

Evidence of an oscillatory density profile in liquid metal surfaces: an asymptotic solution

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 6039

(<http://iopscience.iop.org/0953-8984/4/28/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:19

Please note that [terms and conditions apply](#).

Evidence of an oscillatory density profile in liquid metal surfaces: an asymptotic solution

M Iwamatsu^{††} and S K Lai[†]

[†] Department of Physics, National Central University, Chung-li 32054, Taiwan, Republic of China

^{††} Chiba-Keizai University, Todoroki-cho 3-59-5, Inage-ku, Chiba 263, Japan

Received 8 November 1991, in final form 22 April 1992

Abstract. The asymptotic solution for the Euler–Lagrange equation which describes the surface density profile of liquid metals is derived. The liquid metal is modelled as consisting of a Fermi electron gas and classical one-component-plasma ions. These latter systems are coupled via a first-order electron–ion pseudopotential which is considered to be appropriate for characterizing liquid alkali metals. It is demonstrated here that the density profile can be classified as either a monotonic or an oscillatory type, but our numerical data show that all liquid alkali metals fall into the latter category.

Physically, a liquid metal is a two-component system consisting of a Fermi electron gas and of a neutralizing system of classical ions. These systems are inextricably coupled via Coulombic interactions. At the liquid–vapour interface these interacting Coulombic particles are highly inhomogeneous and their longitudinal single-particle densities vary rapidly from a uniform bulk liquid value to an extremely low-density value characteristic of a vapour system. A prerequisite for the quantitative understanding of liquid metal surface properties is therefore a knowledge of these two interfacial structures. In the literature, these latter quantities have often been obtained from two independent sources. On the one hand, the dense inhomogeneous quantum electron gas is customarily handled by variants of the non-linear, density functional formalism of Hohenberg–Kohn–Sham [1]. The ion interfacial structure, on the other hand, can be approached in two different ways: one can either extract information about the ionic density profile indirectly from experiments which encompass small angular x-ray reflectivity [2, 3], grazing incidence x-ray diffraction [4–6] and high energy electron diffraction [7], or from computer simulation [8] provided one is given a means to construct a total energy expression. The usefulness and the limitations of both techniques of obtaining valuable information on the ion density distribution have been discussed rather thoroughly in a recent review article by Lai [9]. One interesting feature that emerges from these experimental and computer simulation studies is that the ion density profile shows oscillatory behaviour at the liquid–vapour interface. The results of these investigations have subsequently simulated theoretical work [10] and, over the years, have been taken as a guidance for theoretical modelling of the density profile in the variational thermodynamic calculation of surface properties such as the liquid metal surface tension [11–13]. Many of the theoretical works that focus on the calculation of the surface tension for liquid metals, to our knowledge, have been

influenced very much by these findings and have thus proceeded with an *assumed* oscillatory behaviour in a rather arbitrary and parametrized form for the one-particle density profile without any theoretical justification. A question then arises: can we theoretically provide more evidence as to the existence of such oscillatory behaviour? In this paper, we attempt to look at this question.

To make matters simple and yet to keep the physical content in as transparent a form as we could, we follow the pioneering first-order density functional theory of Evans and Hasegawa [14]. It should be noted that although the first-order perturbation theory certainly cannot give an accurate account of the energetics such as the first-order calculations [14–16] (see also the recent work by Hasegawa [11]) for the surface tension of liquid metals, it surely can give a fairly good description for the long-wavelength density fluctuation near equilibrium bulk liquid density [14, 17] where successful calculation of the bulk modulus or the long-wavelength structure factor [17] was already reported. Since we will be primarily interested in the asymptotic behaviour near the bulk liquid side, we expect first-order perturbation theory to be sufficient for this purpose.

