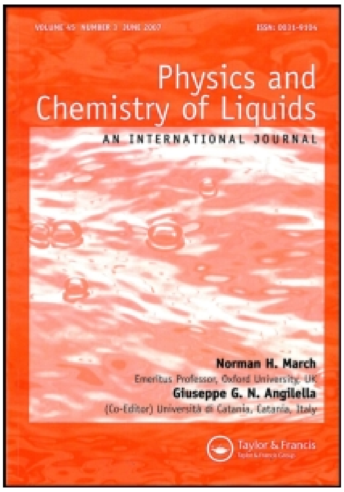

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Asymptotic Behaviour of the Radial Distribution Function in a Quasi-Crystalline Model of Liquids

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By a mathematical analysis of the formulae of a quasi-crystalline model of liquids, i.e. a crystal lattice with smeared out lattice sites, it is shown that this model leads to a nonphysical asymptotic behaviour of the radial distribution function. To remove this defect it is necessary to modify the initial lattice by changing either the coordination numbers or the radii of the coordination spheres. Some ways of such modification are given and illustrated by concrete calculations.

1 INTRODUCTION

One of the best known ways to interpret the radial distribution function (RDF) of liquids obtained in experiments on X-ray or neutron diffraction is perhaps their comparison with RDF for suitable crystal lattices whose sites are smeared out by a certain law. Most often the formalism is used in which the molecular location in a lattice site is given by the Gaussian distribution. Such a model for description of the liquid structure was first proposed by Prins[1] and thus it is reasonable to call it the Prins quasi-crystalline model. Though the physical meaning of the Prins model is quite clear[2], there is no adequate mathematical formulation of the model up to date. So, a correct form of the RDF in this model has been found just recently[3,4]

$$G(R) = \frac{R}{\sqrt{2\pi}} \sum_{i=1}^{\infty} \frac{N_i}{R_i \sigma_i} \left[\exp\left\{ -\frac{(R - R_i)^2}{2\sigma_i^2} \right\} - \exp\left\{ -\frac{(R + R_i)^2}{2\sigma_i^2} \right\} \right]. \qquad (1)$$

Here R_i and N_i are the radii and coordination numbers of the lattice to be smeared out, and σ_i is the dispersion of the Gaussian distribution for i-th coordination sphere. Formula (1) implies that it is the function $G(R)/R$ that can be represented by a series of Gaussian distributions whereas in most of works either RDF itself, G(R), (e.g., in[5-7]) or the pair correlation function $g(R) = G(R)/4\pi\rho R^2$ (e.g., in[1]) are decomposed into Gaussians for intuitive reasons.

In the simplest variant of the model R_i and N_i are chosen equal to the radii and coordination numbers of the successive spheres of a real crystalline lattice and the so called structural diffusion law is used for dispersion

$$\sigma_i^2 = \beta R_i \qquad (2)$$

According to Frenkel[2] the constant $\beta/2$ is designated the coefficient of structural diffusion. Law (2) can be justified for large distances R_i between the molecules when particle distributions around the corresponding points of the lattice are independent.[2] In the neighbouring coordination spheres, however, the molecular distributions are statistically dependent of necessity and thus both law(2) and the assumption of the Gaussian shape of the distribution become incorrect.[4,8,9] These conclusions have been corroborated by recent investigation showing that to fit quantitatively experiment one should deviate from a simple formulation of the model.[9,10]

In the present work we draw attention to another imperfection of the quasi-crystalline model. It turned out that in the simplest variant of the Prins model the differential RDF defined as

$$H(R) = G(R) - 4\pi\rho R^2 \qquad (3)$$

(ρ is the average density of the liquid) rises monotonously with increasing R but does not approach zero as one has to expect on physical grounds. We analyze below the origin of the defect above and propose some ways of its elimination.

