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Conduction regimes in expanded liquid mercury[*]

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In this paper we present a coherent physical picture of four electronic transport regimes in expanded liquid mercury. We propose that the first two metallic regions, i.e., the propagation regime ($\rho > 11.0$ g cm^{-3}) and the diffusion regime ($9.2 < \rho < 11.0$ g cm^{-3}), are separated from the semiconductor regime ($\rho < 7.8$ g cm^{-3}) by a third conduction regime where the material is microscopically inhomogenous with regard to electron transport. Density fluctuations in a one-component system characterized by a mean interatomic spacing $2r_s$ were handled by considering the density-density-correlation function. The latter is characterized by the Ornstein-Zernike decay length ξ and by the Debye short correlation length b. The necessary conditions $b > 2r_s$ and $b > \xi$ imply the existence of structual fluctuations which are independent when separated by more than $2b$. Local electronic structure and local response functions will exist in a disordered material provided that the phase coherence length l of the electronic wave functions is appreciably shorter than b, and given that quantum corrections associated with the inhomogeneities, i.e., tunneling and kinetic-energy contributions, are small. The transport properties of such a system were handled by a general effective-medium theory, which was formally reduced to the problem of transport in a two-component system. Assuming that liquid mercury in the density range 9.3–8.0 (g cm^{-3}) is characterized by a sufficiently large value of b, we were able to provide a complete semiquantitative interpretation of the transport data accounting for the slow variation of the Hall mobility, and for the volume and temperature coefficients of the conductivity in that density region. The analysis of the conductivity data together with our statistical fluctuation theory results in a value of $b = 15$ Å for the average radius of the density fluctuation, whereupon the requirements of internal consistency of our picture are well satisfied. To establish the validity of the semiclassical percolation picture we have provided estimates of the magnitude and relative importance of tunneling and kinetic-energy effects, establishing that these corrections are quantitatively small for this high-temperature system. In the inhomogenous regime, density fluctuations lead to localization and percolation, and the metal-nonmetal transition should be envisioned in terms of a continuous change of the conductivity.

I. INTRODUCTION

A recent series of experimental papers by Hensel[1-7] and colleagues was devoted to the study of the electrical conductivity,[1-5] thermoelectric power,[5,6] and optical properties[7] of subcritical and supercritical mercury, demonstrating the existence of several distinct regimes of electron transport in this one-component system. Subsequently, Even and Jortner[8,9] showed by combined electrical conductivity σ and Hall-effect R measurements that three distinct conduction regimes can be identified at Hg densities ρ above 8.5 g cm^{-3}. For $11 < \rho < 13.6$ g cm^{-3}, the Hall coefficient has the free-electron value $R_{\text{fe}} = (Nec)^{-1}$, and the conductivity exhibits no particular relation to R. For $9.2 < \rho < 11.0$ g cm^{-3}, σ is proportional to $(R_{\text{fe}}/R)^2$, whereupon the Hall mobility follows $\mu_H \propto (R_{\text{fe}}/R)$. Finally, for $8.5 < \rho < 9.2$ g cm^{-3}, μ_H is only weakly dependent on R_{fe}/R. At still lower densities, $5.0 < \rho < 7.8$ g cm^{-3}, Schmutzler and Hensel[5,6] have established a correlation between σ and thermoelectric power S of the form $\ln(\sigma/\sigma_0) = -\alpha e|S|/k$, $\alpha \approx 1$, indicating the existence of a fourth, semiconducting, regime in expanded liquid mercury.

Additional experimental information relevant to the physical nature of electron transport in expanded mercury comes from the dependence of σ and S on indium concentration in dilute amalgams. Zillgit and Hensel[10(a),10(b)] showed that a strong influence on In concentration (in the range 0.75–3%) on σ is exhibited for $\rho \leq 8.6$ g cm^{-3}.[10(c)] To complete this survey we should mention that Hensel has measured the extinction coefficient of supercritical mercury vapor[7] for $\rho \leq 3.89$ g cm^{-3}. Extrapolation of the observed absorption edges resulted in a vanishing energy gap at $\rho \sim 5.5$ g cm^{-3}.

In this paper we are concerned with developing a coherent physical picture of all the four transport regimes in expanded liquid mercury. Before developing our ideas, however, it will be necessary to review briefly the current theoretical background to this problem.

