$$= \sum_{n=0}^{3} \int_{n\pi/2}^{n\pi/2+\Phi} e^{\mp 2i\varphi}\, d\varphi - \sum_{n=0}^{3} \int_{0}^{\Phi} e^{\mp 2i(\varphi' - n\pi/2)} Q_{\pm} e^{-d_{\pm}\varphi'/\omega_c\tau} d\varphi' = 0, \tag{B2}$$

where $\Phi = \frac{1}{2}\pi - \Delta\varphi/4$. Thus the Bragg reflections do not mix the two senses of circular polarization and we have

$$j_{\pm} = 2(2\pi)^{-3} em\hbar^{-2} \int v_{\pm} f_{1\pm}\, d\varphi\, dk_z\,, \tag{B3}$$

where we have integrated over dE and the $\partial f_0/\partial E = -\delta(E - E_F)$ factor in $f_{1\pm}$ causes the $d\varphi dk_z$ integration to be restricted to the Fermi surface. Substituting (5) in (B3) and noting from (6) and (12) that $qv_z/d_{\pm} = (1 - b_{\pm}/d_{\pm})/\tau$ we have

$$j_{\pm} = \frac{2\tau em}{(2\pi\hbar)^2} \frac{1}{2\pi} \int v_{\perp}^2 \left[\frac{e\mathcal{E}_{\pm}}{d_{\pm}} - \frac{im\omega u_{\perp}}{2\tau} \left(1 - \frac{b_{\pm}}{d_{\pm}}\right) \right] \times \left[1 - Q_{\pm} e^{-d_{\pm}(t-t_1)/\tau}\right] d\varphi\, dk_z\,, \tag{B4}$$

where we have dropped a factor of $e^{i(\vec{q}\cdot\vec{R} - \omega t)}$. The entire φ dependence of the integrand is in $(t - t_1)$, which may be replaced by φ/ω_c and integrated over $0 \le \varphi \le \Phi$ in each of the four sections of the hole orbit (for electron orbits there is no φ dependence and a factor 2π is obtained from the φ integration) to yield Eq. (10).

*Research sponsored by the U.S. Air Force Office of Scientific Research, Office of Aerospace Research, under Grant No. AFOSR 68-1507.

†Present address: Universidad Nacional de Ingenieria, Lima, Peru.

[1]T. Kjeldaas, Jr., Phys. Rev. 113, 1473 (1959).

[2]M. H. Cohen, M. J. Harrison, and W. A. Harrison, Phys. Rev. 117, 938 (1960).

[3]S. G. Eckstein, Phys. Rev. Letters 16, 611 (1966).

[4]J. R. Boyd and J. D. Gavenda, Phys. Rev. 152, 645 (1966).

[5]L. Kleinman, Phys. Rev. 182, 686 (1968) (hereafter called I).

[6]A. B. Pippard, Proc. Roy. Soc. (London) A257, 165 (1960).

[7]J. D. Gavenda [Phys. Rev. B 1, 3884 (1970)] has shown that the exact deformation potential in I is equivalent to Pippard's. We had incorrectly stated in I that the FED approximation was equivalent to Pippard's deformation potential.

[8]P. R. Sievert, Phys. Rev. 161, 637 (1967).

[9]See the Appendix in I.

[10]Consider, for instance, an intrinsic semiconductor. The current associated with a long-wavelength phonon is negligible because the valence electrons follow the ions in their motion even though those same electrons give no contribution to the zero-frequency conductivity.

[11]Besides the usually negligible contribution mentioned above collision drag also enters the jellium calculation through the distribution function.

[12]We have corrected an unimportant sign mistake in (15).

[13]From Figs. 1(a) and 1(b) one easily sees that $\Delta\varphi/4 = 2\cos^{-1}(K/2k_{\perp})$, where $k_{\perp}^2 = k_F^2 - k_z^2$.

[14]The -1 in $N(1/G - 1)$ is important only for large fields where it makes the attenuation approach zero.

PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Density of Electronic States in Liquid Aluminum

M. M. Pant, M. P. Das, and S. K. Joshi
Physics Department, University of Roorkee, Roorkee, India

(Received 1 February 1971)

The density-matrix approach due to March and his collaborators is used to obtain the electronic density of states of liquid metals. A model potential is used for liquid aluminum, and the density of states is calculated for both completely random and correlated systems. Results are compared with previous calculations, and nearly-free-electron-like behavior is found for liquid aluminum.

I. INTRODUCTION

In recent years the study of electronic states in liquid metals[1] has received considerable attention. The effort has been mostly directed towards developing formal techniques for tackling the problem of cellular disorder. There have been rather few attempts to evaluate the theoretical expressions numerically for real systems.

Ballentine[2] has calculated the density of states in several liquid metals by using the Green's-function method of Edwards.[3] He used a local energy-independent Heine-Abarenkov-type potential. Ballentine used Edwards's theory but replaced the

free-electron propagator in the second-order self-energy with the exact propagator. This is equivalent to extracting a particular set of diagrams from the self-energy expression and summing these diagrams to all orders in perturbation. There have also been calculations for some liquid metals using a nonlocal optimum model potential employing essentially a perturbation-theory approach.[4]

A nonperturbative approach has also been proposed recently by Rousseau *et al.*[5] They have used a model of independent pseudoatoms to obtain the partition function of a random array as well as a correlated arrangement of scatterers. They have obtained the density of states for liquid Be.

In this paper we report a calculation of the density of states in liquid aluminum using essentially the approach of Rousseau *et al.* Aluminum was chosen because for this system a number of calculations for the density of states have been attempted using other methods.[2,6] The results could therefore be compared with the results of other theoretical investigations and experimental measurements.[7]

In Sec. II we outline the basic approach and approximations of the pseudoatom model. We give in Sec. III the details of applications to aluminum. The results are discussed in Sec. IV.

II. OUTLINE OF THEORY

We shall summarize the theory of independent pseudoatoms due to Rousseau *et al.*[5] in order to establish the notation and provide a framework for the discussion of results. There are two essential steps in the calculation of the density of states in a liquid. First the partition function is obtained for a given configuration. Then the ensemble averaging is done to obtain the density of states.

The total potential $V(\vec{r})$ in the assembly is regarded as a sum of localized potentials $v(\vec{r})$ centered on $\vec{R}_i$, the position of the ith ion:

$$V(\vec{r}) = \sum_{R_i} v(\vec{r} - \vec{R}_i). \tag{1}$$

The partition function is defined by

$$Z(\beta) = \sum_i \exp(-\beta\epsilon_i) = \int C(\vec{r}, \vec{r}; \beta)\, d\vec{r}\,, \tag{2}$$

where ϵ_i is the ith eigenvalue of the single-particle Hamiltonian, $H = -\nabla^2 + V(\vec{r})$, $\beta = 1/kT$, and $C(\vec{r}, \vec{r}_0; \beta)$ is the canonical density matrix given by

$$C(\vec{r}, \vec{r}_0; \beta) = \sum_i \psi_i^*(\vec{r})\psi_i(\vec{r}_0)\exp(-\beta\epsilon_i)\,. \tag{3}$$

If we have a slowly varying potential, the eigenvalues change by V, whereas the wave functions remain essentially unchanged. Then for the potential given in Eq. (1) we can write

$$C(\vec{r}, \vec{r}; \beta) = C_0(\vec{r}, \vec{r}; \beta)\exp[-\beta\textstyle\sum_i v(\vec{r} - \vec{R}_i)]\,, \tag{4}$$

where $C_0(\vec{r}, \vec{r}_0; \beta)$ is the free-particle density matrix. If V is not slowly varying, we generalize (4) to

$$C(\vec{r}, \vec{r}_0; \beta) = C_0(\vec{r}, \vec{r}; \beta)\exp[-\beta U(\vec{r}, \vec{r}_0; \beta)]\,. \tag{5}$$

Here U is called the effective potential matrix. $U(\vec{r}, \vec{r}; \beta) \equiv U(\vec{r}; \beta)$ defines the pseudoatom. We further write $U(\vec{r}; \beta) = \sum_{R_i} u(\vec{r} - \vec{R}_i; \beta)$ so that the system may be looked upon as a collection of independent pseudoatoms described by the above canonical density matrix involving effective potential U instead of actual potential $V(\vec{r})$.

