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Computer "Experiments" on Liquid Metals*

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The liquid structure factor $S(k)$ and velocity autocorrelation function $\psi(t)$ of classical systems of particles interacting by two-body potentials have been computed by Monte Carlo and molecular dynamics techniques. The two-body potentials were chosen with two features which might be present in the effective ion-ion potential of some simple liquid metals: a "soft" repulsive core of Born-Mayer type and long-range oscillations of the form $A\cos 2k_Fr/r^3$. Comparison is made with $S(k)$ and $\psi(t)$ corresponding to a Lennard-Jones potential: The softness of the core increases the damping of the oscillations of $S(k)$ and the oscillatory behavior of $\psi(t)$; the effect of the Friedel oscillations on $S(k)$ and $\psi(t)$ is very small if their amplitude A is of the order of that predicted by theoretical calculations. If A is two to three times larger, Friedel oscillations increase the height of the first peak of $S(k)$ and the oscillations of $\psi(t)$. The dependence of the effect of Friedel oscillations of "realistic" amplitude upon their wave vector $2k_F$ is investigated in a simple model: In that model the height of the first peak of the structure factor, $S(k_0)$, is maximum when $2k_F = k_0$. The possibility of observing such a resonance effect by neutron or x-ray scattering on a liquid Li-Mg alloy is briefly discussed.

I. INTRODUCTION

The interest in considering simple liquid metals as classical fluids received a strong stimulation in 1963 through a paper by Johnson, Hutchinson, and March[1] (JHM): These authors, using approximate relations between the radial distribution function $g(r)$ and the interparticle potential $V(r)$ in classical fluids attempted to extract the interparticle potential from the experimental structure factor of liquid sodium and liquid argon near their respective triple point. For sodium they obtained an ion-ion potential with marked oscillations whereas in the case of argon the potential obtained was of the expected van der Waals type. These results, although now somewhat controversial, drew attention on the eventual possibility of obtaining, through x-ray or neutron scattering experiments, information on the effective interaction between ions in liquid metals.

Further progress in this direction was made in 1966 through two investigations, one by Ashcroft and Lekner[2] (AL) and the other by Paskin and Rahman[3] (PR). AL reached a conclusion nearly opposite to that of JHM by showing that a reasonably good fit of the experimental liquid structure factors (up to the second peak) of seventeen metals near their triple point could be obtained by a zero-parameter model, namely, the Percus-Yevick (PY) structure factor of hard spheres at a packing fraction of 0.45. As to PR, they inverted the JHM results, by use of the molecular dynamics technique of Rahman[4]: Assuming for liquid sodium a potential with oscillations analogous to those found by JHM and with a repulsive core of Born-Mayer type, they obtained a radial distribution function in reasonable agreement with experiment. Furthermore, they obtained the interesting result[5] that the velocity autocorrelation function corresponding to such a potential shows marked oscillations, in contrast to the Lennard-Jones case.[4, 6]

It thus seems that the problem raised by JHM, of extracting from experiments information concerning the interactions between ions in a liquid metal, has to be divided in the following two questions: (a) if the ion-ion potential presented some characteristic theoretically founded features, e.g., Friedel oscillations and, in the case of the alkalis a "soft" Born-Mayer core, would these features have any measurable effect on the quantities accessible to experiment and especially on the scattering of x rays and neutrons? (b) does the ion-ion potential in liquid metals present these features? Obviously, one of the only hopes of answering question (b) is that the answer to question (a) be affirmative. The aim of this paper is to study question (a) using computer "experiments"; it turns out that in the region of temperature and pressure where experimental data exist, namely, the neighborhood of the triple point, and with the current accuracy of the x-ray and neutron scattering experiments, the answer to question (a) is partly negative. This is so because, as noted by AL and, in the case of a Lennard-Jones potential, by Verlet,[7] most of the structure factor of a simple fluid near its triple point can be quantitatively interpreted as stemming from geometrical, excluded volume effects, and is unaffected by the details of the interaction. Some details do, however, show up in certain cases, as we shall show, and it is not impossible that accurate experiments will give unambiguous answers to question (b), regarding some features of the potential.

In Sec. II, after some brief numerical details about the techniques of computer "experiments" used, Monte Carlo and molecular dynamics, we discuss the potentials which we have used to describe two liquid metals: sodium and aluminum. Regarding the reliability of these two-body potentials the philosophy underlying the calculations is different from the one in the rare-gas case in two respects. Firstly, from a theoretical viewpoint the use of classical statistical mechanics is, of course, much less founded in liquid metals, due to the presence of the conduction electrons, than in rare gases. The ion-ion pseudopotential which, in a certain way, takes into account the effect of these electrons is unable to describe correctly the volume-dependent effects and should therefore not be expected to describe accurately the very low k behavior of $S(k)$. [The fact that the AL model fits the isothermal compressibility of liquid alkalis[2, 8] correctly is partly a coincidence due to the use of the PY approximation: The inverse compressibility $\beta(\partial p/\partial \rho)$ of a hard-sphere fluid of packing fraction 0.45, obtained by deriving the Padé 3, 3 approximant of the pressure[9] is 35, whereas the PY approximation yields a value of 39.5, closer to the experimental values for liquid alkalis close to their triple point (41.7 for liquid sodium, 45 for liquid rubidium).] It is indeed unlikely that any reasonable state-independent potential could give rise to an inverse isothermal compressibility $\beta(\partial p/\partial \rho)$ of 100 as observed in lead. The second, less fundamental, difference is the absence, for liquid metals, of any potential as reliable (for volume-independent quantities) as, say, the Lennard-Jones potential for rare gases.