2 ASYMPTOTIC BEHAVIOUR OF THE RADIAL DISTRIBUTION FUNCTION IN THE PRINS MODEL

Let us find the asymptotic behaviour of the RDF defined by equation (1). For large R the second exponent in (1) can be always omitted and summation over the spheres can be replaced by integration with respect to radius when introducing the radial distribution function of the crystal lattice $G_c(R)$. Thus $G_c(R')dR'$ gives the number of particles of the initial lattice in an interval dR' at a distance R' from the origin of coordinates. As a result we obtain

$$G(R) \sim \frac{R}{\sqrt{2\pi}} \int_0^\infty \frac{\exp\left[-\dfrac{(R-R')^2}{2\sigma^2(R')}\right]}{\sigma(R')R'} G_c(R')dR' \qquad (4)$$

instead of (1). At large R for any homogeneous crystal one should assume

$$G_c(R) = 4\pi\rho_c R^2 \qquad (5)$$

where ρ_c is the average density of the crystal used. Using (5) and structural diffusion law (2), equation (4) can be written as

$$G(R) \sim \frac{4\pi\rho_c R}{\sqrt{2\pi\beta}} \int_0^\infty \sqrt{R'} \exp\left[-\frac{(R-R')^2}{2\beta R'}\right] dR'. \qquad (6)$$

The lower limit of integration is assumed to be zero in spite of incorrectness of relation (5) at small R. This can be done since the integration over the region where $|R - R'|$ is large (when $(R - R')^2 \gg 2\beta R'$) gives a negligible contribution to the integral due to the exponent in the integrand. Thus, if R is large enough the form of the function $G_c(R')$ at small R' is unimportant.

The integration in (6) can be performed analytically to give

$$G(R) \sim 4\pi\rho_c(R^2 + \beta R). \qquad (7)$$

Consequently the function H(R) has asymptotic behaviour

$$H(R) \sim 4\pi\rho_c\beta R. \qquad (8)$$

However, for a homogeneous liquid (or crystal) the function H(R) must approach zero because at large distances the local density coincides with the average one. Hence the asymptotic form (8) of the RDF in the Prins model turns out to be nonphysical.

To illustrate this conclusion we obtained RDF by the direct calculation according to formula (1) for two types of crystal lattices. The results which are shown in Figure 1 are in full agreement with equation (8). A monotonic increase of the central line for the function H(R) in the Prins model has been observed also by Franchetti[11]. He did not attribute, however, this defect to be inherent of the model.

The origin of the additional term in the radial distribution function asymptote (7) may be elucidate as follows. Since smearing dispersion of the