A function analogous to the Mayer function in classical statistical mechanics is introduced:

$$f(\vec{r}; \beta) = \exp[-\beta u(\vec{r}; \beta)] - 1\,, \tag{6}$$

so that

$$C(\vec{r}; \beta) = C_0(\vec{r}; \beta)\left(1 + \sum_{R_i} f(\vec{r} - \vec{R}_i; \beta) + \frac{1}{2!}\sum_{R_i}\sum_{R_j} f(\vec{r} - \vec{R}_i; \beta) f(\vec{r} - \vec{R}_j; \beta) + \cdots\right). \tag{7}$$

The series (7) has to be ensemble averaged. In order to find the configurational averages for a set of correlated scatterers, higher-order correlation functions are needed. Three-body correlation functions are expressed in terms of two-body correlation functions by the Abe approximation:

$$\rho^{(3)}(r_1, r_2, r_3) \simeq \tfrac{1}{3}[g(r_{12})g(r_{13}) + g(r_{21})g(r_{23}) + g(r_{31})g(r_{32})]\,. \tag{8}$$

Similarly, the nth-order correlation functions may be expressed in terms of $g(r_{ij})$. Thus

$$Z(\beta) = (2\pi\beta)^{-3/2}\left[1 + \rho\int d\vec{r} f(\vec{r}; \beta) + \int d\vec{r}_1 f(\vec{r}_1, \beta) \times\left(\frac{1}{2!}\rho^2 G(\vec{r}_1) + \cdots + \frac{1}{n!}\rho^n G^{n-1}(\vec{r}_1) + \cdots\right)\right], \tag{9}$$

with $G(\vec{r}) = \int d\vec{r}_2 f(\vec{r}_2; \beta) g(r_{12})$, and so on. The terms in the series (9) can be summed to yield

$$Z(\beta) = (2\pi\beta)^{-3/2}\times\left(1 + \int d\vec{r}_1 \frac{f(\vec{r}_1; \beta)\{\exp[\rho G(\vec{r}_1)] - 1\}}{G(\vec{r})}\right). \tag{10}$$

For a model of random pseudoatoms we have $g(r) = 1$, so that Eq. (10) reduces to

$$Z(\beta) \equiv (2\pi\beta)^{-3/2} \exp[\beta\alpha(\beta)] , \tag{11}$$

where $\alpha(\beta) = (\rho/\beta) \int d\vec{r} f(\vec{r}, \beta)$ and ρ is the number of ions per unit volume.

The partition function $Z(\beta)$ is related to the density of states $n(E)$ by the Laplace transformation

$$Z(\beta) = \int_{-\infty}^{+\infty} n(E) \exp(-\beta E)\, dE . \tag{12}$$

III. APPLICATION TO ALUMINUM

In order to calculate the electronic density of states, we have to start with a suitable choice of the potential. Here we use a potential in the following analytical form due to Green *et al.*[8]:

$$v(r) = 2(N\gamma - z)/r , \tag{13}$$

where

$$\gamma = 1 - \{[\exp(r/d) - H] + 1\}^{-1} , \tag{14}$$

z is the number of nuclear protons, N is the number of core electrons, and H and d are two parameters. These parameters are determined by fitting the energy values and wave functions with those calculated from the Hartree-Fock-Slater method by Herman and Skillman.[9] The values of these parameters for aluminum used by us are $H = 1.8312$ and $d = 0.7290$. This simple analytical form which yields the same energies and wave functions as the Herman-Skillman potential is thus a reasonable choice for the single-center potential. With this choice the effective potential matrix can be determined in an analytical form.