Ziman[11] and Faber[12] have shown in normal liquid metals, where the mean free path considerably exceeds the reciprocal Fermi wave number, that in the lowest-order corrections to the Born approximation there is a cancellation of those changes in the conductivity resulting from changes in the density of states. At the same order the Hall coefficient exhibits changes from R_{fe} which are determined by the ratio of the density of states at the Fermi energy to the free-electron value.[11(b)] Fukuyama *et al.*[13] have predicted that incorporation of high-order effects may result in significant deviations of R from R_{fe}. We term the regime in which a perturbation expansion in powers of the potential converges well the propagation (weak-scattering) regime. Although the theoretical situation concerning the Hall coefficient is confused, we may conclude that in this regime there is no special relation between σ and R_{fe}/R.

Friedman[14] has studied transport in a crystal with a tight-binding s band. He assumes that the wave-function amplitudes are everywhere constant but the phases on different sites are uncorrelated. He then inserts these wave functions into the Kubo-Greenwood formulas and obtains[14]

$$\sigma = \tfrac{2}{3}\pi(e^2/\hbar a)\,zX^2, \tag{1a}$$

$$R = (3\eta\bar{z}/z^2)(a^3/ec)X^{-1}, \tag{1b}$$

$$\mu_H = R\sigma = (2\pi\eta\bar{z}/z)(ea^2/\hbar)X, \tag{1c}$$

where z is the number of nearest neighbors; $\bar{z}$ is the number of triangular closed paths around each lattice site; $\eta \simeq \frac{1}{3}$ is a geometrical factor; a is the internuclear separation; and the parameter

$$X = J\,a^3 n(E_F) \tag{2}$$

contains J, the nearest-neighbor electron-transfer integral, and the density of states $n(E_F)$ at the Fermi energy E_F. Since all parameters except X can be readily estimated in particular situations, it is more convenient[8,6] to relate σ and μ_H to R_{fe}/R,

$$\sigma = \frac{\sigma\pi\eta^2}{z}\left(\frac{\bar{z}}{z}\right)^2\left(\frac{e^2}{\hbar a_0}\right)\left(\frac{\rho}{\rho_0}\right)^{1/3}\left(\frac{R_{\mathrm{fe}}}{R}\right)^2, \qquad \mu_H = \frac{\sigma\pi\eta^2}{z}\left(\frac{\bar{z}}{z}\right)^2\left(\frac{ea_0^2}{\hbar}\right)\left(\frac{\rho}{\rho_0}\right)^{-2/3}\left(\frac{R_{\mathrm{fe}}}{R}\right), \tag{3}$$

where a_0 is the internuclear separation at the density ρ_0. In this form, one can hope that Friedman's results are of more general applicability in this diffusion or Brownian-motion, i.e., strong-scattering, regime than the particular model for which they were derived.

Friedman[14] has related in a rough way the transport coefficients he derived to g, Mott's[15] ratio of density of states to free-electron density of states,

$$R_{\mathrm{fe}}/R \simeq (1/4\eta f)(z/\bar{z})g, \tag{4}$$

where f is a filling factor relating Fermi energy to bandwidth W,

$$E_F = fW, \tag{5}$$

and

$$g = n(E_F)/n_{\mathrm{fe}}(E_F). \tag{6}$$

Similarly σ can be approximately related linearly[15] to g^2.

Mott[15-19] has proposed that a pseudogap, i.e., a range of localized states, can occur in a disordered system when g falls below g^* which he estimates[16,17] to be about $g^* \simeq \frac{1}{3}$. The boundaries of this pseudogap or mobility gap are the mobility edges and within it the mobility is low. Accordingly when E_F lies within this gap, transport is nonmetallic in character. Mott has also pointed out[15] that in a fluid consisting of widely separated mercury atoms, the s and p bands would be separated by a gap and the s band full. Thus, when g falls to $\frac{1}{3}$ as the density is reduced, a metal-semiconductor transition occurs as the pseudogap opens near the Fermi energy.

The nature of the wave functions near the mobility edges and in the pseudogap has been elucidated by Cohen.[20] His basic point is that long-range fluctuations in the potential are crucial for the transition from extended to localized states at a mobility edge. Hence, semiclassical considerations are sufficient there, and the problem reduces to one similar to that first considered by Ziman,[21] percolation of a classical particle in a random potential. Let $C(E)$ be that fraction of the total volume which is classically allowed. The mobility edge E_c occurs when $C(E)$ reaches the percolation value C^*,

$$C(E_c) = C^*. \tag{7}$$

No calculations are available for this continuum site-percolation problem. For the lattice case,[22] C^* ranges from 0.16 for fcc to 0.30 for simple cubic (sc). We estimate C^* to be roughly 0.2, so that

$$C(E_c) = 0.2. \tag{8}$$

Equation (8) is consistent with Zallen and Scher's estimate of C^*.[22(b)]