The potentials were therefore constructed in the following way: In a first step the hard-core diameter σ and depth of the well ϵ were chosen so that the density and temperature of the liquid metal at its triple point, when expressed in units of σ^{-3} and ϵ, be of the order of the reduced density and temperature of argon at its triple point. This ensured that the thermodynamical properties of our artificial fluids were not too unreasonable; an independent check on the value of σ was given by the position k_0 of the first peak of the experimental structure factor. In a second step, several potentials were constructed with the same ϵ and σ but with different core steepness and with or without long-range oscillations.

Results concerning the effect of the steepness of the core are given in Sec. III; a soft Born-Mayer core gives rise, when compared to a "hard" core, say $1/r^{12}$, to the following two differences: on the one hand a stronger damping of the oscillations of the structure factor $S(k)$ and on the other hand marked oscillations of the velocity autocorrelation function $\psi(t)$, as already observed by PR.[5]

In Sec. IV are given the results concerning the effect of the Friedel oscillations for two liquid metals – sodium and aluminum. In the case of liquid sodium, oscillations analogous to those predicted theoretically[10] have no clear-cut effect on $S(k)$: By this we mean that the structure factor corresponding to the same potential with and without these oscillations can be fitted equally well by two slightly different hard-sphere models. As to the velocity autocorrelation function, it is practically unaffected by the presence of these oscillations. We have also studied the effect of oscillations of amplitude two to three times larger: The height of the first peak of $S(k)$ is then increased by 20–30% and the oscillations of $\psi(t)$ slightly enhanced. In the case of aluminum, two potentials were successively used: one suggested by Harrison[11] and Pick,[10] with a narrow bowl and large oscillations, and one suggested by Ashcroft and Langreth[12] with smaller oscillations. The large oscillations have an effect on the structure factor which is most apparent in terms of a deviation from a hard-sphere model. An analogous though smaller deviation can be seen on the neutron and x-ray results; the accuracy of these results is, however, probably not high enough and the parameters of the potential not established well enough to use the experimental results as a test on the potential.

The last section (Sec. V) is devoted to a simple model: For a two-body potential consisting of a hard-sphere repulsion followed by damped Friedel oscillations of "realistic" amplitude, the liquid structure factor is computed for several values of the wave vector $2k_F$ around k_0. The height of the first peak shows a maximum for $2k_F = k_0$. This result indicates that Friedel oscillations might be easier to detect if their wave vector $2k_F$ were allowed to vary around k_0. A brief discussion is made of the possibility of observing such a resonance by x-ray or neutron scattering on a liquid Li-Mg alloy, which seems to be the best candidate: The equivalent hard-sphere diameters of pure liquid Li and Mg are almost equal and $2k_F$ can be made to vary, assuming a free-electron model, between 0.9 k_0 and 1.1 k_0.

II. DESCRIPTION OF COMPUTER "EXPERIMENTS"

We have used both standard methods of "exact" machine computations: the Monte Carlo[13] method when we were interested only in time-independent quantities and the molecular dynamics[4,14,15] method when we were interested in computing time-dependent quantities. In the latter case, the technique used was the one devised by Verlet to study the Lennard-Jones fluid and the reader is referred to Ref. 15 for technical details.

864 particles were enclosed in a cubic box with periodic boundary conditions; the length of one run was of 500 000 configurations in the Monte Carlo case and 1200 steps in time in the molecular dynamics case. The extrapolation of the radial distribution function $g(r)$ to large r, necessary for the Fourier transform of $g(r)$, was done in the same way as in Ref. 7 by assuming that, for r larger than some distance r_C, $g(r)$ satisfies the PY equation. The validity of this procedure was tested empirically by choosing several values of the distance r_C and checking that the resulting $S(k)$ never differed by more than a few percent, and, in one case, by making also a direct calculation of

$$S(k)=\frac{1}{N}\langle \sum_{i\neq j} e^{i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}\rangle.$$

The uncertainty of our results, for instance for the height of the first peak, is believed to be ±0.1.

We now come to the description of the two-body potentials which we have used. In the case of sodium, the units of length and energy chosen are $\sigma=3.24$ Å, $\epsilon=599$ °K. In these units, the density and temperature of sodium at its melting point are $\rho=0.83$, $T=0.62$. (The potentials given in the literature usually have diameter and depth differing from these values: The potential of Pick[10] has $\sigma=2.7$ Å, $\epsilon=1880$ °K and the LR02 potential of PR has $\epsilon=276$ °K.) Calculations were made successively with four potentials, the parameters of which are gathered in Table I:

(i) A potential constructed to fit the oscillations given by Pick[10] and with a repulsive core $1/r^7$, intermediate between the Born-Mayer soft core and the Lennard-Jones hard core. It is shown on Fig. 1 and has the form

$$V_1(r)=[(\cos 2k_{F1}r)/r^3](A_1+B_1/r^2+C_1/r^4)$$
$$+[(\sin 2k_{F1}r)/r^4](E_1+F_1/r^2).$$

