Optical properties of a two-component liquid-metal plasma

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The effect of electron correlations on the high-frequency conductivity of liquid metals is analyzed. A general expression derived for the effective rate of electron-ion collisions reflects both ion-ion and electron-electron correlations when the interaction between the electron and ion subsystems of the metal is weak. Comparison of the theoretical results with experimental data on liquid sodium confirms that the conductivity is increased by electron correlations. In the two-component approach it is possible to pursue the analogy between the high-frequency properties of metals and those of a moderately dense plasma.

1. The optical properties of liquid metals in the infrared region can be described quite well in a qualitative sense by the classical Drude-Lorentz theory. In the optical and ultraviolet parts of the spectrum, in contrast, the theoretical $\sigma(\omega)$ curve differs substantially from the experimental data.[1,2] In these parts of the spectrum it is no longer valid to assume a static collision rate.

Faber[3] has reported a first attempt to determine how a high-frequency field affects collision events in metals for frequencies $\hbar\nu \lesssim \hbar\omega \ll \varepsilon_F$. Helman and Baltensperger[4,5] derived an expression for the high-frequency conductivity for arbirary frequencies $\omega \gg \nu_1$, but for a statically screened electron-ion potential and in the random phase approximation (RPA) for the electrons. The approximation of a static screening is not justified at high frequencies; in particular, it cannot explain the absorption increase due to the excitation of plasma waves at $\omega \gtrsim \omega_p$ (Ref. 6). Petchick[7] derived an expression for $\mathrm{Re}\,\sigma(\omega)$ for frequencies $\omega \sim \omega_p$ in the first approximation in the pseudopotential in the adiabatic approximation for the ions. This expression for $\mathrm{Re}\,\sigma(\omega)$ was subsequently studied numerically[8] in the RPA for electrons.

It should be noted that the description of the absorption is not completely satisfactory even at relatively low frequencies, because of the well-known uncertainties regarding the parameters of the pseudopotential and the way to allow for correlations in the electron fluid.

In this paper we derive an expression for the high-frequency conductivity of liquid metals, working from a two-component plasma model. This approach has been pursued actively in recent years in research on the static properties of metal plasmas and dense gaseous plasmas.[9,10] It has the indisputable advantage of allowing a common description of the properties of a system of charged particles with an increasing "nonideality" (the ratio of the Coulomb interaction energy of a charged particle to its kinetic energy) and with an arbitrary degree of degeneracy. The expression derived for $\sigma(\omega)$ incorporates strong ion-ion and electron-electron correlations and is valid for an arbitrary degree of degeneracy and for arbitrary relations among $\hbar\omega$, T, ε_F, and $\hbar\omega_p$ under the condition $\omega \gg \nu$. Working in the adiabatic approximation, we derive an expression for the frequency-dependent effective mass of the electrons. Calculations carried out for liquid sodium demonstrate that electron-electron correlations must be taken into account in order to reach good agreement with experiment at high frequencies.

2. In the linear-response theory the complex electron conductivity is given by the expression

$$\sigma(\omega) = ine^2/m\omega + \Phi(\omega)/3, \tag{1}$$

where

$$\Phi(\omega) = \frac{1}{\hbar\omega V}\int_{-\infty}^{\infty} dt e^{i\omega t - \varepsilon t}\theta(t)\langle[\hat{\mathbf{J}}(t), \hat{\mathbf{J}}(0)]\rangle_0, \tag{2}$$

$\varepsilon = +0$ turns the field on adiabatically, $\theta(t)$ is the unit step function, n is the electron number density, V is the volume of the system, $\hat{\mathbf{J}}(t) = \int d\mathbf{r}\hat{\mathbf{j}}(t,\mathbf{r})$, and the operator $\hat{\mathbf{j}}(t,\mathbf{r})$, represents the electron current density. Integrating $\Phi(\omega)$ by parts twice, we find

$$\Phi(\omega) = \frac{i}{\omega^3}[Z(\omega) - Z(0)], \tag{3}$$

$$Z(\omega) = \frac{1}{i\hbar V}\int_0^{\infty} dt e^{i\omega t - \varepsilon t}\langle[\dot{\hat{\mathbf{J}}}(t), \dot{\hat{\mathbf{J}}}(0)]\rangle_0. \tag{4}$$