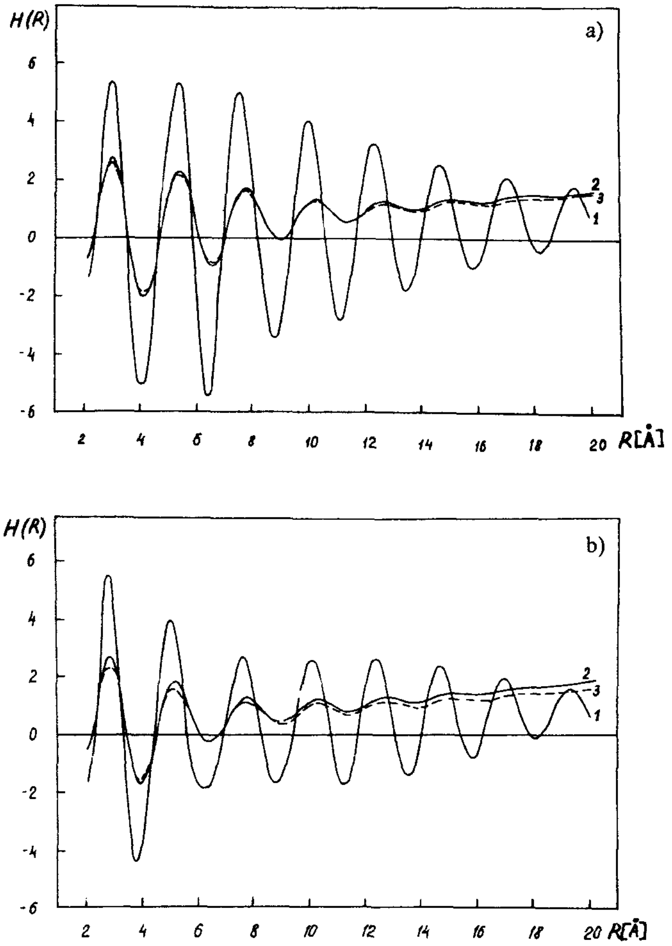


FIGURE 1 Differential RDF calculated according to formula (1). Curves 1 and 2 correspond to $\beta = 0.06$ and 0.12. Curve 3 is similar to curve 2 but all the lattice coordination numbers were multiplied by ρ_l/ρ_c. $\rho_l = 0.0528$ Å^{-3}, $R_1 = 2.85$ Å.
a) The initial lattice of body-centered cubic type. $\rho_c = 0.0561$ Å^{-3}.
b) The initial lattice of face-centered cubic type. $\rho_c = 0.0611$ Å^{-3}.

coordination spheres increases with increasing the sphere radius (according to law (2)), the number of particles which enter into a given coordination sphere from the sphere of the larger radius will be greater than the number of particles which leave this sphere. It is such a character of the particle redistribution that results in a nonphysical increase in the local density as compared with the average one. A correct asymptote can be obtained only at the constant dispersions for all the spheres independently of their radius ($\beta = 0$). But this situation, being typical of a perfect crystal, cannot correspond to a real liquid where the structural diffusion law (2) is undoubtedly valid asymptotically.[1,2]

It should be noted that one might fail to observe this defect of the Prins model if an asymptotic behaviour of the pair correlation function g(R) is investigated. Indeed, according to (7) we have

$$g(R) = \frac{G(R)}{4\pi\rho_c R^2} \sim 1 + \frac{\beta}{R} \xrightarrow[R\to\infty]{} 1,$$

i.e. the model gives a correct asymptote for g(R).

3 CORRECTION OF THE ASYMPTOTIC BEHAVIOUR OF THE RADIAL DISTRIBUTION FUNCTION

To improve the RDF asymptotic behaviour it is necessary to correct the quasi-crystalline model by modification of its basic assumptions. This can be done in different ways: a) by removing some particles from the sites of the initial crystal lattice and by changing the radii of the coordination spheres; b) by substitution of the Gaussian distribution by some other one; c) by rejection the structural diffusion law. We will discuss here only the first way, modification of the initial crystal lattice, since the others lead to unnecessary complications of the model.[7,8] It is reasonable especially as the Gaussian type of distribution and the structural diffusion law appear always to be valid for liquids at large R.

It is shown in Appendix that the correct form of the RDF asymptote in the quasi-crystalline model of liquids is possible only in the case when the RDF of the initial crystal lattice has the asymptote

$$G_c(R) \sim 4\pi\rho(R^2 - \beta R). \tag{9}$$

The simplest way to obtain the structure satisfying condition (9) is to change the lattice coordination numbers according to the law

$$N_i = N_i^0\left(1 - \frac{\beta}{R_i}\right)\frac{\rho_l}{\rho_c} \tag{10}$$

leaving unchanged the coordination sphere radii, $R_i = R_i^0$. Here the index "0" denotes that the corresponding value belongs to the initial crystal lattice with the average density ρ_c. ρ_l is the average density of the liquid the RDF of which has to be built. Indeed, by the definition, the initial lattice RDF is

$$G_c(R) = \lim_{\Delta R\to 0} \sum_{\Delta R(R)} N_i/\Delta R. \tag{11}$$

The sign $\sum\limits_{\Delta R(R)}$ means summation over the coordination spheres which lie in an interval ΔR at a distance R from the origin of coordinates. Substituting transformation (10) into (11), we get

$$G_c(R) = \lim_{\Delta R \to 0} \sum_{\Delta R(R)} \frac{\rho_l}{\rho_c}(1 - \beta/R_i)N_i^0/\Delta R = \\ = \frac{\rho_l}{\rho_c}\left(1 - \frac{\beta}{R}\right) \lim_{\Delta R \to 0} \sum_{\Delta R(R)} N_i^0/\Delta R. \tag{12}$$