(ii) The LR02 potential of Paskin and Rahman

$$V_2(r)=A_2\frac{\cos(2k_{F2}r+B_2)}{r^3}+E_2\exp\left(F_2-G_2\frac{r}{r_0}\right).$$

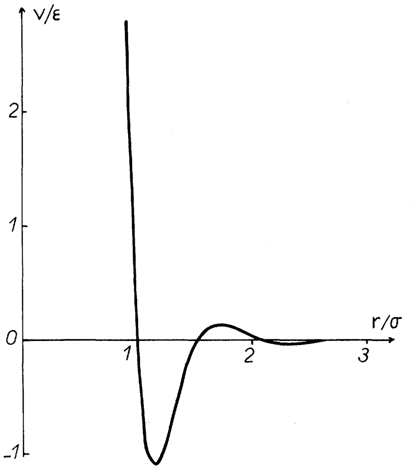

FIG. 1. Interionic potential $V_1(r)$ for liquid sodium.

This potential has oscillations of wavelength $2k_F$ exactly equal to k_0, the position of the first peak of the structure factor, whereas the value $2k_F$ appropriate for liquid sodium is 0.9 k_0. This comes probably from the fact that PR fitted the oscillations of their potential to the ones found by JHM which, in turn, were not completely separated from the oscillations of the potential of average force.[16]

(iii) A potential with the same Born-Mayer repulsive core as V_2 but with a deeper bowl and still larger oscillations

$$V_3(r)=[(\cos 2k_{F3}r)/r^3](A_3+B_3/r^2)+\frac{\sin 2k_{F3}r}{r^4}$$
$$\times(C_3+D_3/r^2)+E_3\exp(F_3-G_3r/r_0).$$

(iv) Finally, a potential with the same oscillations as the preceding one but with a hard $1/r^{12}$ core

$$V_4(r)=(\cos 2k_{F4}r/r^3)(A_4+B_4/r^2)$$
$$+(\sin 2k_{F4}r/r^4)(C_4+D_4/r^2)+E_4/r^{12}.$$

Of these four potentials, only the first one has oscillations of "realistic" amplitude; the remain-

TABLE I. Parameters of the different two-body potentials used in the calculation. For an explanation of the units used, see text.

		A	B	C	D	E	F	G	r_0	$2k_F$
	V_1	0.19	−1.02	−0.08	−0.43	−2.54				5.987
Sodium	V_2	−0.78	0.57			15.11	5.07	10.79	1.15	6.82
	V_3	−0.42	−0.56	−2.96	1.46	15.11	5.07	10.79	1.15	5.987
	V_4	0.32	−5.24	−5.39	5.76	4.06				5.987
Aluminum	V_5	0.66	4.22	−2.61	−0.54	0.67	1.49			8.97

ing three have oscillations which are a caricature of reality, being at least two to three times larger than the eventual oscillations in liquid alkalis.

In the case of aluminum, the units chosen are $\sigma = 2.56$ Å, $\epsilon = 1198$ °K. In these units the melting point of aluminum is $\rho = 0.89$, $T = 0.78$. Calculations were made with the two potentials shown on Fig. 2:

(i) A potential with a hard $1/r^{12}$ core and constructed to fit the potential calculated by Pick[10]

$$V_5(r) = (\cos 2k_{F5} r/r^3)(A_5 + B_5/r^2 + C_5/r^4) + (\sin 2k_{F5} r/r^4)(D_5 + E_5/r^2) + F_5/r^{12}\,.$$

(ii) The potential calculated by Ashcroft and Langreth[12] (taken to be zero for $r > 2.24$).

III. EFFECT OF THE SOFTNESS OF THE REPULSIVE CORE

In this section we present the results of a molecular dynamics calculation done with the potential $V_3(r)$ taken to be zero for $r > 1.5$. The calculation was done at $\rho = 0.83$, $T = 0.64$ and the results are compared with results obtained for the structure factor by Verlet[7] and, for the velocity autocorrelation function, by Levesque *et al.*,[6] with the Lennard-Jones potential at $\rho = 0.84$, $T = 0.73$. Table II shows a comparison of the thermodynamical functions: No striking difference appears. The main difference in the radial distribution functions $g(r)$ is the one expected by intuition, namely, that the rise in $g(r)$ around $r = 1$ is less sharp for a soft potential than for a hard one. This, in turn, has the effect on the structure factor $S(k)$, also intuitively understandable, that the oscillations corresponding to a soft potential are more damped. This is shown on Fig. 3: While both first peaks have the same height, the third peak corresponding to the soft potential is nearly three times smaller than the one corresponding to the hard potential. Also shown on Fig. 3 by triangles and crosses are experimental neutron results [maxima, minima, and points where $S(k) = 1$]. While both potentials give a first peak of 2.75 the experimental value seems to lie between 2.5 and 2.6. As to the height of the third peak, it is hard to know what the accuracy of the experiments at large angles is and whether the better agreement with a "soft" potential is significant or not.