Assuming that the inhomogeneous electron-ion coupling is weak, Evans and Hasegawa showed that the total grand potential for the two-component system is

$$\Omega[\rho, n] = G_i[\rho] + G_e[n] + \frac{1}{2} \int d\mathbf{r} \varphi(\mathbf{r})[n(\mathbf{r}) - Z\rho(\mathbf{r}) - \mu_i] \int d\mathbf{r} \rho(\mathbf{r}) - \mu_e \int d\mathbf{r} n(\mathbf{r}) + \int \int d\mathbf{r}' \rho(\mathbf{r}) n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) \quad (1)$$

where Z is the nominal valence of an ion, $n(\mathbf{r})(\rho(\mathbf{r}))$ is the single-particle density, G_e (G_i) is a unique functional of the electronic (ionic) density representing the non-Coulombic contribution to the intrinsic free energy of the electronic (ionic) system, μ_e (μ_i) is the chemical potential for the electronic (ionic) system, $\varphi(\mathbf{r})$ is given by

$$\varphi(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}') - Z\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2)$$

being the electrostatic potential and w is the non-Coulombic part of a pseudopotential v^{ps} defined by

$$v^{\text{ps}}(\mathbf{r}) = w(\mathbf{r}) - Z/r. \quad (3)$$

To proceed, we note that since $w(\mathbf{r})$ describes a repulsive short-ranged part of $v^{\text{ps}}(\mathbf{r})$ we may approximate the last term in equation (1) as

$$\int \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) \approx \int d\mathbf{r} \rho(\mathbf{r}) n(\mathbf{r}) \tilde{w}(0) \quad (4)$$

where the tilde means a Fourier transform. Following Evans and Hasegawa [14], we use the square-gradient approximation for the first and second terms in equation (1), i.e., we write

$$G_i[\rho] = \int d\mathbf{r} (g_i(\rho(\mathbf{r})) + g_{i2}(\rho(\mathbf{r}))[\nabla\rho(\mathbf{r})]^2 + \dots) \quad (5)$$

$$G_e[n] = \int d\mathbf{r} (g_e(n(\mathbf{r})) + g_{e2}(n(\mathbf{r}))[\nabla n(\mathbf{r})]^2 + \dots). \quad (6)$$

It should be noted here that the use of the square-gradient approximation is justified for the electron gas [18] and also for the one-component plasma (OCP) system [19].

Equations (1)–(6) form the basis of the present analysis. Now, in order to obtain the precise form of the density profile of the surface we have to solve the Euler-Lagrange equations [10, 19] which are given by

$$\mu_i = \frac{\delta G_i[\rho]}{\delta \rho(\mathbf{r})} - Z\varphi(\mathbf{r}) + n(\mathbf{r})\tilde{w}(0) \tag{7}$$

$$\mu_e = \frac{\delta G_e[n]}{\delta n(\mathbf{r})} + \varphi(\mathbf{r}) + \rho(\mathbf{r})\tilde{w}(0). \tag{8}$$

Taking the z -axis to be the normal to the planar liquid surface and inserting equations (5) and (6) into equations (7) and (8), we have, after rearranging

$$2g_{i2} \frac{d^2\rho(z)}{dz^2} + g'_{i2} \left(\frac{d\rho(z)}{dz} \right)^2 + (\mu_i - g'_i) + Z\varphi(z) - \tilde{w}(0)n(z) = 0 \tag{9}$$

$$2g_{e2} \frac{d^2n(z)}{dz^2} + g'_{e2} \left(\frac{dn(z)}{dz} \right)^2 + (\mu_e - g'_e) - \varphi(z) - \tilde{w}(0)\rho(z) = 0 \tag{10}$$

where the prime in each g refers to differentiation with respect to the n or ρ . Note that equations (9) and (10) are coupled differential equations for n and ρ . These one-particle densities are also coupled through Poisson's equation

$$\frac{d^2\varphi(z)}{dz^2} = -4\pi[n(z) - Z\rho(z)]. \tag{11}$$

Further progress can be made if we can calculate the chemical potentials for electrons and ions. To this end, we must consider the free energy density, f , of a uniform system. Within first-order perturbation theory it can be shown [14] that

$$f = g_i(\rho) + g_e(n) + n\rho\tilde{w}(0) \tag{12}$$

which allows us to calculate the μ_i and μ_e from the formulae

$$\mu_i = \left. \frac{\partial f}{\partial \rho} \right|_{n=n_i, \rho=\rho_i} = g'_i(\rho_i) + n_i\tilde{w}(0) \tag{13}$$

$$\mu_e = \left. \frac{\partial f}{\partial n} \right|_{n=n_i, \rho=\rho_i} = g'_e(n_i) + \rho_i\tilde{w}(0) \tag{14}$$

where n_i and ρ_i are the equilibrium densities in a bulk liquid phase and are related by $n_i = Z\rho_i$. The above expressions for chemical potentials can be substituted back into equations (9) and (10) and we arrive at