Since the RDF of the crystal lattice at large R is $4\pi\rho_c R^2$ it follows from (12) that

$$G_c(R) \sim \frac{\rho_l}{\rho_c}\left(1 - \frac{\beta}{R}\right)4\pi\rho_c R^2 = 4\pi\rho_l(R^2 - \beta R). \tag{13}$$

Thus, transformation (10) really leads to a lattice with the necessary asymptote of the RDF.

The factor ρ_l/ρ_c in (10) serves to make the calculated RDF correspond to liquid with the real density ρ_l differing from that of the initial crystal, ρ_c. Note that a simple multiplication of all the lattice coordination numbers by the same factor ρ_l/ρ_c evidently cannot improve the RDF asymptote (see Figure 1).

In Figure 2 the functions H(R) are plotted calculated on the basis of the quasi-crystalline model under the same parameters as for the functions in Figure 1, but with the modification of the coordination numbers of the initial lattice according to law (10). Now the functions H(R) oscillate around zero, i.e. have a correct asymptotic behaviour.

Changing only the coordination numbers is rather a particular case of the crystal lattice modification. Such a modification results, in fact, in no shift of the RDF maxima. However, the experience of fitting the calculations to experimental data shows that maxima of the calculated RDF are often shifted systematically with respect to those of the experimental functions (see Figure 2). Therefore, for a better fitting one has to change in the model the coordination sphere radii too (see, e.g.,[10,11]).

In principle, it is possible to accept arbitrary laws for changes in the coordination sphere radii,

$$R_i = f(R_i^0),\ i = 1,2,\ldots,\infty, \tag{14}$$

and the coordination numbers,

$$N_i = \varphi(R_i)N_i^0. \tag{15}$$

It is necessary only to demand they to ensure a correct asymptotic behaviour of the RDF. This means that between f(R) and φ(R) a dependence must