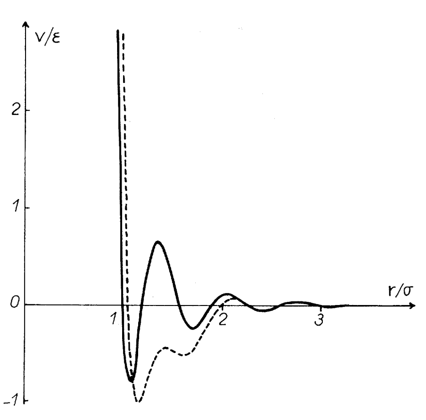

FIG. 2. Interionic potentials for liquid aluminum: (solid line) $V_5(r)$; (dashed line) potential of Ref. 12.

TABLE II. Thermodynamical functions obtained with two potentials of different core steepness: For an explanation of the units used, see text.

Core	ρ	T	$\frac{p}{\rho k T}$	U	$\beta \frac{\partial p}{\partial \rho}$
Lennard-Jones	0.84	0.73	0.25	−6.08	24
Born-Mayer	0.83	0.64	0.5	−4.2	20

Before giving the results concerning the velocity autocorrelation function, let us make a little detour and introduce a way of analyzing structure factors derived from the AL model and which will prove convenient in this section and Sec. IV. Let a_n be the amplitude of the nth extremum of the structure factor to be analyzed, and consider a hard-sphere fluid of packing fraction η_n such that the PY structure factor for such a fluid has an nth extremum of amplitude equal to a_n. To each

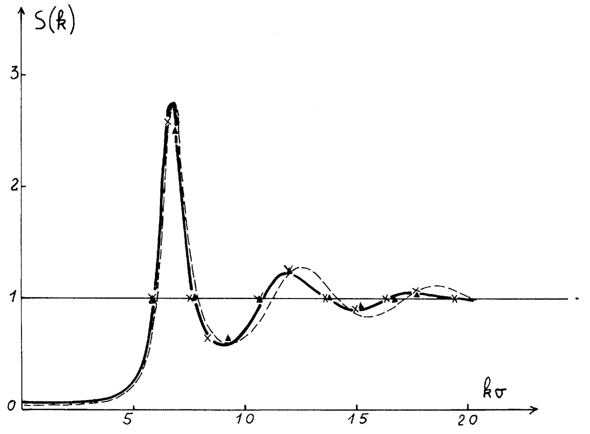

FIG. 3. Structure factors obtained with two potentials of different core steepness: (solid line) V_3 (cut at $r = 1.5$) $\rho = 0.83$, $T = 0.64$; (dashed line) Lennard-Jones (cut at 2.5) $\rho = 0.84$, $T = 0.73$; △ experimental values [extrema and values for which $S(k) = 1$] in liquid sodium according to K. S. Singwi and G. Feldman, in Proceedings of the Symposium on Inelastic Scattering of Neutrons, Bombay, 1964 (International Atomic Energy Agency, Vienna, 1964), Vol. II, p. 85; × experimental values in liquid sodium according to H. Oehme and H. Richter, Naturwissenschaften 53, 16 (1966).

TABLE IV. Hard-core diameters according to AL (in Å).

He	Li	Be					
2.6	2.7	2					
Ne	Na	Mg			Al	Si	
2.8	3.3	2.8			2.5	2.6	
Ar	K	Ca	Cu	Zn	Ga	Ge	As
3.4	4.1	3.5	2.2	2.4	2.5	2.8	2.7
Kr	Rb			Cd	In	Sn	Sb
3.6	4.3			2.7	2.9	2.9	3
Xe	Cs	Ba		Hg	Tl	Pb	Bi
4	4.7	3.9		2.8	2.9	3.1	3.1

peak and valley is thus associated the packing fraction of a hard-sphere fluid. (If, instead of the PY structure factor, one uses the "exact" one,[17] one assigns to each peak and valley a slightly different value of η but the variation of η_n with n is practically unchanged.) The result of such an analysis for several experimental and theoretical structure factors is given in Table III. The first line corresponds to a Lennard-Jones fluid not far from its triple point. The successive η's decrease roughly monotonously as expected, due to the fact that the rise of $g(r)$ around $r=1$ is less abrupt than in the hard-sphere case. The faster decrease of the η's in the case of a soft potential can be seen on the fourth line. In the lower half of Table III are given the η's corresponding to several experiments: some neutron data on sodium,[18] not very recent, and some recent data on potassium,[19] lead,[20] aluminum,[21] zinc,[22] and copper.[23] If one believes the data on sodium and potassium, one is tempted to interpret the fact that the η's decrease more rapidly than for the other metals by saying that the ion-ion potential in the alkalis is softer than in the other metals. Such a view is partly supported by inspection of the hard-core diameters corresponding to several elements shown in Table IV. The hard-core diameters σ are those calculated by AL from the densities of the liquids at their triple point ($\rho\sigma^3=0.86$). Another estimation of the equivalent hard-core diameter σ, possible whenever experimental structure factors exist, is to equate the position k_0 of the first peak of $S(k)$ to the value it has, in reduced units, for argon at its triple point,[7] namely, $k_0\sigma=2\pi/0.93$. The two estimates never differ by more than 5%. In the case of the rare gases, the values given are those determined by second virial measurements. It can be seen on this table that the effective hard-core diameters of the alkalis (except lithium) are 0.5–0.7 Å larger than those of the corresponding rare gases. Thus, although an isolated Na^+ ion has a diameter, equal to that of Ne, of 2.8 Å (and even a little smaller due to the extra nuclear charge), the effective ion-ion hard-core diameter in liquid sodium is 3.3 Å, presumably because of the Coulomb repulsion between ions. But the 0.5 Å thick "skin" between 3.3 and 2.8 Å is presumably soft since it is not until 2.8 Å that the hard Pauli-principle repulsion acts. The fact that the elements of the following columns have again smaller hard-core diameters could be linked to a stronger screening of the Coulomb repulsion by the electrons, and explain the slow decrease of the η's. Obviously, before such an analysis can be taken seriously, some accurate neutron or x-ray data on the damping of the oscillations of $S(k)$ in the liquid alkalis are necessary: Coupled with computer "experiment" results, they

