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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 recently¹ 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 Franchetti³ who derived the following formula for $g(R)$:

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

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 Prins²

$$\sigma_n^2 = \beta R_n \quad (2)$$

was adopted.³

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

$$h(R) = g(R) - 1 \sim \frac{1}{R^2} \quad R \rightarrow \infty \quad (3)$$

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 formulation⁵ 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.,

$$\sigma_n^2 = \beta R \quad (4)$$

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

$$\sigma_n^2 = \beta(R - R_0), \quad R > R_0 \quad (4')$$

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

When either (2) or (4) is substituted into (1), one obtains numerically *practically identical* results⁶ for short and intermediate R , but with (4) one obtains an asymptotic behaviour entirely different from (3) as $R \rightarrow \infty$. Indeed, substituting (4) (or 4') into (1) one can easily convert the expression with the aid of the Poisson sum formula⁵ into the form

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

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}

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

This formula has been confirmed by radial distribution function values derived from computer simulation⁸ 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 formula⁹

$$h(R) \sim -\phi(R)/k_b T \quad (7)$$

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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