

where there is electronic and/or rotational-vibrational excitation of the H_2^+ ion. Since the measurement averages over all states of H_2^+ , our results show that the particular magnetic substate excited in the collision is independent of the rotational-vibrational excitation of the H_2^+ ion. Another possible conclusion, namely that only one final state of the H_2^+ ion contributes to the excitation, seems unlikely, although selection rules may play a role in reducing the number of final states.

At 1.5 keV, 2.33° , and 1.5 keV, 1.00° , the alignment is considerably less than maximal but the atoms could still be in pure states if there is a definite phase relation between the eigenstates $m_l = 0$ and $m_l = \pm 1$. Further measurements of the three alignment parameters and the single orientation parameter are needed to fully characterize these states and show that they are pure states.

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Calculation of the Structure Factor of Liquid Metals*

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We suitably modify the scheme of Singwi *et al.* for calculating the density response function of interacting electron gas to take into account the fact that the pair correlation function vanishes in the highly repulsive hard-core region of the potential for classical liquids. This modified self-consistent iterative scheme is applied to calculate the structure factor for liquid sodium and rubidium. Both equilibrium and dynamical properties of classical liquids can now be calculated from a single theory.

The static structure factor $S(q)$ and the pair correlation function $g(r)$ have been successfully calculated by use of a perturbation theory due to Weeks, Chander, and Andersen (WCA)¹ for the Lennard-Jones fluid.² More recently, this scheme has been applied to calculate thermodynamic properties of liquid metals.³

For the calculation of dynamical properties, on the other hand, one uses either the generalized hydrodynamics⁴⁻⁶ or the theory of Singwi *et al.*⁷ (STLS), which introduces correlations between particles through the equilibrium pair correlation function. In both these schemes, the equilibrium structure given by $S(q)$ or $g(r)$ is as-

sumed to be given.

In the STLS theory,⁷ the dynamical density response function $\chi(q, \omega)$ is expressed as

$$\chi(q, \omega) = \chi_0(q, \omega) / [1 - \psi(q)\chi_0(q, \omega)]. \quad (1)$$

Here, $\chi_0(q, \omega)$ is the dynamical density response function of a free (noninteracting) system and the $\psi(q)$ is defined by

$$d\psi(r)/dr = g(r)d\varphi(r)/dr, \quad (2)$$

$\varphi(r)$ being the pair potential of the system. The fluctuation-dissipation theorem leads to a further relation between the structure factor and the ef-

fective field $\psi(r)$,

$$S(q) = [1 + \rho\beta\psi(q)]^{-1}, \quad (3)$$

where $\rho = N/V$ is the particle number density, $\beta = 1/k_B T$ is the inverse temperature, and $\psi(q)$ is the Fourier transform of $\psi(r)$.

Even though, in principle, $S(q)$ and $\psi(q)$ can be calculated from self-consistent solution of Eqs. (2) and (3), the STLS theory as applied to the collective motion in classical liquids ignores this and treats $\psi(q)$ as a parameter⁸; unlike the interacting electron gas, a direct numerical iteration of Eqs. (2) and (3) for classical liquids does not lead to satisfactory results for $g(r)$ or $S(q)$.⁹ For a highly repulsive interaction potential nothing in the theory guarantees that, for any particular iteration, $g(r)$ vanishes sufficiently rapidly for

$r \rightarrow 0$ so that the Fourier transform of $\psi(r)$ obtained from Eq. (2) is well defined.

Thus, if this unphysical aspect of the theory could be removed, the STLS theory would not only be internally self-consistent but also serve as a complete theory of liquids. Unlike the present situation, both the equilibrium as well as dynamical properties of classical liquids could then be calculated from one single theory.

Pynn¹⁰ assumed that the solution of Eqs. (2) and (3) exists for classical liquids and suggested that the problem is only computational. In our view, on the other hand, this is a major difficulty in the STLS theory because short-range correlations are not being taken into account properly.