TABLE III. Analysis of several theoretical and experimental structure factors in terms of hard-sphere model. The number η_n in the nth column characterizes the amplitude a_n of the nth extremum. It is the packing fraction of a hard-sphere fluid which has a PY structure factor such that its nth extremum has also an amplitude a_n. For an explanation of the units used, see text.

	η	1	2	3	4	5
Theory	Lennard-Jones, $T=0.78$, $\rho=0.85$,	0.47	0.46	0.44	0.45	0.42
	V_1 cut at 1.53	0.47	0.47	0.41	0.41	0.38
	V_1 cut at 3.20	0.44	0.43	0.38	0.37	0.3
	V_3 cut at 1.5	0.47	0.46	0.41	0.36	0.28
	V_5 cut at 1.51	0.45	0.47	0.49	0.5	0.5
	V_5 cut at 3.3	0.43	0.52	0.48	0.49	0.49
Experiment	Sodium (Ref. 18), neutrons	0.45	0.44	0.41	0.3	0.25
	Potassium (Ref. 19), neutrons	0.46	0.45	0.41	0.4	0.32
	Lead (Ref. 20), x rays	0.47	0.47	0.44	0.42	0.41
	Aluminum (Ref. 21), x rays	0.45	0.49	0.43	0.40	0.36
	Zinc (Ref. 22), neutrons	0.44	0.43	0.42	0.37	
	Copper (Ref. 23), neutrons	0.44	0.45	0.43	0.42	0.41

might give insight on the steepness of the ion-ion repulsion.

Let us now come back to the results of the molecular dynamics calculations concerning the velocity autocorrelation function and the diffusion coefficient. The velocity autocorrelation function

$$\psi(t) = (m/3kT)\langle \vec{v}_i(0)\cdot\vec{v}_i(t)\rangle$$

has been computed by the same technique as in the Lennard-Jones case.[6] Figure 4 shows the results compared to the Lennard-Jones one. Marked oscillations, analogous to the ones obtained by PR[5] with a long-range oscillatory soft-core potential, are obtained here with a soft potential with no oscillations. Although the physical reason for which a soft core should give rise to a deeper bowl, followed by oscillations in the velocity autocorrelation function, is not clear to us, we think that it might be linked to the following two facts: On the one hand, the diffusion coefficient, which is equal to the integral of $\psi(t)$ is, as we shall see, rather insensitive to the steepness of the core; the small t behavior of $\psi(t)$, on the contrary is governed by the quantity

$$\rho\int \Delta V(r)g(r)d\vec{r},$$

which is twice as small in the case of a soft potential as in the case of a hard one. The extra positive region under $\psi(t)$ in the case of a soft potential has to be compensated by a larger negative region. Figure 5 shows the Fourier transforms of the curves of Fig. 4,

$$f(\omega) = \int_0^\infty \cos\omega t\,\psi(t)\,dt,$$

together with the experimental[24] curve. Again, the soft potential seems to be in better agreement with the experimental curve but the accuracy of the latter, obtained after extraction of the "self" part of $S(k,\omega)$, and a $k\to 0$ limit, is probably not very high.[25] As to the diffusion coefficient D, it seems to be rather insensitive to the steepness of the core: the soft potential yields $D = 4.4\times 10^{-5}$ cm²/sec and the Lennard-Jones one $D = 4.9\times 10^{-5}$ cm²/sec, whereas, the experimental[26] value in liquid sodium is $D = 4.3\times 10^{-5}$ cm²/sec.