Hilton *et al.*[10] have shown that in the linear approximation [ignoring $\nabla U(\vec{r})$] the effective potential matrix $U(\vec{r}; \beta)$ is written as

$$U(\vec{r}, \vec{r}_0; \beta) = \int \mathcal{G}(\vec{r}, \vec{r}_0, \vec{r}')\, v(\vec{r}')\, d\vec{r}' , \tag{15}$$

with

$$\mathcal{G}(\vec{r}, \vec{r}_0, \vec{r}') = \frac{\exp(|\vec{r} - \vec{r}_0|^2/2\beta)}{2\pi\beta} \frac{|\vec{r} - \vec{r}'| + |\vec{r}' - \vec{r}_0|}{|\vec{r} - \vec{r}'|\,|\vec{r}' - \vec{r}_0|} \exp\left(-\frac{(|\vec{r} - \vec{r}'| + |\vec{r}' - \vec{r}_0|)^2}{2\beta}\right) . \tag{16}$$

We are interested in the diagonal element $U(\vec{r}; \beta)$ given by

$$U(\vec{r}; \beta) = \frac{1}{\pi\beta} \int \frac{d\vec{r}'\, v(\vec{r}') \exp(-2|\vec{r} - \vec{r}'|^2/\beta)}{|\vec{r} - \vec{r}'|} . \tag{17}$$

Using the form (13) for $v(r)$, we obtain

$$U(r, \beta) = -\frac{2Nd}{(1-H)r\beta} \left(\frac{\pi\beta}{2}\right)^{1/2} \sum_n (-1)^{n+1} \exp\left(\frac{-n^2}{2\rho d^2}\right) \times \operatorname{erfc}\left[\left(\frac{2}{\beta}\right)^{1/2} \left(r + \frac{n\beta}{4d}\right)\right] \left\{\left[\exp\left(\frac{nr}{d}\right) - \exp\left(\frac{-nr}{d}\right)\right] d^{-n}\right\} . \tag{18}$$

As mentioned in Sec. II, this approach is valid for

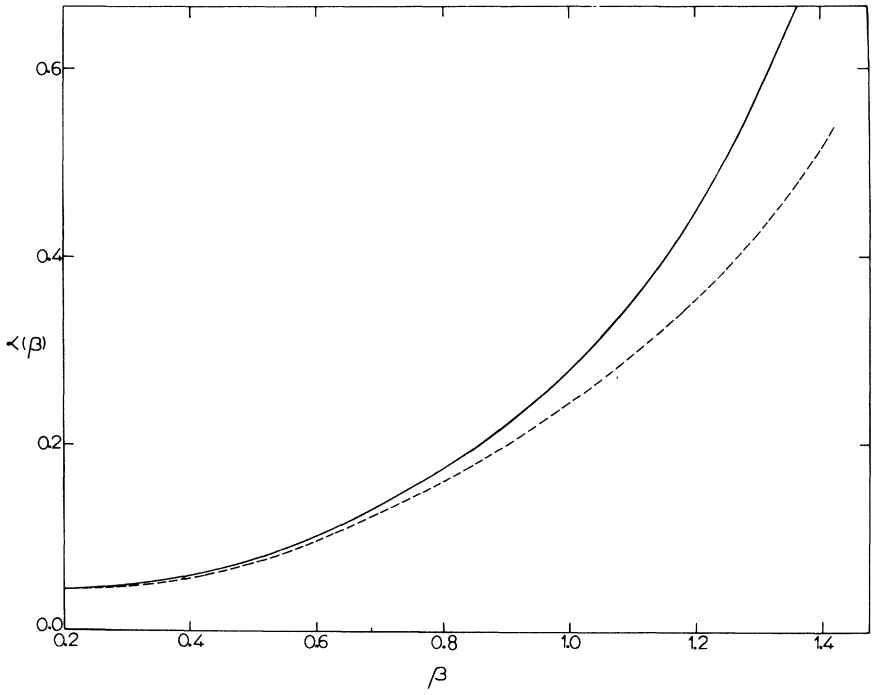

FIG. 1. Plot of $\alpha(\beta)$ vs β in a.u. Solid line represents the results for the random assembly; dashed line shows them for the correlated assembly.