$$2g_{i2} \frac{d^2\rho(z)}{dz^2} + g'_{i2} \left(\frac{d\rho(z)}{dz} \right)^2 - [g'_i(\rho(z)) - g'_i(\rho_i)] + Z\varphi(z) - [n(z) - n_i]\tilde{w}(0) = 0 \tag{15}$$

$$2g_{e2} \frac{d^2n(z)}{dz^2} + g'_{e2} \left(\frac{dn(z)}{dz} \right)^2 - [g'_e(n(z)) - g'_e(n_i)] - \varphi(z) - [\rho(z) - \rho_i]\tilde{w}(0) = 0. \tag{16}$$

We are now in a position to derive the asymptotic behaviour of single-particle densities following the procedure given in [10] and [19]. In the first place, we note that near the bulk liquid region we expect the density profiles to be close to the bulk density. Introducing $m(z) = n(z) - n_l$ and $\sigma(z) = \rho(z) - \rho_l$, these linearized forms for $m(z)$ and $\sigma(z)$ can be used to cast equations (15) and (16) into

$$2g_{i2}(\rho_l) \frac{d^2 \sigma(z)}{dz^2} - g_i''(\rho_l) \sigma(z) + Z\varphi(z) - m(z)\tilde{w}(0) = 0 \quad (17)$$

$$2g_{e2}(n_l) \frac{d^2 m(z)}{dz^2} - g_e''(n_l) m(z) - \varphi(z) - \sigma(z)\tilde{w}(0) = 0 \quad (18)$$

$$\frac{d^2 \varphi(z)}{dz^2} = -4\pi[m(z) - Z\sigma(z)] \quad (19)$$

which are now a set of coupled linear equations. At this point it is trivial to solve these equations by applying the standard procedure. If we introduce the following variables $y_1(z) = m(z)$, $y_2(z) = \sigma(z)$ and $y_3(z) = \varphi(z)$, equations (17)–(19) can be written in a matrix form

$$\frac{d^2 \mathbf{y}}{dz^2} = \mathbf{A} \mathbf{y} \quad (20)$$

where the matrix \mathbf{A} is given by

$$\mathbf{A} = \begin{pmatrix} g_e''(n_l)/(2g_{e2}(n_l)) & \tilde{w}(0)/(2g_{e2}(n_l)) & 1/(2g_{e2}(n_l)) \\ \tilde{w}(0)/(2g_{i2}(\rho_l)) & g_i''(\rho_l)/(2g_{i2}(\rho_l)) & -Z/(2g_{i2}(\rho_l)) \\ -4\pi & 4\pi Z & 0 \end{pmatrix}.$$

It is easily seen that the solution to equation (20) is of the form

$$\mathbf{y} = \mathbf{y}_0 e^{\alpha z} \quad (21)$$

where \mathbf{y}_0 should be fixed by the initial condition. Here α can be determined through the eigenvalue equation

$$\det(\mathbf{A} - \alpha^2 \mathbf{1}) = 0 \quad (22)$$

and the sign of the solutions $\pm\sqrt{\alpha^2}$ has to be chosen to satisfy the appropriate boundary condition. Denoting $x = \alpha^2$, this secular equation (22) can be expanded to read

$$x^3 + ax^2 + bx + c = 0 \quad (23)$$

where

$$a = -\frac{1}{2} \left(\frac{g_e''(n_l)}{g_{e2}(n_l)} + \frac{g_i''(\rho_l)}{g_{i2}(\rho_l)} \right) \quad (24)$$

$$b = \frac{8\pi Z^2 g_{e2}(n_l) + 8\pi g_{i2}(\rho_l) + g_i''(\rho_l) g_e''(n_l) - \tilde{w}^2(0)}{4g_{e2}(n_l) g_{i2}(\rho_l)} \quad (25)$$

$$c = -\frac{4\pi Z^2 g_e''(n_l) + 4\pi g_i''(\rho_l) + 8\pi Z \tilde{w}(0)}{4g_{e2}(n_l) g_{i2}(\rho_l)} = -\pi[\rho_l^2 \chi_T g_{e2}(n_l) g_{i2}(\rho_l)]^{-1} \quad (26)$$

and in equation (26) we have simplified the expression by the isothermal compressibility, χ_T , defined by

$$\chi_T^{-1} = \rho_1^2 g_1''(\rho_1) + n_1^2 g_e''(n_1) + 2n_1\rho_1\tilde{w}(0). \tag{27}$$