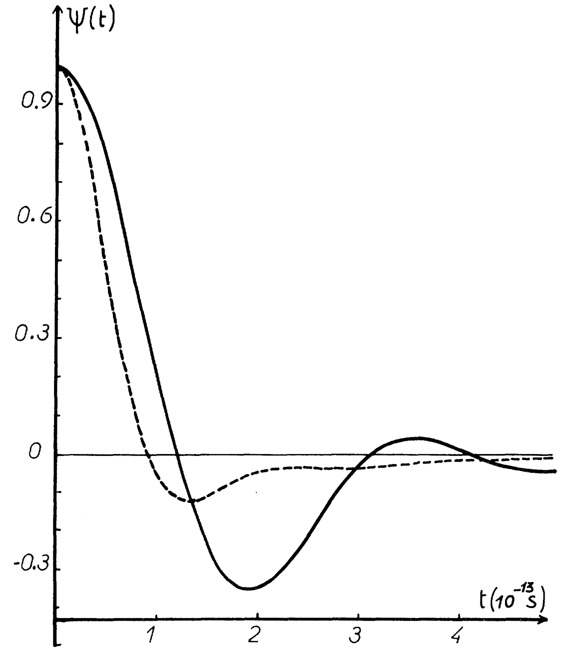

FIG. 4. Velocity autocorrelation functions obtained with two potentials of different core steepness: (solid line) V_3 (cut at $r = 1.5$) $\rho = 0.83$, $T = 0.64$; (dashed line) Lennard-Jones (cut at $r = 2.5$) $\rho = 0.84$, $T = 0.73$.

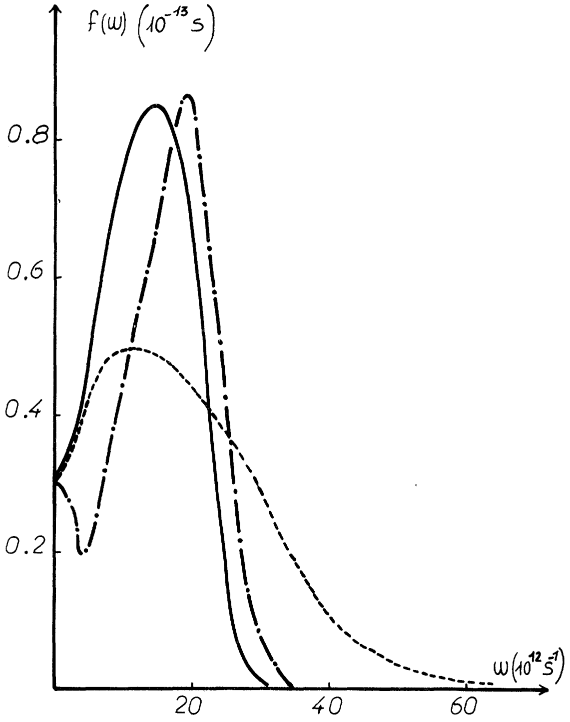

FIG. 5. Fourier transforms of the velocity autocorrelation functions of Fig. 4: (solid line) V_3 (cut at $r = 1.5$) $\rho = 0.83$, $T = 0.64$; (dashed line) Lennard-Jones (cut at $r = 2.5$) $\rho = 0.84$, $T = 0.73$; (dot-dashed line) experimental curve in sodium (Ref. 24).

IV. EFFECT OF FRIEDEL OSCILLATIONS

The structure factor $S(k)$ and velocity autocorrelation function $\psi(t)$ have been computed using the potentials described in Sec. II successively with and without oscillations. In the case of sodium the computation was done in the first place for the potential $V_1(r)$ which has oscillations analogous to the oscillations calculated in solid alkalis at zero temperature,[10] and which are therefore an upper bound to the oscillations one can expect in the liquid. The effect on $S(k)$ is very small as can be seen of Fig. 6 and on line 2 and 3 of Table III: The η's corresponding to V_1 with and without oscillations decrease in an analogous way. As to the effect of the oscillations on $\psi(t)$ (Fig. 7) it is negligible. Since realistic oscillations seemed to give no clear-cut effect, we then used potentials with stronger oscillations. We find that the oscillations of the LR02 potential of PR do have an effect: The height of the first peak is increased by 30% and reaches the value 2.95 for the potential with oscillations. This is in contrast with the result obtained by Paskin[5] who obtained with the same potential a height of 2.4 for $S(k_0)$, in better agreement with the experimental value 2.5. This difference comes probably from the fact that, instead of truncating $g(r)$ at $r = 2.5$, we prolongate it through the PY equation. On $\psi(t)$, the oscillations of the potential have the effect of enhancing the oscillations due to the softness of the core. The potentials V_3 and V_4, in which the oscillations are still larger, yield the same effects: anomalously high value of the height of the first peak $S(k_0)$ and enhancement of the structure of $\psi(t)$.

In the case of aluminum, only the structure factor was computed; the oscillations of the potential V_5 have the effect of lowering the first peak and deepening the first valley. This is shown on Fig. 8 and also on Table III: For the potential V_5, the η's are not monotonously decreasing as for the Lennard-Jones potential, but start by increasing $\eta_1 = 0.43$, $\eta_2 = 0.52$, and so on. Looking at the lower half of the table, it can be noticed that, among all the experimental data gathered there, the results on aluminum are the only ones to show a similar (though less marked) nonmonotonous be-

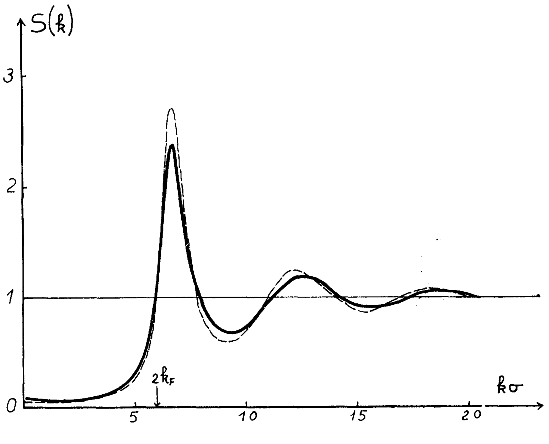

FIG. 6. Structure factors obtained with potential $V_1(r)$, $\rho = 0.83$, $T = 0.97$: (dashed line) cut at $r = 1.53$ (no oscillations); (solid line) cut at $r = 3.20$ (oscillations).