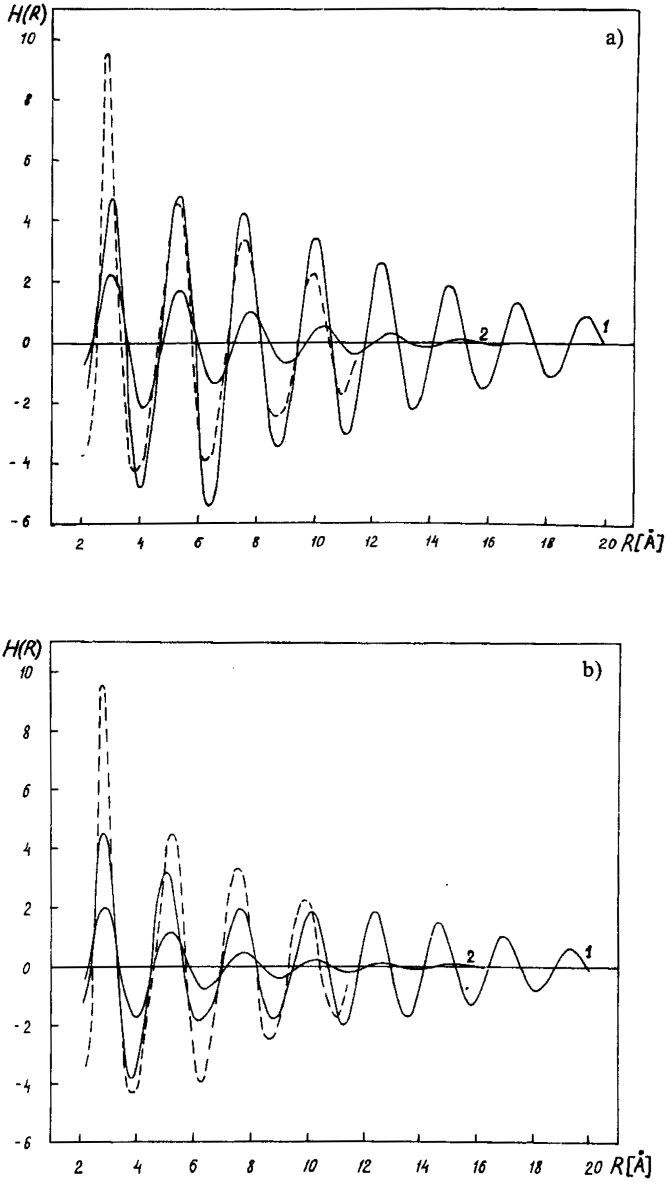


FIGURE 2 Differential RDF calculated according to formula (1') with transformation of the coordination numbers by law (10). For curves 1 and 2 $\beta = 0.06$ and 0.12 respectively. The dotted line is the experimental function H(R) for liquid aluminium[12] at the temperature 670 °C and $\rho_l = 0.0528$ Å^{-3}. The other parameters are the same as in Figure 1.
a) The body-centered cubic lattice.
b) The hexagonal close packing.

exist which can be obtained as follows. Let us count the number of particles in a layer $\Delta R(R)$ of the lattice distorted in accordance with the laws (14) and (15):

$$\sum_{\Delta R(R)} N_i = \sum_{\Delta R(R)} \varphi(R_i)N_i^0 = \varphi(R) \sum_{\Delta R(R)} N_i^0.$$

But the number of sites of the distorted lattice in an interval $\Delta R(R)$ is equal to the number of sites of the initial lattice in a corresponding interval $\Delta R_0(R_0) = \dfrac{df^{-1}(R)}{dR} \Delta R(R)$ where $R_i^0 = f^{-1}(R_i)$ is an inverse to (14) transformation. Therefore at large distances from the origin of coordinates the relation

$$\sum_{\Delta R(R)} N_i = \varphi(R) 4\pi\rho_c R_0^2 \Delta R_0 = 4\pi\rho_c \varphi(R)[f^{-1}(R)]^2 \frac{df^{-1}(R)}{dR} \Delta R$$

is valid. Using (11) and (9), we obtain the dependence to be found

$$\varphi(R_i) = \frac{\rho_1}{\rho_c} \frac{R_i^2 - \beta R_i}{[f^{-1}(R_i)]^2\, df^{-1}(R_i)/dR_i}. \tag{16}$$

Transformation (10) is evidently a particular case of this equation when $R_i^0 = f^{-1}(R_i) = R_i$.

The linear transformation

$$R_i = KR_i^0 + A \tag{17}$$

is the simplest law of changing the radii of the coordination spheres. Together with (16) it gives

$$\varphi(R_i) = \frac{\rho_1}{\rho_c} K^3 \frac{R_i^2 - \beta R_i}{(R_i - A)^2}. \tag{18}$$

Here K is the constant dilatation coefficient of the lattice, and A is a constant which may be expressed via the radius of the first coordination sphere of the lattice, R_1. In the case of simple liquids the first sphere radius is known to be practically invariable at melting. Therefore transformation (17) must leave the first coordination sphere radius invariable what leads to the relation for the constant A:

