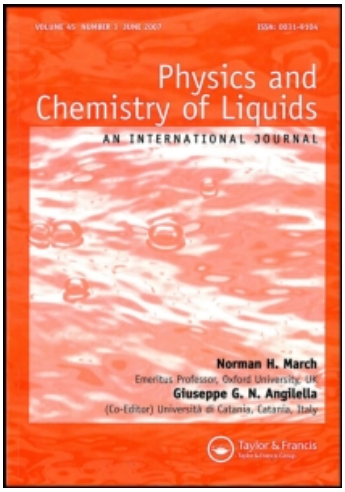

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Some properties of the structure factor $S(q)$ in two-dimensional classical liquids near freezing

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Some properties of the structure factor $S(q)$ in two-dimensional classical liquids near freezing

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We explore general properties of the main peak of the structure factor $S(q)$ near the melting temperature $T_{\rm melt}$ in liquids confined in two dimensions, especially for the one component plasma model and for monatomic liquids interacting through inverse twelfth-power potentials. Those properties are the height of the peak, $S(q_{\rm m})$, where $q_{\rm m}$ is the position of maximum in the peak, and the ratio between $S(q_{\rm m})$ and $q_{\rm m}/\Delta q$, where $2\Delta q$ is the width of the peak. The results obtained are then compared with those for similar systems in three dimensions. Other magnitude that we use to compare two-dimensional and three-dimensional simple liquids is $r_{\rm m}/\Delta r$, where $r_{\rm m}$ is the position of the main peak in the pair distribution function $g(r)$ and $2\Delta r$ is the width of that peak.

Keywords: classical liquids; freezing; two-dimensional systems; structure factor

The one component plasma (OCP) is a model in which a single species of charged particles interacting via the Coulomb potential are immersed in a uniform neutralising background of opposite charge. The OCP is characterised by the plasma coupling parameter Γ defined as

$$\Gamma = \frac{e^2/r_{\rm s}}{k_{\rm B}T}, \tag{1}$$

where $r_{\rm s}$ measures the mean interparticle separation. That is, Γ is the ratio of Coulomb energy $e^2/r_{\rm s}$ to the thermal energy $k_{\rm B}T$. In early work, Ferraz and March [1] utilised available computer simulation results on the classical three-dimensional (3D) OCP and plotted $S(q_{\rm m})$, the maximum height of $S(q)$, that is, the height of the main peak of the structure factor, *versus* Γ. The freezing value of Γ for the 3D classical OCP model is approximately 160, and from that plot they were able to obtain the value of $S(q_{\rm m})$ at freezing, namely $(S(q_{\rm m}))_{T_{\rm melt}} = 2.7$, where $T_{\rm melt}$ indicates the melting temperature. This is in conformity with the so-called Verlet rule [2]. The plot of $S(q_{\rm m})$ *versus* Γ for the 3D OCP is redrawn in Figure 1.

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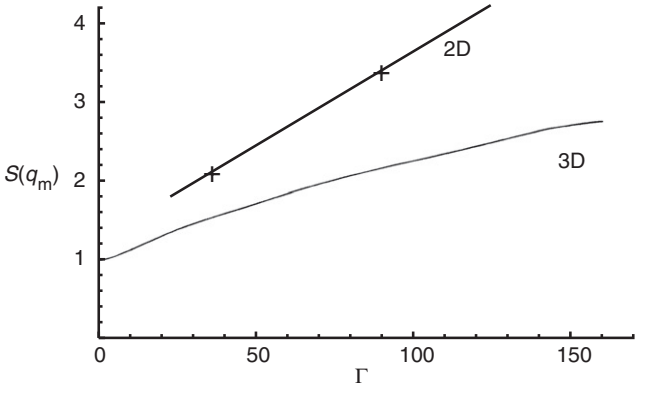

Figure 1. Maximum $S(q_m)$ of liquid structure factor as a function of the coupling parameter Γ defined in Equation (1) for the 3D one-component plasma (redrawn from Ferraz and March [1]). Also shown are two points from available Monte Carlo calculations of the classical 2D one-component plasma by Gann *et al.* [3], and the linear extrapolation to Γ=125.

