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Possible Generalization of the Ashcroft-Lekner Hard-Sphere Model for the Structure Factor

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A generalization of the Ashcroft-Lekner (AL) hard-sphere mode for calculation of structure factor is proposed. The AL model is derived from the Wertheim-Thiele solution of the Percus-Yevick integral equation for the case of hard spheres. This generalization introduces a correct hard-sphere equation of state for dense fluids into the AL model. This allows us to determine one coefficient of the AL model exactly and gives a condition on the other two coefficients in terms of the packing fraction. However, in order to determine all the three coefficients uniquely, we need a third condition which is proposed to be obtained from a fit to the experimental data at one point. Our generalization of the AL model is expected to yield a structure factor for dense systems in better agreement with the experimental data, at least for machine calculations on hard-sphere systems.

I. INTRODUCTION

Recently, there has been renewed theoretical interest in calculating the static structure factor.[1] This renewed interest stems from the recent accurate experimental measurements of the static structure factor $S(k)$ for liquid sodium and potassium.[2] In particular, the Ashcroft-Lekner (AL) hard-sphere model[3] has been used to calculate the structure factor. This model has achieved considerable popularity particularly in the theory of liquid metals because, so far, it is the only closed-form expression for the structure factor. Greenfield, Wiser, Leenstra, and van der Lugt[1] tried to generalize the Ashcroft-Lekner (AL) structure factor $S_{\mathrm{AL}}(k)$ by introducing the hard-core diameter σ as an adjustable parameter in different regions of k. This generalization[1] gives a better fit to the experimental data than the AL model[3] but suffers from the same problems as the AL model itself. For example, no account is taken of the tail of the potential, and also, since the interaction is hard sphere, the potential has infinite discontinuity at the hard-sphere diameter σ.

However, in this paper we are not concerned with these difficulties. In particular, we concern ourselves with the problem that neither the AL hard-sphere model[3] nor its recent generalization by Greenfield *et al.*[1] yields a correct equation of state for dense fluids. In this paper a generalization of the Ashcroft-Lekner hard-sphere model is proposed which incorporates correct hard-sphere equation of state for dense fluids. Our proposed generalization leads to a formulation having one independent parameter. This independent parameter can be determined either by a fit to the experiment data at one point or by a further variational computation to give lowest root-mean-square deviation from the experimental data.

II. ASHCROFT-LEKNER (AL) MODEL

The Ashcroft-Lekner hard-sphere model[3] is based on Wertheim-Thiele[4] (WT) solution of the Percus-Yevick (PY) equation[5] for hard-sphere systems. In the AL model

$$S(k)=\frac{1}{1-C(k)}\,, \tag{1}$$

where

$$\begin{aligned}C(k)=-\frac{24\eta}{(k\sigma)^6}\{&\alpha(k\sigma)^3(\sin k\sigma-k\sigma\cos k\sigma)\\&+\beta(k\sigma)^2[2k\sigma\sin k\sigma-(k^2\sigma^2-2)\cos k\sigma-2]\\&+\gamma[(4k^3\sigma^3-24k\sigma)\sin k\sigma\\&-(k^4\sigma^4-12k^2\sigma^2+24)\cos k\sigma+24]\}.\end{aligned} \tag{2}$$

Here

$$\alpha=(1+2\eta)^2/(1-\eta)^4\,, \tag{3a}$$

$$\beta=-6\eta(1+\tfrac{1}{2}\eta)^2/(1-\eta)^4\,, \tag{3b}$$

$$\gamma=\tfrac{1}{2}\eta(1+2\eta)^2/(1-\eta)^4\,, \tag{3c}$$

correspond to the WT solution[4] of the PY equation[5] for hard spheres. The packing fraction η is related to the hard-sphere diameter σ by

$$\eta=\tfrac{1}{6}n\pi\sigma^3\,, \tag{4}$$

n being the average number density of the molecules.

The compressibility equation of state obtained from the WT solution [Eq. (3)] is

$$nk_BT\chi_T=(1-\eta)^4/(1+2\eta)^2\equiv 1/\alpha. \tag{5}$$

In Eq. (5) χ_T is the isothermal compressibility, T is the temperature, and k_B is the Boltzmann constant. Notice, that Eq. (5) corresponds to Eq. (31) of Thiele.[4] Furthermore, since in the limit $k\to 0$, $S(0)=nk_BT\chi_T$, we conclude that

$$\lim_{k\to 0} S(k) = 1/\alpha \; . \qquad (6)$$

Note that Eq. (6) can be directly obtained from Eqs. (1) and (2) by calculating $C(k)$ in the limit $k\to 0$.

