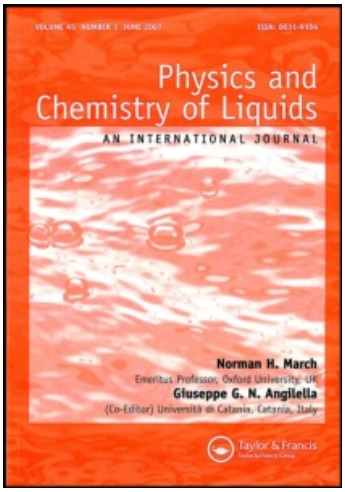

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Comment on the Asymptotic Form of the Radial Distribution Function in a Quasi-Crystalline Model of Liquids

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The asymptotic behaviour of the radial distribution function $g(R)$ for a liquid was reexamined recently[1] in a model defining the molecular correlations in terms of a fluctuating local crystalline structure (the quasi-crystalline model). Several different versions of this model have been presented since the earliest one given by Prins.[2] A more recent version was given by Franchetti[3] who derived the following formula for $g(R)$:

$$g(R) = \frac{1}{4\pi\rho}\frac{1}{\sqrt{2\pi}}\frac{1}{R}\sum_n \frac{1}{\sigma_n R_n}\left[\exp\left\{-\frac{(R-R_n)^2}{2\sigma_n^2}\right\} - \exp\left\{-\frac{(R+R_n)^2}{2\sigma_n^2}\right\}\right] \tag{1}$$

Here the n-summation extends over all the points of a certain chosen lattice, with R_n the distance from a central lattice site and σ_n^2 a suitably chosen dispersion assigned to the corresponding lattice point. This result was obtained from a minimization procedure applied to a certain functional of the lattice structure. To make (1) more specific, the so-called structural diffusion law given by Prins[2]

$$\sigma_n^2 = \beta R_n \tag{2}$$

was adopted.[3]

Formula (1), together with (2) has been found to lead to the incorrect asymptotic form

$$h(R) = g(R) - 1 \sim \frac{1}{R}, \qquad R \to \infty \tag{3}$$

This form exhibits the type of long range correlations found in a crystal but is unacceptable for a liquid. To rectify this inconsistency, it was proposed[1,4]

to modify the model by varying the lattice coordination numbers or the radii of the coordination spheres of the near neighbors to the central molecule in such a way as to force the desired asymptotic form. However such an alteration in the lattice structure turns out to be entirely unnecessary when one adopts yet another general formulation[5] of the quasi-crystalline model, based on a Fokker-Planck type equation for the spatial correlations between local lattice structures. This formulation leads to the same equation as (1) but the dispersion law (2) is now replaced by an R-dependent σ_n, i.e.,

$$\sigma_n^2 = \beta R \tag{4}$$

(Some refinement can be achieved in taking account of the finite molecular exclusion diameter R_0 by replacing (4) by

$$\sigma_n^2 = \beta(R - R_0), \qquad R > R_0 \tag{4'}$$

with $g(R)$ necessarily equal to zero for $R \leqslant R_0$).

When either (2) or (4) is substituted into (1), one obtains numerically *practically identical* results[6] for short and intermediate R, but with (4) one obtains an asymptotic behaviour entirely different from (3) as $R \to \infty$. Indeed, substituting (4) (or 4') into (1) one can easily convert the expression with the aid of the Poisson sum formula[5] into the form

$$g(R) = 1 + \sum_{\nu}{}' e^{-1/2\beta b_\nu^2(R-R_0)} \frac{\sin b_\nu R}{b_\nu R} \tag{5}$$

Here the ν-summation extends over all the points of the *reciprocal* lattice, excluding a central site, the b_ν being the distances of the points from the central site.† For large R, the dominant contribution to the sum in (5) comes from the first few terms with the smallest b_ν. Thus (5) conforms to the well known asymptotic formula found by Fisher.[7,4]

$$h(R) \sim \frac{A_1}{R} e^{-A_2 R} \sin(A_3 R + A_4) \tag{6}$$

This formula has been confirmed by radial distribution function values derived from computer simulation[8] as well as x-ray scattering data for liquid Argon.

It is an altogether different problem how to reconcile (6) with another currently adopted asymptotic formula[9]

$$h(R) \sim -\phi(R)/k_b T \tag{7}$$

where $\phi(R)$ is the pair potential and k_b is Boltzmann's constant. We suggest here only that (7) might be obtained from (6) by some smoothing procedure which does wash out the long range oscillations in $h(R)$.

† The reciprocal lattice adopted in (5) is larger in linear scale by a factor 2π, compared to the reciprocal lattice adopted in ref. 5.

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