At this stage, it is appropriate to emphasize two relevant points. Firstly, because $\chi_T, g_{e2}(n_1)$ and $g_{i2}(\rho_1)$ are positive definite, c is negative definite leading to at least one of the solutions of equation (23) being real and positive, α_1^2 say. Secondly, we see from equation (23) that the asymptotic forms for $m(z), \sigma(z)$ and $\varphi(z)$ all obey the same single differential equation given by

$$\frac{d^6 y}{dz^6} + a \frac{d^4 y}{dz^4} + b \frac{d^2 y}{dz^2} + c = 0 \tag{28}$$

in which $y(z) = m(z), \sigma(z)$ or $\varphi(z)$. Because of this property, the asymptotic forms of ρ, n and φ should separately have the same functional form

$$y(z) \sim Ae^{\alpha_1 z} + Be^{\alpha_2 z} + Ce^{\alpha_3 z}. \tag{29}$$

in which A, B and C are constants and should be determined separately for ρ, n and φ in order to satisfy the boundary condition that they vary smoothly to match exactly the density profiles around the surface [19]. The values α_2 and α_3 should shed light on the detailed behaviour of the density profiles. To make a further analysis, we therefore return to equation (23). This cubic equation has solutions dependent on the discriminant

$$\Delta = 4 \left(b - \frac{a^2}{3} \right)^3 + 27 \left(c - \frac{ab}{3} + \frac{2a^3}{27} \right)^2. \tag{30}$$

Bearing in mind the one real solution mentioned above, the other two possible solutions α_2^2 and α_3^2 depend on the sign of Δ . When $\Delta > 0$ we have both solutions complex, corresponding to a damped oscillation superimposed on the real solution $\exp[\alpha_1 z]$, giving

$$y(z) \sim Ae^{z/L_1} + B'e^{z/L_2} \cos(z/\lambda + C'). \tag{31}$$

In equation (31) B' and C' are new constants and we have chosen signs for α_i such that the boundary condition $y(z) \rightarrow 0$ as $z \rightarrow -\infty$ is satisfied, that is, we write

$$\alpha_1 = 1/L_1 \tag{32}$$

$$\alpha_2 = [1/L_2 + i/\lambda] \tag{33}$$

$$\alpha_3 = [1/L_2 - i/\lambda]. \tag{34}$$

and from the famous Cardano's formulae

$$\alpha_1^2 = -\frac{a}{3} + A^{1/3} + B^{1/3} \tag{35}$$

$$\alpha_2^2 = -\frac{a}{3} + \omega A^{1/3} + \omega^2 B^{1/3} \tag{36}$$

$$\alpha_3^2 = -\frac{a}{3} + \omega^2 A^{1/3} + \omega B^{1/3} \tag{37}$$

with

$$A = -\left(c - \frac{ab}{3} + \frac{2a^3}{27}\right)/2 + \sqrt{\frac{\Delta}{108}} \quad (38)$$

$$B = -\left(c - \frac{ab}{3} + \frac{2a^3}{27}\right)/2 - \sqrt{\frac{\Delta}{108}} \quad (39)$$

$$\omega = \frac{-1 + i\sqrt{3}}{2}. \quad (40)$$

On the other hand, when $\Delta < 0$, we have two additional real solutions, which describe monotonic behaviour. We stress, in particular, that a negative real solution is unphysical as this characterizes infinite oscillations and the equilibrium value of the density is never recovered. This latter solution should therefore be discarded. Accordingly, the question of whether or not an oscillatory behaviour of the density profile will exist depends crucially on the value of Δ . To make our discussion more concrete, we present in figure 1 our numerical data of the decayed lengths L_1 and L_2 as well as the wavelength of oscillation $2\pi\lambda$ for five liquid alkali metals Li, Na, K, Rb and Cs. These numerical estimates are calculated using the empty core pseudopotential with the core radius of each metal chosen to give the observed equilibrium value within first-order theory [12]. We first summarize several interesting points:

(i) For all liquid alkali metals, our present theory yields $\Delta > 0$ and oscillatory density profiles are thus predicted in accordance with indirect experiments [3, 7] and computer simulations [8, 20].