$$A = (1 - K)R_1^0. \tag{19}$$

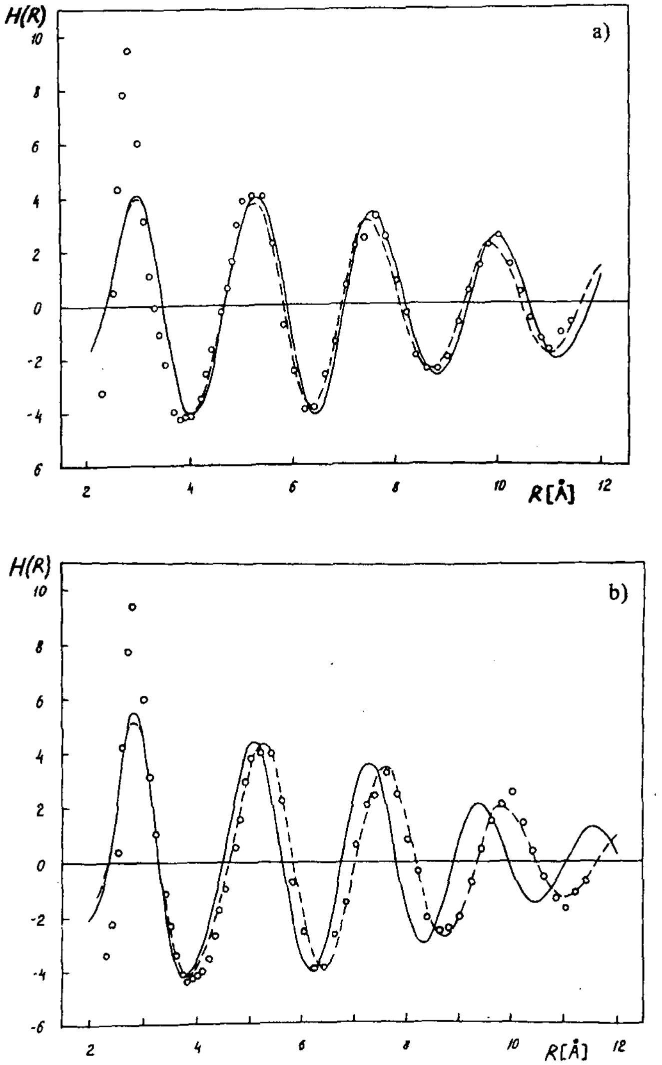
On the other hand, the nonlinear lattice dilatation by the laws

$$R_i = R_i^0(1 - cR_i^0), \qquad N_i = (1 + 2cR_i^0)^2 N_i^0,$$

postulated by Franchetti[11] surely does not satisfy condition (16) and thus leads to an incorrect RDF asymptote.

4 COMPARISON WITH EXPERIMENT

To illustrate the possibilities of the modified quasi-crystalline model we applied the formalism of the linear lattice distortion described by formulae (17), (18), and (19) to reconstruction of the radial distribution function of liquid aluminium. We chose aluminium as its experimental RDF contains the greatest number of oscillations among all data compilated in.[12] Figure 3 gives a comparison of the calculations with the experiment. First of all we see that the model does not allow one to describe simultaneously both the



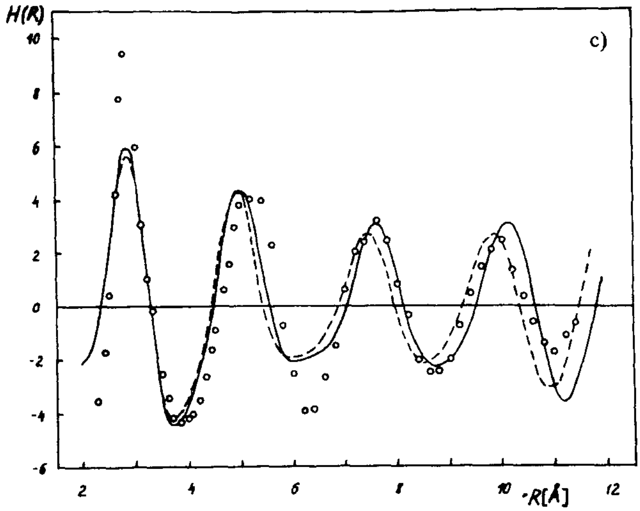


FIGURE 3 Comparison of the functions H(R) calculated according to (1) with modification of the lattice by formulae (17), (18) and (19) with experiment. $R_1 = 2.85$ Å, $\rho_1 = 0.0528$ Å^{-3}.
a) The body-centered cubic lattice.
$\beta = 0.07$. For the solid line $K = 1$, for the dotted one $K = 0.98$.
b) The hexagonal close packing.
For the solid line $K = 1$, $\beta = 0.05$. For the dotted one $K = 1.07$, $\beta = 0.06$.
c) The face-centered cubic lattice. $\beta = 0.046$.
For the solid curve $K = 1$, for the dotted one $K = 0.96$.

