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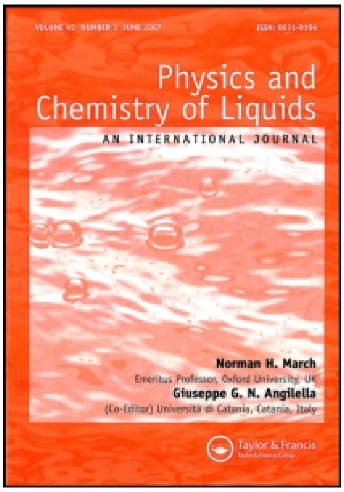

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Letter: freezing theory of rbcl

M. Rovere[a]; M. P. Tosi[b]; N. H. March[c]
[a] International School for Advanced Studies, Trieste, Italy [b] International Centre for Theoretical Physics, Trieste, Italy [c] Theoretical Chemistry Department, University of Oxford, Oxford, England

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Letter

Freezing Theory of RbCl

M. ROVERE,
International School for Advanced Studies, Trieste, Italy.

and

M. P. TOSI,
International Centre for Theoretical Physics, Trieste, Italy.

and

N. H. MARCH,
*Theoretical Chemistry Department, University of Oxford, 1 South Parks Road,
Oxford OX1 3TG, England.*

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A criterion for freezing of alkali halides in terms of the principal peak of the liquid charge–charge structure factor $S_{QQ}(k)$ has been given in earlier work.[1] Subsequently, a theory of freezing of both neutral binary alloys and alkali halides has been developed,[2] based on partial liquid structure factors as input information.

The purpose of the present letter is to report results calculated from this theory, using the neutron determined partial structure factors for RbCl.[3] The important quantity for the present approach is the fractional volume change on melting $(V_L - V_S)/V_S \equiv \eta$, L and S referring to liquid and solid respectively.

As shown in Ref. 2, the difference $\Delta\Omega$ in thermodynamic potential between the two phases in equilibrium can be written

$$\frac{\Delta\Omega}{Nk_BT} = -\eta + c_{NN}(0)(\eta + \tfrac{1}{2}\eta^2) + 2\sum_{\mathbf{G}}{}' [c_{NN}(\mathbf{G})|\rho_{\mathbf{G}}|^2 \cos^2(\tfrac{1}{2}\mathbf{G}\cdot\mathbf{h}) + c_{QQ}(\mathbf{G})|\rho_{\mathbf{G}}|^2 \sin^2(\tfrac{1}{2}\mathbf{G}\cdot\mathbf{h})]. \tag{1}$$

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Here the sum extends over all the reciprocal lattice vectors $\mathbf{G}$ different from zero, $\rho_{\mathbf{G}}$ is the Fourier component of the number density of either species, $\mathbf{h}$ is the vector joining the two ions in the unit cell of the crystal structure while $c_{NN}(\mathbf{G})$ and $c_{QQ}(\mathbf{G})$ are the partial Ornstein–Zernike direct correlation functions in the liquid, just above the freezing point. Actually at the freezing point, the difference in thermodynamic potential $\Delta\Omega$ is zero.

The Euler equations (3.11) and (3.12) of Ref. 2 were rearranged into the forms

$$1 + \eta = \exp[\eta c_{NN}(0)] \int \frac{d\mathbf{r}}{V} \exp[F_1(\mathbf{r}) + F_2(\mathbf{r})] \tag{2}$$

and

$$2\rho_{\mathbf{G}} = \exp[\eta c_{NN}(0)] \int \frac{d\mathbf{r}}{V} \exp(-i\mathbf{G}\cdot\mathbf{r}) \exp[F_1(\mathbf{r}) + F_2(\mathbf{r})], \tag{3}$$

with

$$F_1(\mathbf{r}) = \sum_{\mathbf{G}}{}' \rho_{\mathbf{G}} c_{NN}(\mathbf{G})[1 + \exp(i\mathbf{G}\cdot\mathbf{h})] \exp(i\mathbf{G}\cdot\mathbf{r}) \tag{4}$$