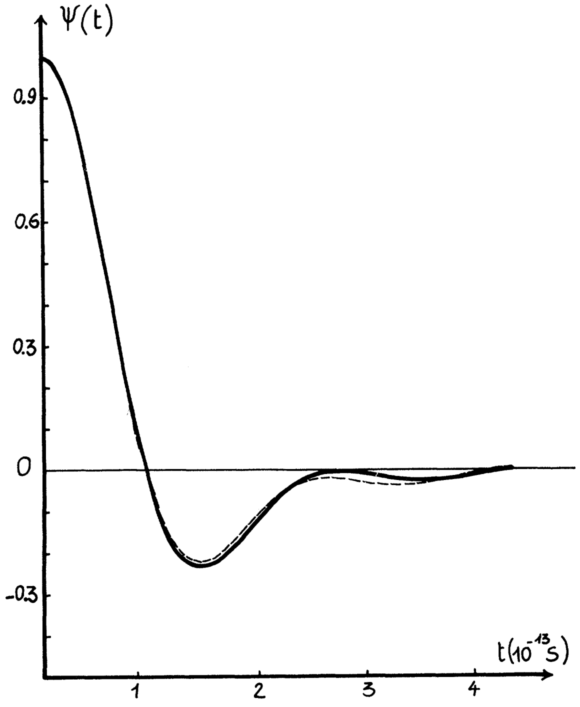

FIG. 7. Velocity autocorrelation functions obtained with potential $V_1(r)$, $\rho = 0.83$, $T = 0.97$: (dashed line) cut at $r = 1.53$ (no oscillations); (Solid line) cut at $r = 3.20$ (oscillations).

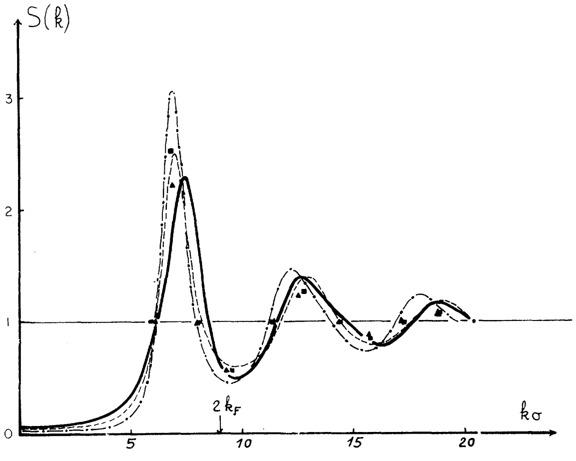

FIG. 8. Structure factors obtained with the potentials of Fig. 2: (dashed line) $V_5(r)$ cut at $r = 1.2$, $\rho = 0.89$, $T = 0.78$; (solid line) $V_5(r)$ cut at $r = 3.3$, $\rho = 0.89$, $T = 1.08$; (dot-dashed line) potential of Ref. 12 $\rho = 0.89$, $T = 0.78$; □ experimental x-ray results (Ref. 21) on liquid aluminum [extrema and values where $S(k) = 1$]; △ experimental neutron results (according to K. E. Larsson *et al.*, in Proceedings of the Symposium on Inelastic Scattering of Neutrons, Bombay, 1964 (International Atomic Energy Agency, Vienna, 1964), Vol. II, p. 117, on liquid aluminum.

havior of the η's: $\eta_1 = 0.45$, $\eta_2 = 0.49$, and so on. This is, however, not enough to conclude to the existence of oscillations in the ion-ion potential of liquid aluminum, especially since the experimental x-ray results,[21] shown on Fig. 8, seem in better agreement with the structure factor obtained by the potential with no oscillations.

We have also made a Monte Carlo calculation with the potential proposed, for liquid aluminum, by Ashcroft and Langreth (dashed curved of Fig. 2). The resulting $S(k)$, shown on Fig. 8, has too much structure. One possible explanation for this might be the following: Since the potential has a large negative region, it is possible that the corresponding melting point is higher than the melting point of liquid aluminum. The structure factor which we have computed would then be that of a metastable supercooled fluid.

