Comment on "Hard-Sphere-Like Dynamics in a Non-Hard-Sphere Liquid"

Recently, Scopigno *et al.* [1] have reported on measurements of the spectral linewidth of a liquid semimetal such as Ga for wave vectors comprising Q_p where the static liquid structure factor $S(Q)$ shows its maximum. For such spatial scales, the coherent spectral width may be described by means of an expression derived by Cohen *et al.* [2] on the grounds of the revised Enskog theory (RET),

$$\Delta\omega = D_E Q^2/S(Q)[1 - j_0(Q\sigma) + 2j_2(Q\sigma)], \quad (1)$$

with D_E being the Enskog diffusion coefficient and σ a hard-sphere diameter. The Eq. (1) is known to approximately account for data measured for non-hard-sphere systems [2,3], provided that estimates for D_E and σ are chosen and used together with the experimental $S(Q)$.

Here we comment on the fact that the agreement between theory and experiment shown in Ref. [1] can only be reached if both $S(Q)$ together with a value D_E close to the experimental estimate for the self-diffusion coefficient are chosen and both quantities largely differ from those expected for a hard-sphere liquid. In fact, $S(Q)$ shows a complicated structure that unveils the action of forces of different nature, and the best estimate for D_E comes to be significantly below that calculated from RET.

The analysis of data reported on [1] can be carried out without leaving any adjustable parameter. On the basis of our own neutron data [4] measured with a resolution in energy transfers of 0.43 meV (FWHM) [2.8 meV quoted in [1]], we can access both collective and single-particle properties in a single experiment. The latter can be followed up to $Q \approx 1.4$ Å^{-1} where coherent effects are minimal. From its linewidth $\Delta\omega_{\rm inc} = 2\hbar D_s Q^2$ one then derives an estimate for the self-diffusion coefficient $D_s = 0.132$ Å^2 meV [versus 0.114 Å^2 meV [1]]. As regards the hard-sphere diameter entering Eq. (1), the adequate value comes to be 2.79 Å which matches that where the static pair distribution $g(r)$ shows its maximum, and therefore corresponds to the most probable interatomic distance rather than to a particle diameter.

The data are shown in Fig. 1 together with curves calculated using two different $S(Q)$, setting σ and D_E to values given above. The agreement between experiment and calculation is confined within 2.0 Å$^{-1} \leq Q \leq$ 3.5 Å^{-1} and outside such a range it depends upon details of the $S(Q)$ used for the calculation. Both the minimum about Q_p and the shoulder at about 3 Å^{-1} are well accounted for. Such a double-peak structure cannot obviously be reproduced if a single-peak, hard-sphere $S(Q)$ is plugged into Eq. (1).

Summarizing, the linewidths about Q_p on molten Ga can only be reproduced using Eq. (1) if input quantities [i.e., $S(Q), D_E, \sigma$] are chosen by, or very close to, experiment. They show large deviations from those expected for a hard-

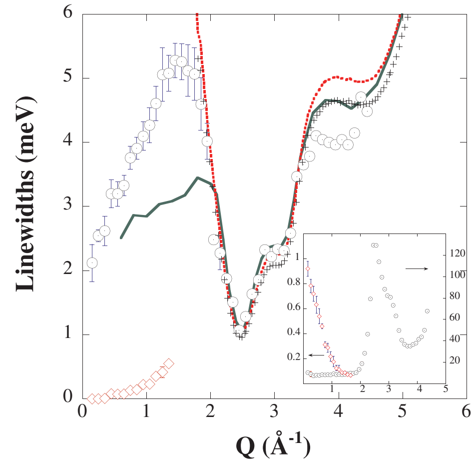

FIG. 1 (color online). Circles: coherent linewidth (FWHM) of liquid Ga at 315 K. Lozenges: incoherent linewidths. Solid line: Eq. (1) setting $\sigma = 2.79$ Å, (see text) and using the $S(Q)$ of Ref. [5]. Dashed line: same as before but with the $S(Q)$ of Ref. [6]. Crosses depict the result using the best estimate for D_E given in [1]. Inset: relative amplitudes of the coherent (circles) and incoherent scattering (lozenges) signals.

sphere liquid and therefore the presence of hard-sphere-like dynamics cannot be inferred from analysis of data based upon these. Furthermore, the best value found for σ that would correspond to unphysically high packing is yet another reminder of the inadequency of portraying the dynamics of liquid Ga in terms of a dense packing of hard spheres. In consequence, it cannot be taken as an indication of the "supra-atomic" nature of the "effective particles" as suggested in Ref. [1].

F. J. Bermejo,[1] I. Bustinduy,[1] C. Cabrillo,[1] S. J. Levett,[2] and J. W. Taylor[2]
[1]Department of Electricity and Electronics
University of the Basque Country
P.O. Box 644, 48080 Bilbao, Spain
and Instituto de Estructura de la Materia
C.S.I.C.
Serrano 123, E-28006 Madrid, Spain
[2]Rutherford Appleton Laboratory
Chilton, Didcot
Oxon OX11, 0QX, United Kingdom

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