Thus, a knowledge of the number density, the temperature, and the isothermal compressibility gives $S(0)$ and, therefore, fixes α from Eq. (6). Equations (3a) and (4) then yield appropriate values of η and σ. Solution of Eqs. (1)–(3) is straightforward and gives the Ashcroft-Lekner hard-sphere-model structure factor $S_{\mathrm{AL}}(k)$.

III. PROPOSED GENERALIZATION

As pointed out before, the compressibility equation of state, Eq. (5), obtained from the WT solution[4] of the PY equation[5] for hard spheres is known to be quite inadequate for dense hard-sphere fluids studied by machine calculation. In fact, hard-sphere machine data on equation of state has been analyzed by Carnahan and Starling.[6] On the basis of this analysis, they proposed an equation of state given by

$$P/nk_BT = (1+\eta+\eta^2-\eta^3)/(1-\eta)^3 \; . \qquad (7)$$

This equation of state has, in fact, been confirmed by Verlet and Weiss[7] in their machine calculation of hard-sphere systems. Direct differentiation of Eq. (7) yields

$$nk_BT\chi_T = (1-\eta)^4/[(1+2\eta)^2+\eta^3(\eta-4)]. \qquad (8)$$

This differs from Eq. (5) by the extra term $\eta^3(\eta-4)$ appearing in the denominator of Eq. (8) on the right-hand side.

We now propose that a new expression for α consistent with the hard-sphere equation of state, Eqs. (7) and (8), be used instead of Eq. (3a). Thus, use of Eqs. (5), (6), and (8) leads to a new value of α given by

$$\alpha = [(1+2\eta)^2+\eta^3(\eta-4)]/(1-\eta)^4 \; , \qquad (9)$$

appreciably different from the WT solution Eq. (3a). Furthermore, Eqs. (1) and (6) give

$$C(0) = 1-\alpha \; , \qquad (10)$$

whereas, from Eq. (2) in the limit $k\to 0$, $C(0)$ is given by

$$C(0) = -8\eta(\alpha+\tfrac{3}{4}\beta+\tfrac{1}{2}\gamma) \; . \qquad (11)$$

Equations (10) and (11) give rise to the relationship

$$6\beta+4\gamma = [\alpha(1-8\eta)-1]/\eta \; . \qquad (12)$$

Note that with β and γ given by Eqs. (3b) and (3c), and α given by (3a), Eq. (12) is identically satisfied. (This, of course, corresponds to the AL model.) However, with α given by (9), Eq. (12) is no longer satisfied. Accordingly, Eq. (12) should be regarded as a constraint on whatever values β and γ take. Regarding Eq. (12) as a constraint, Eqs. (9) and (12) still do not form a closed set to determine α, β, and γ uniquely. We need, yet, another relationship on β and γ. If there were other sum-rule-type conditions to be satisfied, we would automatically get a closed set of equations to determine α, β, and γ.

Thus, in our generalization of the AL hard-sphere model for the static structure factor, we propose to (i) continue to use Eqs. (1) and (2) to calculate the structure factor, (ii) use the value of α given by Eq. (9), (iii) use Eq. (12) as a (sum-rule-type) condition on β and γ, and (iv) match the position of one point in the experimental data on $S(k)$ to uniquely determine β and γ. A further variation in values of β and γ consistent with Eq. (12) could enhance the agreement somewhat.

IV. CONCLUSIONS

We compute $S(k)$ for liquid sodium[8] at temperature 200 °C and compare with the AL static structure factor as well as the experimental data.[2] The values of different parameters are listed in Table I. For the AL model, we use Eqs. (3), (4), and (6). For our model (modified AL model), Eqs. (4), (6), and (9), as well as (12), are used. $S(0)$ is the experimental value at $k=0$. In the modified AL model, that value of β and γ is considered as giving best fit to the experimental data on $S(k)$ for which root-mean-square deviation from the experimental data on $S(k)$ is the least. Thus, the values of β and γ obtained by a fit to the experimental data at $k=1.73$ Å^{-1} were varied a little [subject to Eq. (12)] to get the best fit. The static structure factor $S(k)$ is plotted in Fig. 1. For comparison, the AL struc-

TABLE I. Values of different parameters in the AL model and this calculation (modified AL model) for the static structure factor for liquid sodium at 200 °C.

AL model[a,b]					Present Calculation (modified AL model)[b]				
η	σ(Å)	α	β	γ	η	σ(Å)	α	β	γ
0.424	3.247	31.025	−33.95	6.577	0.434	3.27	31.056	−34.65	7.196

[a] Value of σ listed here is an improvement over that given in Table I, in Ref. 1.