We then use an equation of motion for $\mathbf{J}(t)$:

$$\frac{d\hat{\mathbf{J}}(t)}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{\mathbf{J}}(t)], \tag{5}$$

where $\hat{H}$ is the Hamiltonian of the system in the absence of an external field. We should point out here that in our two-component model of the plasma the Hamiltonian is written

$$\hat{H} = \hat{H}_{ee} + \hat{V}_{ei} + \hat{H}_{ii}, \tag{6}$$

where $\hat{V}_{ei}$ is the local pseudopotential of the electron-ion interaction. It can then be shown that

$$\frac{d\hat{\mathbf{J}}}{dt} = -\frac{e}{m}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\partial V_{ei}(\mathbf{r}_1 - \mathbf{r}_2)}{\partial \mathbf{r}_1}\hat{n}_i(\mathbf{r}_1, t)n_e(\mathbf{r}_2, t), \tag{7}$$

where the operator $\hat{n}_\alpha(\mathbf{r}, t)$ is the number density of the particles of species α. Substituting (7) into (4), we find

$$Z(\omega) = \frac{e^2}{m^2}\frac{1}{i\hbar V}\int_0^{\infty} dt e^{i\omega t - \varepsilon t}\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \nabla_{\mathbf{r}_1} V_{ei}(\mathbf{r}_1 - \mathbf{r}_2)$$
$$\times \nabla_{r_3} V_{ei}(\mathbf{r}_3 - \mathbf{r}_4)\langle[\delta\hat{n}_e(1)\delta n_i(2),$$
$$\delta\hat{n}_e(3)\delta\hat{n}_i(4)]\rangle_0 \big|_{t_1 = t_2 = t;\ t_3 = t_4 = 0}, \tag{8}$$

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where $\delta\hat{n} = \hat{n} - n$ is a fluctuation in the number density of the particles. In deriving (8) we replaced the commutator of the densities by the commutator of their fluctuations, without changing the value of the integral in (8):

$$\langle[\delta\hat{n}_e(1)\,\delta\hat{n}_i(2),\ \delta\hat{n}_e(3)\,\delta\hat{n}_i(4)]\rangle_0 \Leftarrow \langle[\hat{n}_e(1)\,\hat{n}_i(2),\ \hat{n}_e(3)\,\hat{n}_i(4)]\rangle_0. \tag{9}$$

In this manner, the problem reduces to one of determining a four-particle correlation function.

Examining the diagram representation of the four-density Green's function corresponding to this correlation function, we easily see that for an arbitrary electron-ion interaction we can write

$$\begin{aligned}\langle\delta\hat{n}_e(1)\,\delta\hat{n}_i(2)\,\delta\hat{n}_e(3)\,\delta\hat{n}_i(4)\rangle_0 &= \langle\delta\hat{n}_e(1)\,\delta\hat{n}_e(3)\rangle_0\,\langle\delta\hat{n}_i(2)\,\delta\hat{n}_i(4)\rangle_0\\ &+ \langle\delta\hat{n}_e(1)\,\delta\hat{n}_i(2)\rangle_0\,\langle\delta\hat{n}_e(3)\,\delta\hat{n}_i(4)\rangle_0\\ &+ \langle\delta\hat{n}_e(1)\,\delta\hat{n}_i(4)\rangle_0\,\langle\delta\hat{n}_i(2)\,\delta\hat{n}_e(3)\rangle_0 + J.\end{aligned} \tag{10}$$

Here J is the irreducible part, which has no uncoupled contributions. In the frequency range of interest here, $\omega \gg \nu$, and for a relatively weak electron-ion interaction, it is sufficient to consider only the uncoupled contributions in (10). In this case the correlation functions $\langle\delta\hat{n}_a\delta\hat{n}_b\rangle_0$ are generally point correlation functions in a two-component electron system. Do we need to consider the two-component nature of the correlation functions in (10) if at the same time we are discarding J, which is of order V_{ei}^2? It might seem that retaining the two-component functions $\langle\delta\hat{n}_a\delta\hat{n}_b\rangle_0$ would be equivalent to seeking an accuracy not possible in this approximation, but we must note that, while the potential V_{ei} is small in the integral sense, at small values of k it is purely Coulomb and thus not small. It is for this reason that the terms proportional to V_{ei} prove important in calculations of the structure factors in a two-component system: Their behavior changes at small values of the momentum transfer.[11]

The coupled part of J contains the potential V_{ei} only in the integrand and in this sense is small from the integral standpoint, comparable in magnitude to V_{ei}, so that we can ignore it under the conditions assumed here.