Conductivity above the mobility edges occurs through percolation channels, as it does at E_F when $C(E_F) \gtrsim 0.2$. Thus, as Kirkpatrick[23] has emphasized, one has transport within a submacroscopically inhomogeneous medium. For $C(E_F) > 0.4$, Kirkpatrick's numerical results[23] imply that the simple effective-medium theory[24] is adequate, when $\sigma \propto [\frac{3}{2}C(E_F) - \frac{1}{2}]$, and he claims that $R \propto P^{-1}[C(E_F)]$ where P is the percolation probability. For $C(E_F) < 0.4$, his detailed numerical calculations[23] show that

$$\sigma \propto [C(E_F) - C^*]^{8/5}, \tag{9}$$

when the conductivity of the "excluded" paths is negligible. We shall see that for Hg it is essential to include contributions to σ from the low-conductivity regions.

Eggarter and Cohen[25] have used the semiclassical picture for electrons in dense He vapors. They find agreement with the measured mobility over six orders of magnitude utilizing a statistical sampling length of 1.7 times the De Broglie wavelength. Cohen and Sak[26] have developed a semiclassical theory of the metal-semiconductor transition in liquid or amorphous binary alloys. Electrons near the Fermi energy are excluded from clusters of the compound composition in the alloy by Bragg reflection. The density of states is then approximately[26]

$$n(E) = n_0(E)C(E), \tag{10}$$

where $n_0(E)$ is the density of states of a homogeneous metal having the composition of the material outside the clusters. There is no reason for $n_0(E)$ to be the free-electron density of states, so that we must write

$$g(E) = g_0(E)C(E). \tag{11}$$

The condition for pseudogap formation is then

$$\min_E[C(E)] = C^* \cong 0.2 \tag{12}$$

as distinct from

$$\min_E[g(E)] = g^* \cong \tfrac{1}{3} \tag{13}$$

as proposed by Mott.[16-20]

The validity of the semiclassical picture just at the mobility edge has been challenged by Mott.[27] His main point appears to be that potential fluctuations large enough for tunneling to be ineffective in erasing classical inhomogeneities in the electron motion are improbable except where the fluctuations are very slowly varying, as near a critical point.[27(b)] In his view, one can consider the wave-function amplitude as everywhere comparable except in the latter special case. This implies, via the Kubo-Greenwood formalism and the assumption of random phases, that the conductivity decreases abruptly from the diffusion limit to zero at the mobility edge at $T = 0$ in contrast to Eq. (9). In our view, the energy range in which percolation effects within the semiclassical picture are important depends on the Debye short correlation length[28] and the amplitudes of the fluctuations. In the case where the Debye short correlation length b is long, as for clusters, the inhomogeneities in the potential are smooth enough, within a deformation-potential-type of formalism, that the semiclassical picture is quantitatively valid. If, further, the potential fluctuations have a Gaussian distribution in amplitude with rms width σ_V, percolation effects are important within an energy range of about $2\sigma_V$, inside the mobility edge. As the Debye short correlation length decreases, tunneling indeed reduces the effects of short-range fluctuations in the potential. We think that these can be projected out of the Hamiltonian so as to obtain an equation of motion for a smooth envelope function which becomes semiclassical in the vicinity of the mobility edge, and that the shorter the b, the smaller the range of energy within which semiclassical percolation is important. One test of the qualitative accuracy of the percolation picture is the magnitude of the mean tunneling probability. We include in this paper a technique of estimation for the latter which we prefer to that of Mott.[27]

In summary, the use of the semiclassical theory near a mobility edge has not yet been given a completely rigorous justification. There are two possible approaches, one being the development of the formal theory and the other being the exploration of the consistency of the semiclassical picture with experimental data. Mott has interpreted low-temperature transport data for disordered solids in terms of his picture. We show here that a consistent interpretation of the liquid-Hg data can be constructed on the basis of the semiclassical picture but that the Mott picture[15-19] has difficulties with liquid Hg.

II. MICROSCOPIC INHOMOGENEITIES IN LIQUID Hg

Even and Jortner,[8,9] on the basis of the general arguments advanced by Mott,[15-19] have proposed the following scheme of interpretation of their experimental data. For $\rho > 11$ g cm^{-3} the propagation regime holds. Note that R_{fe}/R is observed to be unity, and that no completely adequate interpretation has been given. In the range $9.2 < \rho < 11$ g cm^{-3}, the diffusion regime applies, and both σ and μ_H are in quantitative agreement with Friedman's theory[14] in the form of Eq. (3). The breakdown of Eq. (3) for σ and μ_H in the range $8.5 < \rho < 9.2$ g cm^{-3} was attributed by Even and Jortner[8] to the opening of a pseudogap at $\rho = 9.2$ g cm^{-3} according to the Mott criterion[16-19] of $g(E_F) = g^* = \frac{1}{3}$.

