$  must be the position of the maximum of  $g(r)$  and  $D_E$  be evaluated by equation (3). For the liquid of repulsive Ga, the  $Z(q)$  function shows a minimum at  $q_M$  and is monotonically ascendant as  $q$  increases from  $q_M$  up to  $40 \text{ nm}^{-1}$ . As evidenced by our simulations, the shoulder originally appearing in the  $Z(q)$  of liquid Ga no longer exists once the Friedel oscillations in the interatomic pair potential are truncated. This strongly suggests that in the realistic case the physical origin of the shoulder

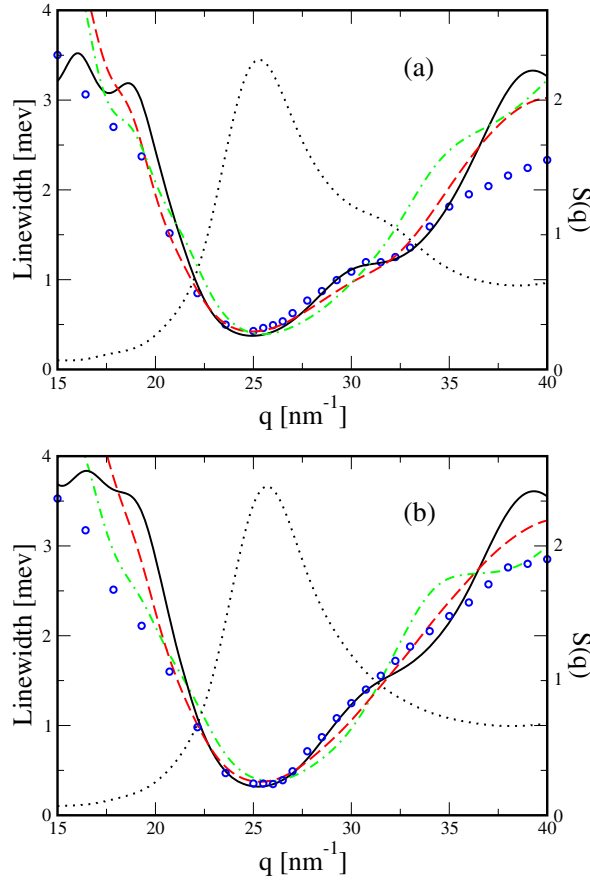


**Figure 2.** The dynamic structure factors of liquid Ga close to the melting point. The solid lines are obtained by our calculations at  $T = 323$  K. Each line is the simulated result weighted by the detailed balance factor and then convoluted with an instrumental resolution, which has a full width at half maximum of 2.8 meV. The circles are the experimental data of IXS at  $T = 315$  K [12].

in  $Z(q)$  should be associated with the Friedel oscillations, which also cause the shoulder in  $S(q)$ .

More information is obtained, as the  $Z(q)$  of the repulsive Ga liquid is predicted by the revised Enskog theory. With the same parameters for  $\sigma_{\text{hs}}$  and  $D_E$  as for successfully producing the anomaly in the  $Z(q)$  of liquid Ga, the prediction of the theory for the repulsive Ga liquid deviates somewhat from the simulation data at wavevectors between 30 and 35  $\text{nm}^{-1}$ . This suggests that in liquid Ga the Friedel interactions make the collective dynamics with wavevectors around the shoulder in  $Z(q)$  behave more like the HS fluid. Also, shown in figure 3, by comparing the predictions with and without  $d(q)$  in equation (1), we find that the dynamic factor  $d(q)$  associated with the cage diffusion is essential to get a good agreement between the theory and simulation for the wavevectors around the shoulder. This information suggests that the mechanism giving rise to the shoulder in  $Z(q)$  should be related to the cage diffusion.

Based on our study by simulations, we suggest that the physical origin of the shoulder in  $Z(q)$  of liquid Ga can be understood through the picture of cage diffusion [20]. For the single-particle dynamics, the cage diffusion in a liquid is usually depicted as that a particle, which frequently collides with its neighbours, is confined in a cage in a short timescale but diffuses out of the cage in a longer timescale. Alternatively, from the viewpoint of collective dynamics, the cage diffusion can be considered as the relaxation of the cage structure, whose relaxation time is related to the stability of the cage. In a liquid metal, as the density fluctuations of the positively charged ions have the same wavelength as that of the Friedel oscillations induced by the conduction electrons, the density waves of electrons and ions are coherent, and the overall attractions between the two systems are expected to integrate constructively and enhance the stability of the cage structure of each ion. This enhancement in the stability of the cage structures causes a relatively slower relaxation of the ion-density fluctuations at low temperatures. However, the enhancement is so small that its effect on the relaxation of collective dynamics is overwhelmed by the thermal motions at high temperatures. For liquid alkali metals, where the wavenumber of the Friedel oscillations is close to  $q_M$  [10, 11], this small enhancement in the stability of the cage structures is not manifested, since it is only superimposed on the liquid structure mostly determined by the repulsive cores of the ions.



**Figure 3.** The spectral linewidth (HWHM) of dynamic structure factor as a function of wavevector for the simulated liquids of Ga (a) and repulsive Ga (b) at  $T = 323$  K. In each panel, the symbols stand for the results of simulation. The lines are the predictions of the revised Enskog theory with different choices of  $\sigma_{\text{hs}}$  and  $D_E$ . For the solid line,  $\sigma_{\text{hs}}$  is chosen to be the distance at the first-peak position of  $g(r)$  and  $D_E$  is evaluated by equation (3) with this  $\sigma_{\text{hs}}$ . The dashed line is the similar results for the same  $\sigma_{\text{hs}}$  and  $D_E$ , except that the dynamic factor  $d(q)$  in equation (1) is excluded. The dot-dashed line is the prediction of the theory with  $\sigma_{\text{hs}} = 2\pi/q_M$  and  $D_E$  replaced by the self-diffusion coefficient  $D_s$  of the liquid. Referred to the scale on the right axis, the dotted line is the static structure factor of the corresponding liquid.

However, for liquid Ga, in which the wavenumber of the Friedel oscillations apparently deviates from  $q_M$ , this minor effect on the cage stability becomes manifest and produces a shoulder in  $Z(q)$  observable in the experiments of inelastic scattering at temperatures close to the melting point.

In conclusion, by simulations with an interatomic pair potential, we have reproduced the high- $q$  shoulders in the static structure factor  $S(q)$  and the linewidth  $Z(q)$  of the dynamic structure factor of liquid Ga close to the melting point. Our results indicate that the Friedel oscillations induced by the conduction electrons are the physical origin for shoulders in both  $S(q)$  and  $Z(q)$ . The shoulder in  $Z(q)$  can be well described by the revised Enskog theory, with an effective HS diameter determined by the distance at the first peak of the radial distribution function. We conclude that the occurrence of the shoulder in  $Z(q)$  is caused by the enhanced

stability on the ion-cage structures due to the constructive attractions between ions and electrons at the Fermi surface.

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