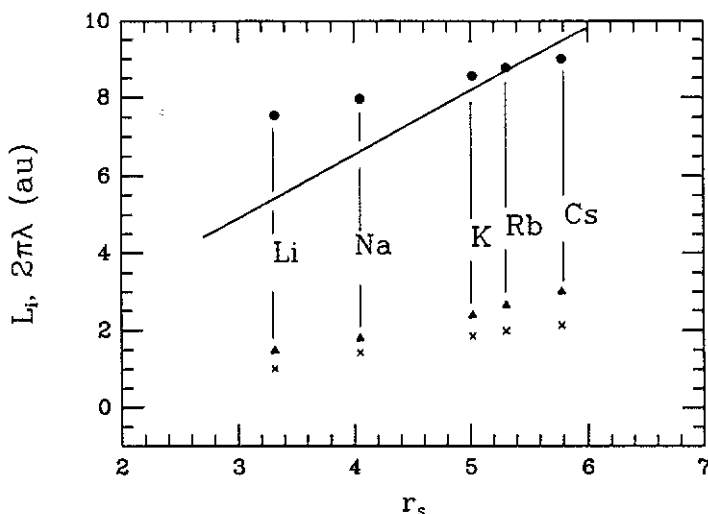


Figure 1. Wavelength of oscillation, $2\pi\lambda$ (solid circles) and decayed length, L_i (crosses for L_1 and solid triangles for L_2) versus electronic density parameter, r_s (in units of the Bohr radius) for five alkali metals near melting temperatures. The full curve refers to π/k_F , the wavelength of the Friedel oscillation (see text).

(ii) The oscillation for low density materials (in the present case liquid Cs) appears to be stronger than that for the higher density metals (in the present case liquid Li) as implied from the general trend of our work and the works of Lang and Kohn [21], Allen and Rice [22] and Hasegawa [11].

(iii) Since the density profiles for both the electrons and ions are similar but in general not the same, we have here an incomplete overlap of the electron and ion particle densities, a feature consistent with the existence of a double layer at the liquid-vapour interface.

(iv) The origin of these oscillatory behaviours derives from the electrostatic term φ as can be readily shown by examining its effect (ignoring φ in equations (7) and (8) and proceeding as in text) on the solutions.

It is thus obvious that an oscillatory behaviour of electrons and ions at the liquid-vapour interface is a common feature for liquid metals. We further note that the wavelength of oscillation $2\pi\lambda$ given in figure 1 when examined against density (from Li to Cs) is approximately $\frac{1}{3}\pi/k_F$. This differs somewhat from that wavelength of the Friedel oscillation

$$\pi/k_F \approx 1.6r_s \tag{41}$$

which was found by Lang and Kohn [21] (see table 1 in [21]) to exhibit a density dependence of oscillation for the electronic density profile calculated in the context of the Kohn-Sham-type equation. The correlation between $2\pi\lambda$ and π/k_F , however, is merely a fortuitous coincidence and the interpretation of the oscillation arising from the Friedel oscillation may not be correct. We stress again that not only electronic density but also the ionic density and the electrostatic potential follow the same functional form, that is,

$$y(z) \sim Ae^{z/L_1} + B'e^{z/L_2} \cos(6k_F z + C') \tag{42}$$

where use is made of the relation $2\pi\lambda = \frac{1}{3}\pi/k_F$ in equation (31). Furthermore, except for the very special case when $B' = 0$, which seems very unlikely, we always have the oscillating profile.

Finally, we comment further on the qualitative behaviours of the decayed lengths L_1 and L_2 as well as on the wavelength of oscillation $2\pi\lambda$. First, we approximate $a \sim b \sim 0$, and, by virtue of equations (26) and (27), express α_i in equations (35)–(37) by the observable χ_T , being the isothermal compressibility. Then, it is straightforward to show that

$$L_1 = [\rho_i^2 \chi_T g_{e2}(n_i) g_{i2}(\rho_i) / \pi]^{1/6} \tag{43}$$

$$L_2 = 2[\rho_i^2 \chi_T g_{e2}(n_i) g_{i2}(\rho_i) / \pi]^{1/6} = 2L_1 \tag{44}$$