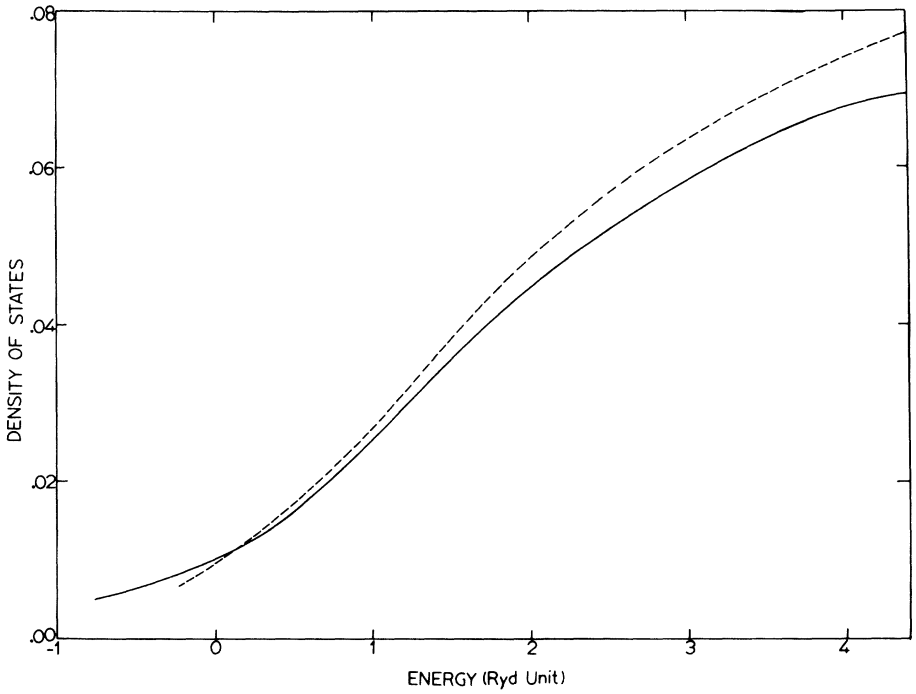

FIG. 2. Calculated densities of states. Solid line is for the random assembly; dashed line is for the correlated one.

a slowly varying potential or a weak potential. We cannot apply the method in this form for a real metal having strongly attractive potentials and possessing bound states. Hence it is necessary to orthogonalize the density matrix to the known bound states of the system following the method due to Hilton *et al.*[10] The orthogonalized-density-matrix approach is applicable for a strong scattering potential also.[5,11]

Now the orthogonalized density matrix is used to calculate $Z(\beta)$ for both random and correlated assembly. In the latter case the required radial dis-

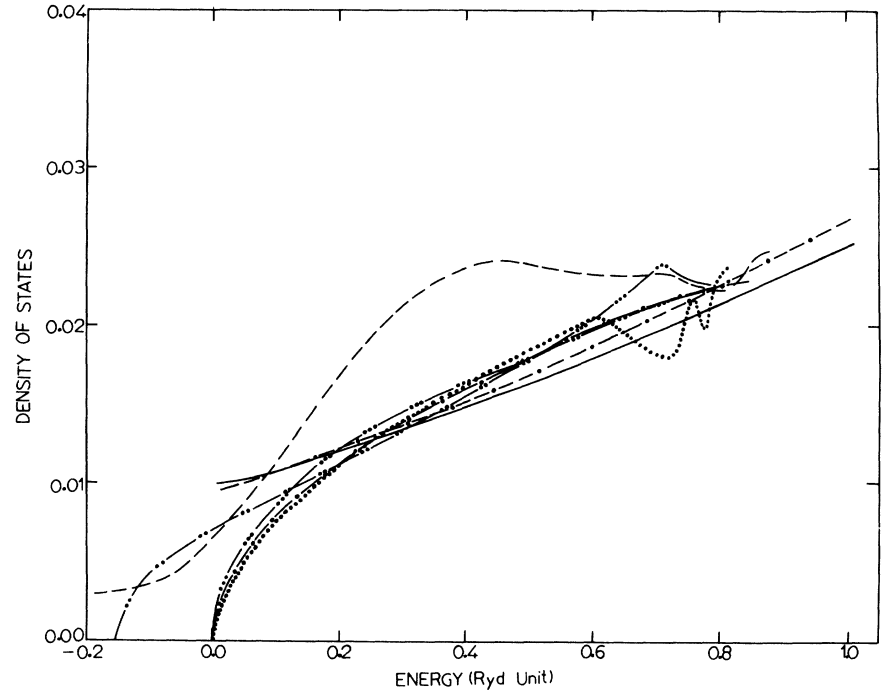

FIG. 3. Comparison of densities of states--·-, free-electron scheme; -···-, Edwards's theory (Ref. 2); -····-, pseudopotential method (Ref. 14); ···, Monte Carlo method (Ref. 6); ---, soft x-ray measurements of Rooke (Ref. 7); -, present calculation for random assembly; --·--, present calculation for correlated system.