We can thus write the complex electron conductivity as

$$\begin{aligned}\sigma(\omega) = \frac{ine^2}{m\omega} + \frac{ie^2}{3\hbar m^2\omega^3}\int\frac{d^3k}{(2\pi)^3}k^2|V_{ei}|^2\int\frac{d\omega_1 d\omega_2}{(2\pi)^2}\\ \times(1-e^{-\beta\hbar(\omega_1+\omega_2)})\,\{S_{ee}(k,\omega_1)S_{ii}(k,\omega_2) - S_{ei}(k,\omega_1)S_{ie}(k,\omega_2)\}\\ \times\left\{\frac{1}{\omega-\omega_1-\omega_2+i\varepsilon} - \frac{1}{-\omega_1-\omega_2+i\varepsilon}\right\},\end{aligned} \tag{11}$$

where

$$S_{ab}(k,\omega) = \int d\mathbf{r}\int dt\,e^{i\omega t - i\mathbf{k}\mathbf{r}}\langle\delta\hat{n}_a(1)\,\delta\hat{n}_b(2)\rangle_0|_{t=t_1-t_2;\ \mathbf{r}=\mathbf{r}_1-\mathbf{r}_2}$$

is a dynamic structure factor. We define the effective rate at which electrons collide with ions by an expression analogous to the expression ordinarily used for a hot plasma[12]:

$$\mathrm{Re}\,\sigma(\omega) = \frac{1}{4\pi}\frac{\omega_p^2}{\omega^2}\nu(\omega).$$

From (11) we find an expression for $\nu(\omega)$:

$$\begin{aligned}\nu(\omega) = \frac{2\pi e^2}{3m^2\omega_p^2}\frac{1-e^{-\beta\hbar\omega}}{\hbar\omega}\int\frac{d^3k}{(2\pi)^3}k^2|V_{ei}|^2\\ \times\int\frac{d\omega_1}{2\pi}\{S_{ii}(k,\omega_1)S_{ee}(k,\omega-\omega_1)\\ - S_{ei}(k,\omega_1)S_{ie}(k,\omega-\omega_1)\}.\end{aligned} \tag{12}$$

Taking the formal limit $\omega \to 0$ in (12), we find the collision rate derived previously by Boercker *et al.*[13] for the static conductivity.

In a classical plasma, this static collision rate, $\nu(0)$, in turn converts into the collision rate corresponding to the Lenard-Balescu kinetic equation, as was shown by Boercker *et al.*[13] In a degenerate metal plasma, it converts into the collision rate corresponding to a metallic conductivity incorporating strong ion-ion correlations.

3. At frequencies $\omega \gg \omega_i$, where w_i are the characteristic ion frequencies, we use the expression derived by Triger[11]:

$$S_{ei}(k,\omega) = -\frac{2\hbar}{1-e^{-\beta\hbar\omega}}V_{ei}\,\mathrm{Im}\left[\frac{\Pi_{ee}{}^R(k,\omega)}{\varepsilon_e{}^R(k,\omega)}L_{ii}{}^R(k,\omega)\right], \tag{13}$$

where $\varepsilon_e{}^R(k,\omega) = 1 - V_{ee}\Pi_{ee}{}^R(k,\omega)$ is the retarded dielectric function of the electron subsystem, Π_{ee}^R is the exact polarization operator of the electron subsystem, and L_{ii}^R is the retarded density correlation function of the ion subsystem (we will omit the superscript R below). Working from (13) we can easily show that the terms quadratic in S_{ei} are small. In this case we have

$$\nu(\omega) = -\frac{1}{3m\omega}\int\frac{d^3k}{(2\pi)^3}k^2|V_{ei}|^2 S_i(k)\frac{\mathrm{Im}\,\Pi_{ee}{}^o(k,\omega)}{|\varepsilon_e{}^o(k,\omega)|^2}, \tag{14}$$

where

$$S_i(k) = \frac{1}{n_i}\int S_{ii}(k,\omega)\frac{d\omega}{2\pi}$$

is the ion structure factor in the two-component system. We have also used

$$\begin{aligned}S_{ee}(k,\omega) &= -\frac{2\hbar}{1-\exp(-\beta\hbar\omega)}\mathrm{Im}\frac{\Pi_{ee}{}^0}{\varepsilon_e{}^0}\\ &= -\frac{2\hbar}{1-\exp(-\beta\hbar\omega)}\frac{\mathrm{Im}\,\Pi_{ee}{}^0}{|\varepsilon_e{}^0|^2}\end{aligned} \tag{15}$$