[b] We also use slightly different density ($\rho=0.904$ g cm^{-3}) for liquid Na at $T=200$ °C than that ($\rho=0.903$ g cm^{-3}) used in Ref. 1. To calculate the density, we use the interpolation formula $\rho(\mathrm{Na})=0.948-2.13\times10^{-4}T-3.30\times10^{-8}T^2$ given in J. P. Stone *et al.*, Naval Research Laboratory Report No. 624, 1965 (unpublished). This density is also listed in Table V of M. G. Kim, K. A. Kemp, and S. V. Letcher, J. Acoust. Soc. Am. 49, 706 (1971).

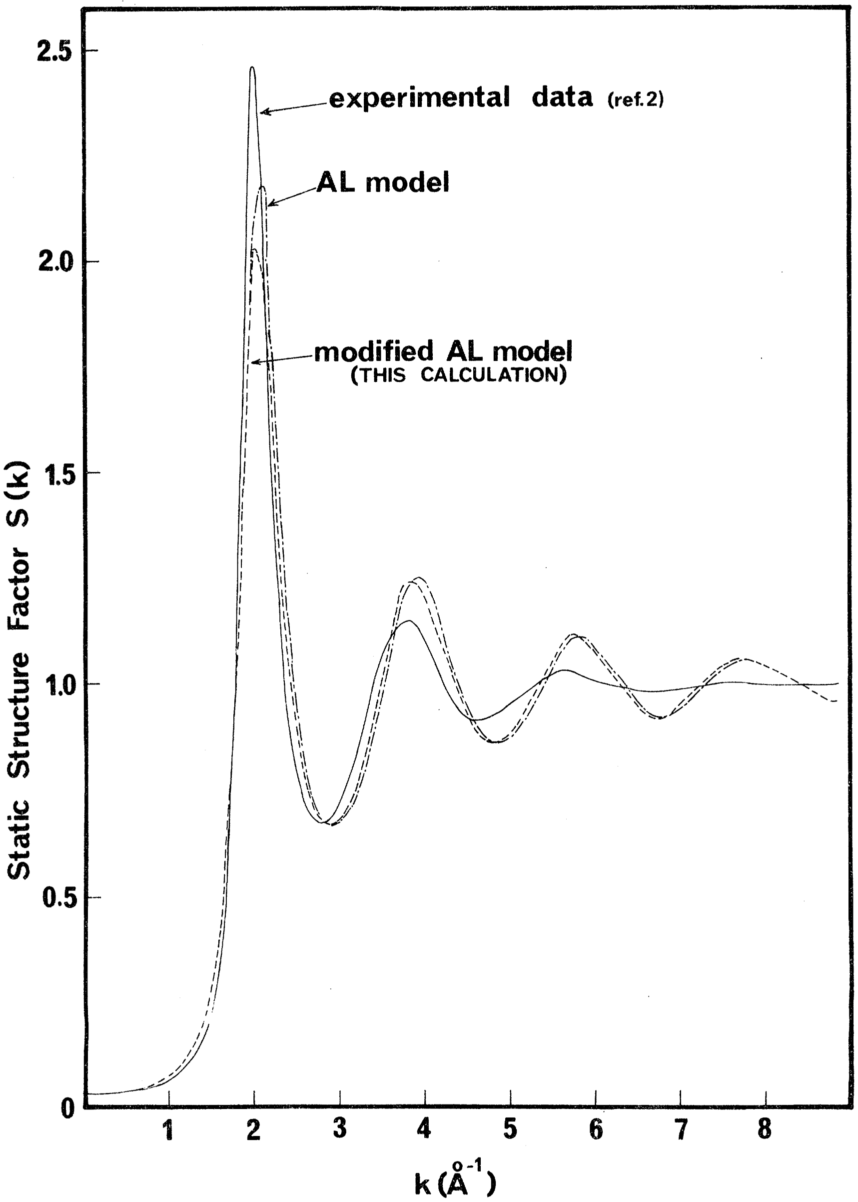

FIG. 1. Structure factor $S(k)$ for liquid sodium at 200 °C; solid line, experimental data (Ref. 2); dash-dot line, AL model; dashed line, modified AL model (this calculation).

ture factor as well as the experimental data are also shown.

It is surprising that our model does not give any better results than the AL model itself. However, it gives the first peak in $S(k)$ at $k = 2.00$ Å^{-1} as observed experimentally. Furthermore, if we restrict ourselves to a fit in a small region of k up to 4 Å^{-1} or so, we can obtain a better fit.