V. FRIEDEL OSCILLATIONS OF VARYING WAVELENGTH

The results of Sec. IV indicate that Friedel oscillations of the type that might be present in liquid alkalis are probably very hard to detect by a measure of the structure factor of the pure liquid. A more sensitive way might be to compare the structure factors obtained by varying the wavelength of the oscillations and leaving the rest of the potential unchanged. Such an experiment might be feasible by mixing two liquid metals of equal hard-core diameters and of different valence. Lithium and magnesium are the best candidates since they have nearly equal hard-core diameters: The experimental structure factors of the pure liquids[18,27] have first peaks at the same position, and of equal height. Since we were interested only in a qualitative estimate of the effect, we made the following two approximations: (a) The repulsive part of the potential was represented by a hard-sphere potential (with a diameter $\sigma = 2.7$ Å); (b) the structure factor was computed in the PY approximation. The amplitude of the Friedel oscillations was chosen to be of the order of the ones predicted for solids at 0°K (see Table V). A very crude estimate of the mean free path of electrons in a Li-Mg alloy can be made using the experimental[28] resistivities of dilute solutions of Mg in Li and yields $\lambda = 13$ Å $\simeq 5\ \sigma$. The oscillations were accordingly damped by a factor $e^{-r/5}$. The PY equation was then solved for a potential of the form

$$
\begin{aligned}
V(r) &\to \infty, && r < 1\\
&= C\cos(2k_F r + \Phi)e^{-r/5}/r^3, && r > 1
\end{aligned}
$$

with Φ adjusted so that $V(1) = 0$, $C/kT_m = 0.4$ (see Fig. 9), at $\rho = 0.86$, $T_m = 0.62$, for several values of $2k_F$ varying between 5.9 and 7.4 (the values of $2k_F$ in pure liquid Li and Mg, respectively). The resulting height $S(k_0)$ is shown on Fig. 10 as a

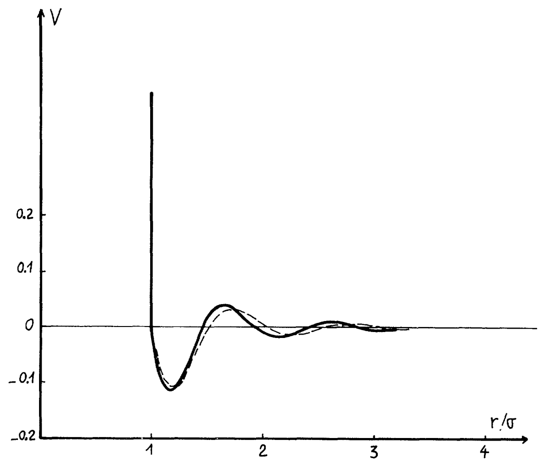

FIG. 9. Model potential hard-sphere and damped Friedel oscillations for two values of $2k_F$: (solid line) $2k_F\sigma = 6.8$; (dashed line) $2k_F\sigma = 6$ (note that the scale in energy is 5 times larger than in Figs. 1 and 2.

TABLE V. Amplitude A of the asymptotic form of the interionic potential $A(\cos 2k_F r)/r^3$, in units k_B × melting temperature, for several simple metals, according to two calculations.

	Li	Na	K	Be	Mg	Al
Pick[a]	0.7	0.04	0.8	13	0.6	0.8
Schneider-Stoll[b]		0.002	0.05		0.2	0.15

[a] Reference 10.

[b] T. Schneider and E. Stoll, Solid State Commun. 5, 837 (1967).

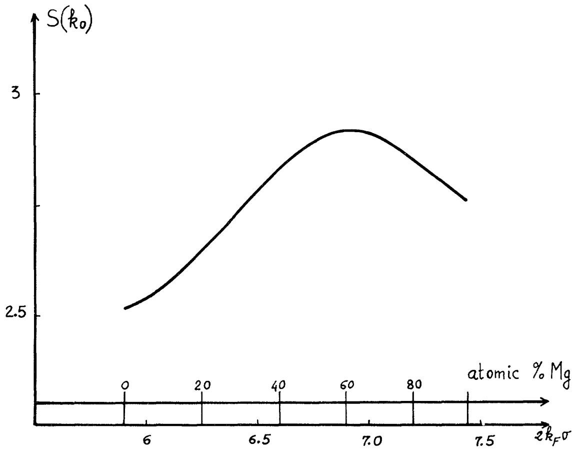

FIG. 10. Maximum value of the PY structure factor obtained, at $\rho = 0.86$, $T = 0.62$, with the potential of Fig. 9, as a function of $2k_F\sigma$ or of the atomic concentration of Mg in a Li-Mg liquid alloy.

function of the atomic concentration calculated on the basis of a free-electron model. A maximum occurs at $2k_F = k_0 = 6.8$, i.e., around 60% Mg. It might be interesting to investigate whether such a "resonance" is indeed observed in Li-Mg alloys.

VI. CONCLUSION

We have studied by computer experiments the effects on measurable quantities of two features which might be characteristic of the interionic potential in liquid metals – soft core and Friedel oscillations. A soft repulsive core of Born-Mayer type shows up clearly in a strong damping of the oscillation of the structure factor and in marked oscillations of the velocity autocorrelation function. The steepness of the ion-ion repulsion in liquid alkalis might thus be investigated by accurate measures of the structure factor up to the third peak, together with as accurate as possible experimental determination of the velocity autocorrelation function. On the contrary, Friedel oscillations of the type of those predicted by theory do not give rise to any qualitative effect. However, using a simple model we have shown that, if one were able to vary the wavelength of the oscillations, their detection might be possible by a comparative measure of the maximum of the structure factors. A liquid Li-Mg alloy seems to be the best candidate for such an investigation.

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