Following Pynn's suggestion,¹⁰ it is assumed that Eq. (2) is valid for all r greater than a distance r_0 which might be thought of roughly as a hard-sphere diameter. For $r < r_0$,

$$\psi(r) = a + b \left(1 - \frac{r}{r_0}\right) + \left(1 - \frac{r}{r_0}\right) \sum_{n=0}^{\infty} c_n P_n \left(\frac{2r}{r_0} - 1\right) \quad (4)$$

is assumed where P_n 's are the Legendre polynomials [in this region, $\psi(r)$ is denoted by ψ_{sr} and in the region $r > r_0$, by ψ_{tr}]. The c_n 's are to be determined by minimization of a functional \mathcal{G} of the form,

$$\mathcal{G}(\psi) = \int d^3r [1 - g(r)] \psi(r) - [\beta\rho^2(2\pi)^3]^{-1} \int d^3q \{ \rho\beta\psi(q) - \ln[1 + \rho\beta\psi(q)] \}. \quad (5)$$

The functional $\mathcal{G}(\psi)$ plays the role of Helmholtz free energy and is obtained as follows: The random-phase-approximation (RPA) expression for the excess Helmholtz free energy given in Ref. 2 reduces to

$$\mathcal{Q} = -\frac{1}{2}\beta\rho^2 \int d^3r \varphi(r) + [1/2(2\pi)^3] \int d^3q \{ \beta\rho\varphi(q) - \ln[1 + \beta\rho\varphi(q)] \} \quad (6)$$

when the ideal gas is considered as the reference system, and the structure factor becomes

$$S_{\text{RPA}}(q) = [1 + \beta\rho\varphi(q)]^{-1}. \quad (7)$$

Note that Eq. (3) reduces to the RPA expression, Eq. (7), when the effective field $\psi(r)$ is replaced by the pair potential $\varphi(r)$. (STLS theory can therefore be regarded as a generalization of RPA.) The functional $\mathcal{G}(\psi)$ is obtained from Eq. (6) by the replacement of $\varphi(r)$ by the effective field $\psi(r)$, and the requirement that

$$\delta\mathcal{G}/\delta\psi(q) = 0 \quad (8)$$

be consistent with Eq. (3).¹¹ The derivatives

$$\partial\mathcal{G}/\partial c_n = 0, \quad n = 0, 1, 2, \dots, \quad (9)$$

therefore, determine the parameters c_n , $n = 0, 1, 2, \dots$.

The parameters a and b are fixed by the continuity condition for $\psi(r)$ in the regions $r < r_0$ and $r > r_0$. Starting with an approximate input set of parameters c_n and a given value of $g(r)$, the iter-

ative procedure now consists of calculating ψ_{tr} from Eq. (2) and ψ_{sr} from Eq. (4) and substituting in Eq. (1) to get $S(q)$. This $S(q)$ and its smoothed Fourier transform $g(r)$ ¹² is substituted in Eq. (9) to calculate new values of the parameters c_n . With this new set, and the new input $g(r)$ calculated from

$$g_{n+1}^{\text{in}}(r) = (1 - \gamma)g_{n-1}^{\text{in}}(r) + \gamma g_n^{\text{out}}(r), \quad 0 < \gamma < 1, \quad (10)$$

the procedure is repeated until self-consistency is achieved.

The modified STLS procedure is applied to two liquid metals: (i) liquid sodium at 200°C and density of 0.904 g cm⁻³, for which accurate data on the structure factor $S(q)$ is available in the literature,¹³ and (ii) a liquid-rubidium-like system at 319°K and density of 1.502 g cm⁻³, for which molecular-dynamics data¹⁴ as well as the pair potential of Price and co-workers¹⁵ used in molecular-dynamics calculation are accessible to us. In

TABLE I. Best fit values of parameter c_n , $n=0, 1, 2, 3, 4$, for liquid sodium at 200°C and a density of 0.904 g/cm³ and liquid rubidium at 319°K and a density of 1.502 g/cm³.

| | r_0 (Å) | a | b | c_0 | c_1 | c_2 | c_3 | c_4 |
|----|--------------|-------|-------|-------|-------|-------|-------|-------|
| Na | 2.858 | 0.099 | 0.109 | 1.214 | 1.311 | 0.951 | 0.290 | 0.146 |
| Rb | 3.202 | 0.182 | 0.154 | 0.469 | 0.383 | 0.021 | 0.071 | 0.012 |

our calculations, the Shyu, Singwi, and Tosi model potential¹⁶ is used for liquid sodium. The liquid rubidium calculation is based on the potential of Price and co-workers,¹⁵ and provides a direct test of our procedure. A value of r_0 corresponding roughly to the hard-sphere diameter is chosen. The choice of r_0 is, however, not critical as long as the derivative $d\phi(r)/dr$ at $r=r_0$ is not large. A set of five c_n 's, $n=0, 1, 2, 3, 4$, is used in calculating the structure factor $S(q)$, though all these five parameters are probably not necessary to get a convergent $S(q)$ or $g(r)$. The next set of values of c_n 's are obtained by calculating the roots of Eq. (9). Our best fit values of the c_n 's, $n=0, 1, 2, 3, 4$, for these two liquid metals are listed in Table I. The resulting $S(q)$ for liquid sodium and liquid rubidium are shown in Figs. 1 and 2, respectively, and compared with the data^{13,14} as well as the predictions of WCA perturbation theory.^{1,3b}