In the two-dimensional case (2D), the data available for the classical OCP is more limited. Gann *et al.* [3] have performed Monte Carlo simulations for this system and found that the freezing transition occurs at $\Gamma = 125$. These authors do not plot the structure factor for this special value of Γ. However, they report the structure factors corresponding to $\Gamma = 36$ and $\Gamma = 90$, and we have plotted the corresponding values of $S(q_m)$ also in Figure 1. An extrapolation to $\Gamma = 125$ gives an estimate of the value of $S(q_m)$ at freezing, that is, $(S(q_m))_{T_{melt}} = 4.2$, in the 2D case.

We next turn to discuss the calculation of $S(q)$ by Broughton *et al.* [4] on a second model of a 2D dense fluid, but now with inverse twelfth-power interaction. These authors plot in their figures 11 and 12 two structure factors in the stable fluid region for different densities ρ, that is, particles per unit area. The approximate 2D peak heights are $S(q_m) = 4.4$ for $\rho = 0.971$ (their state a) and $S(q_m) = 5.3$ for $\rho = 0.986$ (state b), the last one practically corresponds to the freezing density. The difference with respect to the OCP can be attributed to the different interparticle interaction. At the same time as that work, Ramakrishnan [5] presented a density wave theory of freezing in two dimensions following earlier work by Ramakrishnan and Yussouff [6] on the liquid–solid transition in 3D. It is relevant here to note that in [6], a basic justification for the Verlet rule [2] was put forward, based however on the hypernetted chain (HNC) approximation in classical statistical mechanics. The later independent studies of Haymet and Oxtoby [7] and March and Tosi [8] showed that the HNC was essential in the theory of freezing developed in [6]. Ramakrishnan [5] quoted the value of 5.0 for the height of the main peak of the structure factor near freezing in two dimensions.

Other properties of $S(q)$ in three dimensions were subsequently discussed by Bhatia and March [9]. These authors were concerned with relating the position of the main peak of $S(q)$ in dense monatomic liquids, denoted again by q_m, with the shape of that peak. This they chose to characterise by the distance between the two adjacent nodes of $S(q) - 1$ which embrace the peak maximum at q_m: this peak width being denoted in [9] by $2\Delta q$. The semiquantitative estimate for 3D structure factors

Table 1. Results for $\frac{q_m}{\Delta q}$, $\frac{S(q_m)}{q_m/\Delta q}$ and $\frac{r_m}{\Delta r}$ from the computer simulations of Gann *et al.* [3] for the 2D one component plasma and of Broughton *et al.* [4] for monatomic liquids interacting via inverse twelfth-power potentials.

Metal	$\frac{q_m}{\Delta q}$	$\frac{S(q_m)}{q_m/\Delta q}$	$\frac{r_m}{\Delta r}$
Gann ($\Gamma = 36$)	5.57	0.37	4.87
Gann ($\Gamma = 90$)	7.32	0.46	5.71
Gann ($\Gamma = 120$)	–	–	5.59
Broughton ($\rho = 0.9706$)	10.2	0.43	6.29
Broughton ($\rho = 0.9858$)	10.2	0.51	6.29

Notes: q_m is the position of the main maximum in the structure factor $S(q)$ and Δq is the width of that peak. r_m is the position of the main peak in the pair distribution function $g(r)$ and Δr is the width of that peak.

was $S(q_m) \approx 0.3 q_m/\Delta q$. On the other hand, in a semiempirical estimate using five experimental $S(q)$ curves, Bhatia and March obtained in 3D

$$S(q_m) \approx \frac{3}{8}\frac{q_m}{\Delta q}. \tag{2}$$

This result essentially follows from the condition that the liquid pair function $g(r)$, such that $g(r) - 1$ is the Fourier transform of $S(q) - 1$, vanishes at $r = 0$. The constant $3/8 = 0.375$ is slightly larger than the semiquantitative estimate 0.3.