tribution functions are taken from the numerical solutions of Percus-Yevick equations of the hard-sphere assembly.[12]

In principle, the inversion of the partition function gives the density of states, but difficulty arises in a calculation, because $Z(\beta)$ is known numerically for certain values of β. We perform the inversion by making use of the method of first-order steepest descent due to Hoare and Ruijgork.[13] They have shown that this method gives reasonably good results when compared to exact analytical solutions for some simple cases.

IV. DISCUSSION

In Fig. 1 we plot $\alpha(\beta)$ for both the random and correlated cases. It is seen that the difference between the results for random and correlated assembly increases with increasing β. For small values of β the curve for the random assembly lies close to that for the correlated one.

The density of states is shown in Fig. 2 for both the random and correlated systems for a wide range of energy. As mentioned above, an analytical evaluation of the density of states from the partition function is not possible here; therefore, we have calculated numerically the density of states by Laplace inversion of (16) using six values of β ($\beta = 0.3$, 0.5, 0.7, 0.9, 1.1, and 1.3 in a. u.).

The density of states for liquid aluminum obtained by the present method is compared with the results of other calculations in Fig. 3. The calculations by other workers were based on free-electron scheme, Edwards's theory,[2] Monte Carlo calculations,[6] and the pseudopotential method.[14] The density-of-states curve obtained from the soft x-ray emission measurements of Rooke[7] is also shown. The pseudoatoms tend to lower the value of the density of states at higher energies as compared to free-electron results. For locating the low-energy conduction edge we shall have to undertake tedious calculations using values of $Z(\beta)$ at many values of β higher than those used here.

The singularities in the density of states are washed out in our calculations for the disordered assembly. We also find that our results for the density of states are close to those for the free-electron scheme. This shows the nearly-free-electron-like behavior of electrons in liquid aluminum.

ACKNOWLEDGMENTS

We are thankful to the authorities of Tata Institute of Fundamental Research, Bombay, for use of their computer facilities. One of us (M. M. P.) is grateful to Professor N. H. March for helpful discussions and correspondence. He is also grateful to the Department of Atomic Energy, Government of India, and another of us (M. P. D.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for financial support.

[1] P. Phariseau and J. M. Ziman, Phil. Mag. 8, 1487 (1963); see also a conference report, Advan. Phys. 16 (1967).

[2] L. E. Ballentine, Can. J. Phys. 44, 2533 (1966).

[3] S. F. Edwards, Proc. Roy. Soc. (London) A267, 518 (1962).

[4] R. W. Shaw, Jr. and N. V. Smith, Phys. Rev. 178, 985 (1969).

[5] J. Rousseau, J. C. Stoddart, and N. H. March, Proc. Roy. Soc. (London) A317, 221 (1970).

[6] D. Brust, Phys. Rev. B 2, 818 (1970).

[7] See, for example, G. A. Rooke, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland, Amsterdam, 1966), p. 336.

[8] A. E. S. Green, D. L. Sellin, and A. S. Zadur, Phys. Rev. 184, 1 (1969).

[9] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[10] D. Hilton, H. H. March, and A. R. Curtis, Proc. Roy. Soc. (London) A300, 391 (1967).

[11] N. H. March and J. C. Stoddart, Rept. Progr. Phys. 31, 533 (1968).

[12] G. J. Throop and R. J. Bearman, J. Chem. Phys. 42, 2408 (1965).

[13] M. R. Hoare and Th. W. Ruijgrok, J. Chem. Phys. 52, 113 (1970).

[14] See, for example, N. W. Ashcroft, cited in G. Wiech, in *Soft X-ray Band Spectra*, edited by J. Fabian (Academic, New York, 1968), p. 59.