Our results for both these liquid metals are in good agreement with the data^{13,14} and are, in fact, somewhat better than the WCA predictions.^{3b} For $q \rightarrow 0$, our calculated $S(q)$ does not yield the compressibility limit. This is not surprising

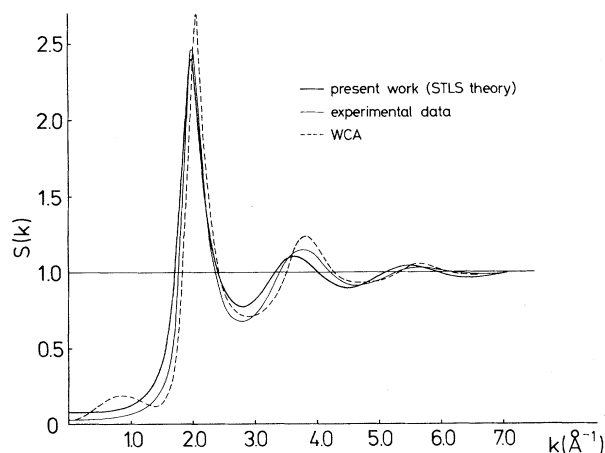


FIG. 1. Structure factor $S(q)$ for liquid sodium at 200°C and a density of 0.904 g/cm³.

and could be improved by replacing Eq. (2) by

$$d\psi(r)/dr = [g(r) + \frac{1}{2}\rho \partial g(r)/\partial \rho] d\phi(r)/dr \quad (11)$$

as given by Vashishta and Singwi¹⁷; for the electron gas, excess buildup around the test particle is greatly reduced by this assumption and for one-component classical plasma the compressibility sum rule is exactly satisfied.¹⁷ However, Eq. (11) involves the density derivative of $g(r)$ and further complicates the numerical procedure without changing the overall quality of the results.

We would like to conclude with a note of caution. The numerical procedure discussed above to calculate the structure factor seems to be sensitive to the initial set of input parameters. This difficulty, however, is common to most self-consistent methods involving integral equations. Our theory *does* provide an initial input value for the parameters a and b based on the continuity of $\psi(r)$ at $r=r_0$.

The modified version of the STLS theory⁷ could well be regarded as a complete internally self-

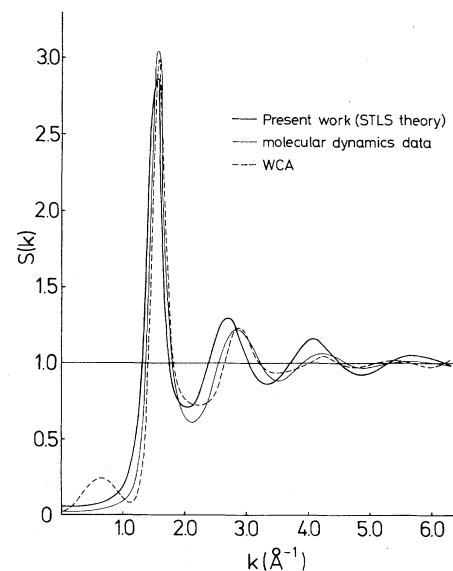


FIG. 2. Structure factor $S(q)$ for liquid rubidium at 319°K and a density of 1.502 g/cm³.

consistent theory of classical liquids in that both equilibrium and nonequilibrium properties can now be calculated within the same framework. At present, the theory, however, describes the dynamical properties reasonably only for large q and ω . Improvements are needed for the theory to describe the dynamics for all q and ω .

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Unusual Dynamical Properties of Self-Interstitials Trapped at Co Impurities in Al†

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Mössbauer spectroscopy was used to study the dynamics of Al self-interstitials trapped at ⁵⁷Co impurities. When a single interstitial atom is trapped at the ⁵⁷Co atom, the Debye-Waller factor decreases rapidly by more than a factor 4 in the temperature interval between 13 and 20 K. We try to explain this anomaly by the following model: The ⁵⁷Co atom jumps between six different positions, thereby forming mixed Co-Al dumbbells with changing Al partners.

In recent years the study of interstitials in metals and especially of their dynamical properties has received increasing interest. Experimental studies indicated a remarkable lattice softening¹⁻⁴

due to interstitials in fcc metals. Mössbauer measurements on dilute AlCo alloys⁵⁻⁷ gave a direct indication^{6,7} of low-frequency vibrations of self-interstitials trapped at Co atoms together