

Electronic Supplementary Information

Extended Short-Range Order Determines the Overall Structure of Liquid Gallium

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Computational details

We performed *ab initio* molecular dynamics simulations of equilibrium liquid gallium at various temperatures from the temperature range $T = [325; 3000]$ K along the isobar $p = 1.0$ atm. These simulations were realized within the Car-Parrinello method as implemented in the Quantum Espresso package¹⁻³ with the exchange-correlation functional taken within the local density approximation by the Perdew-Zunger parametrization^{4,5}. The simulation cell had the shape of a parallelepiped and included five hundred atoms of gallium. To avoid the size effects, we applied in our simulations the periodic boundary conditions, according to which the simulation cell is duplicated in all the directions.

The electronic states expanded in a plane-wave basis have been truncated at 35 Ry. The time-step used to integrate numerically the equations of motion is 8.2682 a.u. (0.2 fs). A fictitious mass of 500 a.u. was assigned to the electronic degrees of freedom. To calculate the electronic structure it was used the Kohn-Sham formulation of DFT. All the Car-

Parrinello molecular dynamics simulations were done within the NpT -ensemble, with the pseudo-Hamiltonian being conserved within 10^{-5} au/ps. The temperature was controlled by means of the Nose-Hoover chain of thermostats⁶ applied to the ionic and electronic degrees of freedom.

Fit of the radial distribution function by a linear combination of the Gaussian functions: The Brute-force method

We apply the brute-force method to solve the optimization problem associated with estimating the parameters of the following expansion for the first peak of the radial distribution function over the Gaussian functions:

$$g(r) = \sum_i \frac{n_i}{2\pi\xi_i^2} \exp\left(-\frac{(r - \sigma_i)^2}{2\xi_i^2}\right). \quad (\text{S1})$$

Here, σ_i is the i th correlation length, n_i is the i th coordination number, and ξ_i is the effective dispersion, which determines the width of the i th Gaussian function. Applying relation (S1) allows one to realize the idea that the dynamics of two particles separated by a distance comparable with a correlation length obeys the Gaussian statistics. Extending this idea we obtain that each peak of $g(r)$ is reproduced either by a single Gaussian or by a linear combination of the Gaussian functions. We perform a fit of the first peak of the ‘experimental’ function $g(r)$ by relation (S1) according to the routine based on the next rules. First, it is necessary to determine the minimum number of the Gaussian functions that allows one to reproduce the contour of $g(r)$ with the required accuracy $\varepsilon = 0.003$. Second, trial values of the parameter σ_i are taking from the range restricted by the distance corresponding to the first nonzero value of $g(r)$ and by the distance $r_{1/2}$ (see Fig. 3). Trial values of both the parameters ξ_i and n_i are interrelated and these values are choosing so that the width and height of a model function $g(r)$ do not exceed values of the experimental function $g(r)$. Third, the fitting procedure starts with use of a single Gaussian, and then their number

increases successively until the required accuracy is achieved.

What information about interaction of neighboring particles can be obtained from distribution $P(\sigma)$?

Appearance of the non-zero values of the distribution $P(\sigma)$ at the lengths $\sigma < \sigma_0$ display the effect of overcoming the repulsion of neighboring particles due to their thermal motion. The width ξ of the left wing of the distribution $P(\sigma)$, as shown in Fig. 6, can be used to recover the features of particle repulsion at the short distances $r \leq \sigma_0$. Namely, assuming that the effective interaction $u(r)$ of particles in the neighborhood of the distance value $r = \sigma_0$ is spherically symmetric, we have

$$u(\sigma_0) - u(\sigma_0 - \xi) \simeq k_B T. \quad (\text{S2})$$

Then, within the harmonic approximation

$$u(\sigma_0 - \xi) \simeq u(\sigma_0) - \frac{1}{2} \left. \frac{\partial^2 u(r)}{\partial r^2} \right|_{r=\sigma_0} \cdot \xi^2 + \mathcal{O}(\xi^4), \quad (\text{S3})$$

we obtain

$$\xi^2 \simeq 2k_B T \left[\left. \frac{\partial^2 u(r)}{\partial r^2} \right|_{r=\sigma_0} \right]^{-1}, \quad (\text{S4})$$

where k_B is the Boltzmann constant.

References

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