$$2\pi\lambda = \frac{4\pi}{\sqrt{3}} [\rho_i^2 \chi_T g_{e2}(n_i) g_{i2}(\rho_i) / \pi]^{1/6} = \frac{4\pi}{\sqrt{3}} L_1 \tag{45}$$

a form which bears a close resemblance to the bulk correlation length ξ which is defined for a one-component classical fluid to be [23]

$$\xi = [\rho_i^2 \chi_T \kappa]^{1/2} \tag{46}$$

where \mathcal{K} is the square-gradient coefficient of the free energy density. This latter equation has been frequently used in explaining the narrowness of the surface width. Note that equation (44) is different from that found in symmetric molten salts [24]. For example, we have here determined an exponent $1/6$ in equation (44) whereas symmetric molten salts [24] yield $1/2$. The reasons are due, firstly, to the fact that in the latter case, the electrostatic potential vanishes identically because of symmetry and, secondly, to the fact that only one equation which describes the total density variation survives among the three coupled Euler-Lagrange equations. The second point in particular is contrary to the present calculation where we retain the electrostatic coupling and solve the three equations together. A simple analogy is thus inappropriate.

Acknowledgments

This work was supported in part by the National Science Council under contract number NSC81-0208-M008-01. One of the authors (MI) gratefully acknowledges the invitation of the NSC for offering a research fellowship. We are also thankful to both the Department of Physics of the National Central University and the Ministry of Education, Computer Center for support of computing facilities.

References

- [1] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864
- [2] Kohn W and Sham L J 1965 *Phys. Rev. A* **140** 1133
- [3] Lu B C and Rice S A 1978 *J. Chem. Phys.* **68** 5558
- [4] Bosio L and Oumenzine M 1984 *J. Chem. Phys.* **80** 959
- [5] Marra W C, Eisenberger P and Cho A Y 1979 *J. Appl. Phys.* **50** 6927
- [6] Barton S W, Thompson B N, Novak F, Weber P M, Harris J G, Dolmer P, Bloch J M and Rics S A 1986 *Nature* **321** 685
- [7] Thomas B N, Barton S W, Novak F and Rice S A 1987 *J. Chem. Phys.* **86** 1036
- [8] Hasegawa M and Ichikawa T 1990 *J. Non-Cryst. Solids* **117/118** 662; 1991 *J. Phys.: Condens. Matter* **3** 2769
- [9] Rice S A, Gryko J and Mohanty U 1986 *Fluid Interfacial Phenomena: Structure and Properties of Liquid-Vapour Interface of Simple Metals* (Oxford: Pergamon)
- [10] Lai S K 1991 *Proc. Nat. Sci. Council. ROC (A)* **15** 181
- [11] Iwamatsu M 1991 *J. Phys. Soc. Japan* **60** 1272
- [12] Hasegawa M 1988 *J. Phys. F: Met. Phys.* **18** 1449
- [13] Stroud D and Grimson M J 1984 *J. Non-Cryst. Solids* **68** 231
- [14] Zeng Z C and Stroud D 1987 *J. Phys. F: Met. Phys.* **17** 2345
- [15] Evans R and Hasegawa M 1981 *J. Phys. C: Solid State Phys.* **14** 5225
- [16] Goodisman J and Rosinberg M L 1983 *J. Phys. C: Solid State Phys.* **16** 1143
- [17] Lai S K 1986 *Phys. Status Solidi* **136** 685
- [18] Evans R and Sluckin T J 1981 *J. Phys. C: Solid State Phys.* **14** 3137
- [19] Ma C Q and Sahni V 1977 *Phys. Rev. B* **16** 4249; 1979 *Phys. Rev. B* **19** 1290
- [20] Ballone P, Senatore G and Tosi M P 1983 *Physica A* **119** 356
- [21] D'Evelyn M P and Rice S A 1983 *J. Chem. Phys.* **78** 5225
- [22] Lang N D and Kohn W 1970 *Phys. Rev. B* **1** 4555
- [23] Allen J W and Rice S A 1977 *J. Chem. Phys.* **67** 5105; 1978 *J. Chem. Phys.* **68** 5053
- [24] Fisk S and Widom B 1969 *J. Chem. Phys.* **50** 3219
- [25] Telo da Gama M M, Evans R and Sluckin T J 1980 *Mol. Phys.* **41** 1355