(the superscript "o" corresponds to the one-component system, but with correlations in this system being taken into account exactly).

It can be seen from (14) that taking the electron correlations into account does not reduce to the customary replacement of ε_e^{RPA} by ε_e^o, which might be expected on the basis of heuristic considerations, but instead involves taking into account an additional factor which arises from the difference between $\mathrm{Im}\,\Pi_{ee}^o(k,\omega)$ and $\mathrm{Im}\,\Pi_{ee}^{RPA}(k,\omega)$. The occurrence of this effect was first pointed out for the static case by Klyuchnikov and Triger,[14,15] who studied the static conductivity of metals by working with a kinetic equation which incorporates electron exchange approximately. In our notation and for the high-frequency case, this factor is found from the condition

$$\mathrm{Im}\,\Pi_{ee}{}^o(k,\omega) = \mathrm{Im}\,\Pi_{ee}^{RPA}(k,\omega)\,\beta(k,\omega). \tag{16}$$

For a hot plasma, in which correlations are unimportant, and at frequencies $\omega \gg \omega_p$, the integral in (14) can be evaluated easily, since

$$\varepsilon_e^\circ(k,\omega)\approx 1,\quad S_i(k)=1,\quad \Pi_{ee}^\circ=\Pi_{ee}^{RPA}.$$

Using the expression for Im $\Pi_{ee}^{RPA}(k,\omega)$, we find

$$\begin{gathered}\nu(\omega)=\nu_0\frac{2T}{\hbar\omega}\operatorname{sh}\left(\frac{\hbar\omega}{2T}\right)K_0\left(\frac{\hbar\omega}{2T}\right),\\ \nu_0=\frac{2}{3}\pi\left(\frac{e^2}{T}\right)^2 n\left(\frac{8T}{\pi m}\right)^{1/2},\end{gathered} \tag{17}$$

where K_0 is the modified Hankel function. Expression (17) is the same as the result derived by Perel' and Éliashberg.[16]

In the adiabatic approximation, the following expression can be derived for the imaginary part of the conductivity for the ion subsystem:

$$\operatorname{Im}\sigma(\omega)=\frac{ne^2}{m\omega}+\frac{\omega_p^2}{4\pi\omega}\gamma(\omega), \tag{18}$$

$$\gamma(\omega)=\frac{1}{12\pi e^2\omega^2}\times\int\frac{d^3k}{(2\pi)^3}k^4|V_{ei}|^2S_i(k)\operatorname{Re}\left(\frac{1}{\varepsilon_e^\circ(k,\omega)}-\frac{1}{\varepsilon_e^\circ(k,0)}\right), \tag{19}$$

where we have used the Kramers-Kronig relation for $1/\varepsilon(k,\omega)$.

Expression (17) for $\gamma(\omega)$, even taken in the *RPA*, differs from the result derived by Helam and Baltensperger,[4] because the dynamic nature of the screening has been taken into account here. Taking into account the relationship between the complex high-frequency conductivity and the dielectric constant,

$$\varepsilon(\omega)=1+\frac{4\pi i}{\omega}\sigma(\omega), \tag{20}$$

we find

$$\varepsilon(\omega)=1-\frac{\omega_p^2}{\omega^2}\left(1+\gamma(\omega)-\frac{i\nu(\omega)}{\omega}\right) \tag{21}$$

in the adiabatic approximation for the ion subsystem, where $\gamma(\omega)$ and $\nu(\omega)$ are taken from (19) and (17), respectively.