Of course, this generalization is based on a hard-sphere model for pair potential and, accordingly, suffers from the usual difficulties. First, no account is taken of the attractive tail of the potential. In fact, the existence of any kind of potential beyond the hard-sphere diameter σ is ignored. Second, a hard-sphere potential has an infinite discontinuity at the interparticle distance σ leading to a corresponding singularity in the radial distribution function $g(r)$. Thus, its Fourier transform $S(k)$ will automatically lead to spurious oscillations at high k. It seems to us that the difficulties associated with the use of the hard-sphere model are much more serious than the use of the low-density solution of the PY equation.

A perturbation scheme recently proposed by Andersen, Weeks, and Chandler,[9] and tested as well as further expanded on by Verlet and Weis,[7] bypasses these difficulties reasonably successfully.

Our effort to generalize the AL hard-sphere model should, therefore, be viewed only as an attempt to extend the model to higher densities. Accordingly, the success or failure of such an attempt should be judged by a comparison with the hard-sphere static structure factor as obtained by machine calculations. Since such data is not available to us, we can simply express the belief that at least in this case, our attempt to modify the AL model so as to extend it to higher densities should be well worth the effort. This is obvious because a variable parameter is built in our model.

However, for any comparison with real liquids or liquid metals, this attempt seems to be as much a failure as the AL hard-sphere model itself. This is, of course, not very surprising in view of the hard-sphere nature of such models.

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[1] A. J. Greenfield, N. Wiser, M. R. Leenstra, and W. van der Lugt, Physica 59, 571 (1972).

[2] (a) A. J. Greenfield and N. Wiser, Phys. Letters 34A, 123 (1971); (b) A. J. Greenfield, J. Wellendorf, and N. Wiser, Phys. Rev. A 4, 1607 (1971).

[3] N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).

[4] M. S. Wertheim, Phys. Rev. Letters 10, 321 (1963); E. Thiele, J. Chem. Phys. 39, 474 (1963).

[5] J. K. Percus and G. J. Yevick, Phys. Rev. 110, 1 (1958).

[6] N. F. Carnahan and K. E. Starling, J. Chem. Phys. 51, 635 (1969).

[7] L. Verlet and J. J. Weis, Phys. Rev. A 5, 939 (1972).

[8] Liquid sodium at 200 °C was chosen for comparison because for some unspecified reason, the values of $S(0)$ given in Ref. 1 above for liquid Na at 100 °C as well as liquid K do not match those given in Ref. 2(b).

[9] H. C. Andersen, J. D. Weeks, and D. Chandler, Phys. Rev. A 4, 1597 (1971). Perturbation schemes to treat the long-range part of the potential have been proposed earlier. For a more-complete list of references, the reader is referred to an excellent review by L. Verlet, in *Statistical Mechanics—New Concepts, New Problems, New Applications*, edited by S. A. Rice, K. F. Freed, and J. Light (University of Chicago Press, Chicago, 1972), p. 379.

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Steady States and Quasienergies of a Quantum-Mechanical System in an Oscillating Field*†

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A general formalism is presented for a system whose Hamiltonian is periodic in time. The formalism is intended to deal with the interactions between *bond* electrons and an external electromagnetic field, which can be treated semiclassically, such as electric and magnetic polarizations, optical rotation, and transitions among discrete levels. A particular bound-state solution of the Schrödinger equation which belongs to an irreducible representation of the time-translation symmetry group is defined as a steady state, and the characteristic number of the irreducible representation as a quasienergy. It is shown that the defined steady states and quasienergies behave in a newly constructed Hilbert space like stationary states and energies of a conservative system in many respects. It is also shown that for a resonant case the unperturbed quasienergy becomes degenerate and the transitions among discrete levels can be accounted for by the familiar degenerate perturbation procedure. Using a suitable Hilbert space, the steady states are established as firmly as the stationary states stand in the theory of a conservative system.

I. INTRODUCTION

It is well known in solid-state physics that for a spatially periodic Hamiltonian, there exist quasimomenta and corresponding Bloch wave functions. Analogously, for a periodically time-dependent Hamiltonian, one expects the existence of quasienergies and Bloch-type states. For these states Young *et al.*[1] coined the term *quasiperiodic states*; we prefer to use the term *steady states*. Such steady states have been discussed and used in the theories of susceptibilities,[1,2] and in the theories of multiple-quantum transitions among discrete levels.[3-5]

In spite of the widespread utilization of steady states for the study of the semiclassical interation between bound electrons and an external electromagnetic field, many aspects of steady states have been discussed only partially and superficially in the literature and apparently require further investigation. The essential points missed by previous workers are the introduction of a Hilbert space suitable for steady states and the uniform treatment of steady states in this space. The introduction of such a Hilbert space not only makes the formalism transparent, but also introduces new