and

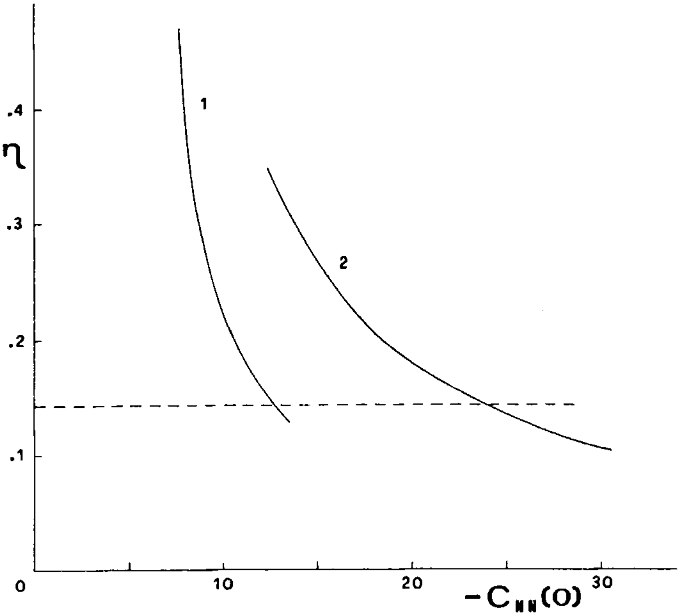
$$F_2(\mathbf{r}) = \sum_{\mathbf{G}}{}' \rho_{\mathbf{G}} c_{QQ}(\mathbf{G})[1 - \exp(i\mathbf{G}\cdot\mathbf{h})] \exp(i\mathbf{G}\cdot\mathbf{r}), \tag{5}$$

which were used in the calculations reported below. We have here used the fact that for RbCl the coupling between the number and charge correlation functions is sufficiently small that we can neglect c_{NQ}.

Though no previous calculations exist on two-component systems, experience has been gained on such a structural theory for monatomic liquids and in particular argon.[4,5] There the calculations[4] were performed in two stages, first including only the Fourier components of the density corresponding to the shortest set of reciprocal vectors $\{\mathbf{G}_1\}$ and then in the second stage including the second set $\{\mathbf{G}_2\}$. This is also a convenient route to adopt in the case of RbCl treated here.

In RbCl, the reciprocal vectors are those of the fcc lattice. In the first stage, we include only $\{\mathbf{G}_1\}$ corresponding to the first peak in $S_{QQ}(k)$ and only $F_2(\mathbf{r})$ enters the calculation. By numerical iteration, the above Euler equations plus $\Delta\Omega = 0$ were solved simultaneously for $\rho_{\{\mathbf{G}_1\}}$, η and $c_{QQ}(\mathbf{G}_1)$ for a given choice of $c_{NN}(0)$. Curve 1 of the Figure shows the fractional volume change η as a function of $c_{NN}(0)$.

One finds from the above calculation that the value of $S_{QQ}(\mathbf{G}_1)$ is always too large to agree with the neutron experiments,[3] a situation similar to that found for argon.[4] Including the next two sets of reciprocal lattice vectors corresponding to the first peak in $S_{NN}(k)$, $F_1(\mathbf{r})$ must also be calculated. Again, by numerical iteration, curve 2 of the Figure was obtained. Now



Fractional volume change η of freezing in RbCl as a function of $c_{NN}(0)$, calculated by including only the first set (curve 1) and the first and second sets (curve 2) of reciprocal lattice vectors. The broken horizontal line gives the experimental value of η.

the value of $c_{QQ}(\mathbf{G}_1)$ was taken from experiment and then $c_{NN}(\mathbf{G}_2)$ was found from the calculation to be in quite reasonable agreement with experiment.

Returning to the Figure, we note that to obtain the experimentally measured value[6] of η, namely 0.14, $c_{NN}(0)$ must be chosen to correspond to a compressibility which is not the same as the measured value for the liquid. However, as for liquid argon, the value obtained for the effective compressibility lies between that of the liquid and that of the hot solid.

We conclude that the structural theory of freezing for RbCl gives results of comparable quality to those obtained for a monatomic system like argon. The new feature in RbCl is that it is an interplay between S_{QQ} and S_{NN} that leads to physically reasonable values of the freezing parameters.

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