We can use this result to construct a rigorous basis for the concept of an effective mass for describing the real part of the dielectric constant:

$$\operatorname{Re}\varepsilon(\omega)=1-\omega_p^{*2}/\omega^2, \tag{22}$$

where

$$\omega_p^*=\left(\frac{4\pi ne^2}{m^*}\right)^{1/2},\quad m^*(\omega)=\frac{m}{1+\gamma(\omega)}. \tag{23}$$

In summary, expressions (14), (19), and (21) for the complex dielectric constant at frequencies $\omega \gg \nu$ have been derived by a pseudopotential approach in the adiabatic approximation for the ion subsytem, with allowance for strong ion-ion and electron-electron correlations.

4. To carry out calculations on the optical properties of liquid metals we need to know the Fourier component of the pseudopotential, the dielectric constant of the electron gas, and the ion structure factor, as can be seen from (14) and (19). We have calculated the high-frequency conductivity of liquid sodium at $T = 400$ K, and we have compared the results with the experimental data of Ref. 1. As the structure factor for the ion subsystem we adopted that for a hard-sphere potential,[17] which is a good approximation for liquid alkali metals. To determine the packing parameter we used the limiting relation[18]

$$\lim_{k\to 0}S_i(k)=n_iT\chi_T,\quad \chi_T=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \tag{24}$$

where χ_T is the isothermal compressibility.

To describe the electron-ion interaction we adopted the Ashcroft pseudopotential

$$V^A(r)=\begin{cases}0, & r\leqslant R\\ -e^2/r, & r>R\end{cases}. \tag{25}$$

Its Fourier component is

$$V_k^A=-\frac{4\pi e^2}{k^2}\cos(kR). \tag{26}$$

We have only a single adjustable parameter here. It is customary to use the *RPA* to describe a degenerate electron gas, although we know that at real densities this approximation has some important shortcomings, which rule out a good quantitative agreement with experiment. A question of independent interest is how the electron correlations in a degenerate electron gas, primarily the exchange correlations, affect the properties of the system as a whole. Furthermore, if a good quantitative agreement with experiment can be achieved then a suitable description of the dielectric constant of the electron gas would make it possible to determine the adjustable parameter of the pseudopotential, *R*.

Many theoretical papers have addressed the problem of taking exchange-correlation effects into account in the dielectric constant of a degenerate electron gas in an approximate way. These effects are customarily described by some function $G(k,\omega)$:

$$\varepsilon_e^\circ(k,\omega)=1-\frac{V_{ee}\Pi_{ee}^{RPA}(k,\omega)}{1+G(k,\omega)V_{ee}\Pi_{ee}^{RPA}(k,\omega)}. \tag{27}$$

For the values of the electron-electron interaction pa-

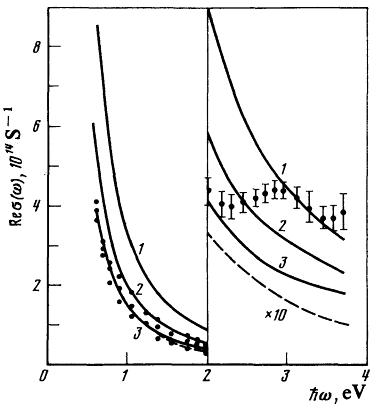

FIG. 1. High-frequency conductivity of liquid sodium at $T = 400$ K vs the frequency (ω) of the external field with $R = 1.67$ a.u. For high frequencies the vertical scale has been multiplied by a factor of 10. 1—theoretical, with the function $G(k,0)$ from Ref. 19; 2—theoretical, with $G(k,0)$ from Ref. 21; 3—theoretical, RPA; dashed curve—calculation from the Drude formula with $\nu = \lim_{\omega\to 0}\nu(\omega)$; points—experimental data.[1]

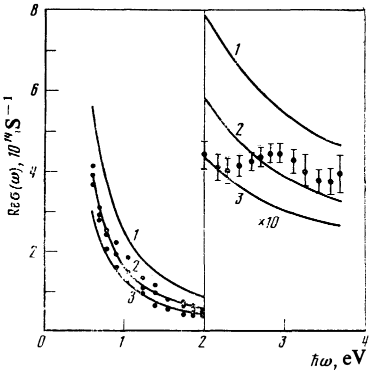

FIG. 2. High-frequency conductivity of liquid sodium at $T = 400$ K vs the frequency (ω) of the external field with $R = 1.8$ a.u. At high frequencies the vertical scale has been multiplied by a factor of 10. 1—theoretical, with the function $G(k,0)$ from Ref. 21; 2—theoretical, with $G(k,0)$ from Ref. 20; 3—theoretical, RPA; points—experimental data.[1]