first and the following maxima of the RDF. This fact, established before on the basis of the nonmodified Prins model,[9] means that the dispersion of the first coordination sphere does not follow the structural diffusion law due to correlation of motions of the neighbouring particles. Therefore we shall further pay attention only on the second and the following maxima of the RDF.

Figure 3a shows that the body-centered cubic lattice well describes the H(R) of liquid aluminium practically without any distortion in the sphere radii (K = 1). A more complicated situation is observed for the hexagonal close packing. Here the good fitting can be obtained only after dilatation of the lattice, K = 1.07 (Fig.3b). At last, for the face-centered cubic lattice it is impossible to choose such K and β parameters which would allow us to fit all the maxima of the function H(R) to experiment (Fig.3c).

5 CONCLUSION

It goes without saying that the model intended to describe liquids must satisfy some general requirements characterizing the essence of the liquid state. The asymptotic behaviour of the differential radial distribution function, $H(R) \xrightarrow[R\to\infty]{} 0$, is the most general requirement of that kind. From the present work it follows that the simplest variant of the Prins model does not satisfy this requirement and thus cannot be considered appropriate for description of liquids. However, this defect of the model is easily removed if the initial crystal lattice is distorted in a certain way, e.g., by law (17) and (18). In this work we do not discuss the meaning of the modified lattice with an unusual asymptote (9) of its RDF. We consider the quasi-crystalline model only as an algorithm for description of the liquid structure. In this algorithm the final structure but not intermediate constructions must have a physical content.

Appendix

The RDF of the modified lattice might be given in general case in the form

$$G_c(R) = 4\pi\rho\left(R^2 + a_0R + a_1 + \frac{a_2}{R} + \ldots + \frac{a_{n+1}}{R^n} + \ldots\right). \tag{A1}$$

The only limitation we assume here for $G_c(R)$ is that the latter must increase not faster than R^2. Substituting (A1) into (4) and using (2), we get

$$\begin{aligned} G_c(R) &\sim \frac{4\pi\rho R}{\sqrt{2\pi\beta}}\int_0^\infty dx\, \exp\left[-\frac{(R-x)^2}{2\beta x}\right]\left(\sqrt{x} + \frac{a_0}{\sqrt{x}} + \frac{a_1}{x\sqrt{x}} + \ldots + \frac{a_n}{x^n\sqrt{x}} + \ldots\right) \\ &= 4\pi\rho R\left[f_{-1}(R) + a_0f_0(R) + \ldots + a_nf_n(R) + \ldots\right] \end{aligned} \tag{A2}$$

where

$$f_n(R) = \frac{1}{\sqrt{2\pi\beta}}\int_0^\infty \frac{dx}{x^n\sqrt{x}}\exp\left[-\frac{(R-x)^2}{2\beta x}\right].$$

It is easy to show that $f_{-1}(R) = R + \beta$, $f_0(R) = 1$ and that the recurrent relation $Rf_{n+1}(R) = f_n(R) - \beta(df_n/dR)$ is valid. On that ground at $n \geqq 1$ all the f_n are homogeneous polynoms of $1/R$ with positive coefficients. Therefore (A2) may give the asymptote for liquid of the form $G(R) = 4\pi\rho R^2$ only at $a_0 = -\beta$, $a_1 = a_2 = \ldots = a_n = \ldots = 0$. Substituting this into (A1), we obtain (9).

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