We have reworked the 3D analysis of Bhatia and March [9] in 2D, and retaining the notation $2\Delta q$ for the distance between the two adjacent nodes of $S(q) - 1$ which embrace the peak maximum at q_m we find the semiquantitative result $S(q_m) \approx 0.5 q_m/\Delta q$, which should be compared with Equation (2). Again, we can obtain a semiempirical estimate using the 2D structure factors from the computer simulations [3,4] and the results are given in Table 1. The value of $S(q_m)/(q_m/\Delta q)$ from the computer simulations for the 2D OCP at $\Gamma = 90$ performed by Gann *et al.* [3] is 0.46. The simulations of Broughton *et al.* [4] for the 2D dense fluid with inverse twelfth-power interaction give $S(q_m)/(q_m/\Delta q) = 0.43$ and 0.51 for the two states with densities $\rho = 0.971$ and 0.986, respectively. The average of these three values is 0.47.

In three dimensions, Bhatia and March [9] also looked at the radial distribution function $g(r)$. Calling r_m the position of the main peak of $g(r)$, and defining the width of the peak, $2\Delta r$, as the distance between the two adjacent nodes of $g(r) - 1$ which embrace the peak maximum at r_m, they estimated very approximately that

$$\frac{q_m}{\Delta q} \approx \frac{r_m}{\Delta r} \tag{3}$$

in dense monatomic fluids. Table 1 contains the results for $r_m/\Delta r$ in 2D from the computer simulations discussed above. The ratio $q_m/\Delta q$ is in every case larger than the ratio $r_m/\Delta r$. If we write $q_m/\Delta q = C r_m/\Delta r$, the value of the constant C is 1.14 and 1.28 for the two OCP states, respectively, and 1.62 for the fluid with inverse twelfth-power interaction, but at least the data in the table shows that $r_m/\Delta r$ increases when $q_m/\Delta q$ increases.

In [9], it is pointed out that there is a direct connection with Lindemann's Law of melting in 3D. Thus, using $(S(q_m))_{T_{melt}} = 2.8$ yields from Equations (2) and (3) the estimate $\Delta r/r_m \approx 0.11$. If we define the mean interatomic separation r_A in 3D through $\rho = 3/(4\pi r_A^3)$, where ρ is the atomic number density, then according to Faber [10], Lindemann's law gives $(\Delta r/r_A)_{T_{melt}} \approx 0.2$ if we identify here Δr as the root mean square displacement of the atoms. Since $r_m \approx 1.8 r_A$, these results are pointed out in [9], to be quite consistent in 3D.

While relating to Lindemann's law, we have recently considered one version sometimes quoted that this law implies that $S_{T_{melt}}(0) =$ constant for all monatomic liquids near freezing. But as shown in [11], this is a poor relation. Fitting to one metal, Rb, for a wide variety of metals considered, $S_{T_{melt}}(0)$ is then found to vary by a factor of 10. Invoking the very recent study of Lawson [12] in 3D, his Figure 2 shows that $k_B T_{melt}/B\Omega$, where B is the bulk modulus and Ω the atomic volume, correlates with Gruneisen's constant. But

$$S_{T_{melt}}(0) = (\rho k_B T K_T)_{T_{melt}} = \left(\frac{k_B T}{B\Omega}\right)_{T_{melt}} \tag{4}$$

and hence $S_{T_{melt}}(0)$ correlates also with Gruneisen's constant.

In the future it would be of obvious interest, in 2D systems like graphene (a problem is the very high melting temperature of graphite, $T_{melt} \approx 4600$–4800 K [13]), or, say, thin monatomic metallic films, to examine such correlations that we know to exist in 3D. But we are not presently aware of any systematic experimental studies of Gruneisen's constant in such 2D-like materials.

To conclude, we note that long ago Peierls [14] and Landau [15] both stressed that a 2D solid does not have the conventional long-range order of the 2D crystal. Due to long-wavelength phonon fluctuations, the mean square displacement of a particle from its ideal site in a lattice will diverge as $\ln N$, where N denotes the number of particles. However, for realistic values of N, Broughton *et al.* [4] pointed out that these phonon fluctuations have only a very small effect on the mean-square displacement.

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