rameter r_s characteristic of metals, 2–6, we do not have a regular procedure for evaluating the function $G(k,\omega)$. We are thus forced to use approximate methods based on physically reasonable approximations which satisfy the well-known exact relations for $\varepsilon_e^0(k,\omega)$ (the sum rule for the compressibility, etc.). This approach naturally leads to some ambiguity in $G(k,\omega)$, and different approximations, seemingly similar in a qualitative sense, can lead to large numerical discrepancies in the description of the properties of real metals. The corresponding questions are discussed in detail by Utsimi and Ichimaru,[19] for example, who also give a detailed bibliography.

Toigo and Woodruff[20] have shown that

$$G(k,\omega) \approx G(k,0). \tag{28}$$

They used expressions derived in Refs. 19 and 21 for $G(k,0)$. It can be seen from Figs. 1 and 2 that taking the exchange-correlation effects in an electron gas into account has a strong effect on the conductivity over the entire frequency range studied. The conductivity values calculated with allowance for electron correlations are far higher than the values calculated in the RPA. We are furthermore struck by the substantial difference in the results found when different approximations are used for $G(k,0)$.

It can be concluded from this calculation of the conductivity that an increase in the pseudopotential parameter R reduces the conductivity at relatively low frequencies and increases the conductivity at higher frequencies. Evidently the only way to identify some preferred approximation of the function $G(k,0)$ and a preferred model pseudopotential is to compare the theoretical and experimental data over broad ranges of the frequency and the temperature. For the experimental data available,[1] we find a good agreement between theory and experiment by using Hubbard's[21] function $G(k,0)$, and $R = 1.8$.

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[1] T. Inagaki, E. T. Arakawa, R. D. Birkhoff, and M. W. Williams, Phys. Rev. **B13**, 5610 (1976).
[2] N. V. Smith, Adv. Phys. **16**, 629 (1967).
[3] T. E. Faber, Adv. Phys. **5**, 547 (1966).
[4] J. S. Helman and W. Baltensperger, Phys. Condens. Matter. **5**, 60 (1966).
[5] J. S. Helman and W. Baltensperger, Phys. Rev. **B15**, 4109 (1977).
[6] J. J. Hopfield, Phys. Rev. **A139**, 419 (1965).
[7] C. J. Petchick, Phys. Rev. **B2**, 1789 (1970).
[8] K. Sturm and E. Pajanne, J. Phys. F **3**, 199 (1973).
[9] M. Baus and J.-P. Hansen, Phys. Rep. **59**, 1 (1980).
[10] D. B. Boercker, Phys. Rev. **A23**, 1969 (1981).
[11] S. A. Trigger, Phys. Lett. **56A**, 325 (1976).
[12] V. P. Silin and A. A. Rukhadze, Élektromagnitnye svoĭstva plazmy i plazmopodobnykh sred (Electromagnetic Properties of Plasmas and Plasma-Like Media), Atomizdat, Moscow, 1961.
[13] D. B. Boercker, F. J. Rogers, and H. E. DeWitt, Phys. Rev. **A25**, 1623 (1982).
[14] N. I. Klyuchnikov and S. A. Triger, Dokl. Akad. Nauk SSSR **238**, 565 (1978).
[15] N. I. Klyuchnikov and S. A. Triger, Teor. Mat. Fiz. **39**, 368 (1967).
[16] V. I. Perel' and G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **41**, 886 (1961) [Sov. Phys. JETP **14**, 633 (1962)].
[17] D. Wertheim, Phys. Rev. Lett. **10**, 321 (1963).
[18] H. Watabe and M. M. Hasegawa, The Properties of Liquid Metals, London, 1973, p. 133; J. Chihara, p. 137.
[19] K. Utsimi and S. Ichimaru, Phys. Rev. **A26**, 603 (1982).
[20] F. Toigo and T. O. Woodruff, Phys. Rev. **B4**, 4312 (1971).
[21] J. Hubbard, Proc. R. Soc. London **A243**, 336 (1958).

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