There are then difficulties with the detailed interpretation of the experiments of Hensel and colleagues.[1-7] The correlation between thermopower and conductivity[6] exhibits clearly marked semiconducting behavior only below $\rho = 7.8$ g cm^{-3} If the pseudogap had opened[8,9] at $\rho = 9.2$ g cm^{-3}, derivations of the conductivity-thermopower correlation from metallic behavior should have set in there. We conclude that the opening of a pseudogap occurs at densities lower than 9.2 g cm^{-3} and that the near constancy[8] of μ_H in the range $8.5 < \rho < 9.2$ g cm^{-3} arises from some other cause.

The marked semiconducting behavior at densities below 7.8 g cm^{-3} is to be contrasted with the clearly metallic behavior above densities of 9.2 g cm^{-3}. The electronic structure changes drastically with density in that range. Density fluctuations can therefore cause significant local modifications of the electronic structure and transport properties when the mean density lies in that range. In other words, we have the strong possibility that liquid Hg is microscopically inhomogeneous in its electronic structure and transport in the density range within which it undergoes a metal-semiconducting transition.

We therefore propose the existence of four transport regimes in expanded liquid Hg. The first two are the propagation ($\rho > 11$ g cm^{-3}) and diffusion ($9.2 < \rho < 11$ g cm^{-3}) regimes as proposed by Even and Jortner.[8,9] The fourth is the semiconducting regime ($\rho < 7.8$ g cm^{-3}) as proposed by Hensel.[6] In these three regimes the material may be regarded as homogeneous in the respect to electron transport. In the third regime, however, ($8.0 < \rho < 9.2$ g cm^{-3}) we propose that the material is inhomogeneous as regards electron transport,[29] and that this inhomogeneity is the cause of a continuous metal-semiconductor transition in this disordered system.

III. DENSITY FLUCTUATIONS IN LIQUID Hg

The density-density correlation function in a simple, one-component liquid such as mercury $G(R)$ is

$$G(R) = \langle \hat{n}(\vec{r})\hat{n}(\vec{r}+\vec{R})\rangle - \langle \hat{n}(\vec{r})\rangle\langle \hat{n}(\vec{r}+\vec{R})\rangle, \tag{14}$$

where $\hat{n}(\vec{r})$ is the completely microscopic number density,

$$\hat{n}(\vec{r}) = \sum_i \delta(\vec{r}-\vec{r}_i). \tag{15}$$

The sum on i runs over all nuclei, $\vec{r}_i$ is the nuclear position, and the average is over all nuclear configurations in thermodynamic equilibrium. $G(R)$ has the following features of interest to us. First, away from the critical point it decays asymptotically[30] as

$$G(R) = (\text{const})e^{-R/\xi}/R, \tag{16}$$

where ξ is the Ornstein-Zernike[30] decay length conveniently expressed as

$$\xi = s[a(0) - 1]^{1/2}, \tag{17}$$

with $a(0)$ the structure factor at zero wave number

$$a(0) = nkT\kappa_T. \tag{18}$$

In Eq. (18), n is the mean number density

$$n = \langle \hat{n}(\vec{r})\rangle, \tag{19}$$

and

$$\kappa_T = n^{-1}(\partial n/\partial p)_{T_s}$$

is the isothermal compressibility. The microscopic length s is given by

$$s^2 = \tfrac{1}{6}\int_0^\infty dR\, R^4 c(R) \Big/ \int_0^\infty dR\, R^2 c(R), \tag{20}$$

where $c(R)$ is the direct correlation function.

There are no accurate treatments of $G(R)$ in the theory of liquid metals from which one can obtain direct numerical values of s. Instead we make reasonable estimates of s by the technique of Ashcroft and Lekner.[31(a)] They showed, and later work by Ashcroft[31(b)] confirmed in detail, that the hard-core Percus-Yevick model[31(c)] gave good fits to the radial distribution function of simple liquids, including liquid metals, to densities closer to the critical density than those we are considering here. The Percus-Yevick theory gives[31(c)]

$$s^2 = \frac{nAa(0)d^2}{a(0)-1}, \tag{21}$$

where

$$\begin{aligned} A &= \tfrac{2}{3}\pi d^3(\tfrac{1}{5}\alpha + \tfrac{1}{6}\beta + \tfrac{1}{7}\gamma), \\ \alpha &= (1+2\eta)^2/(1-\eta)^4, \\ \beta &= -6\eta(1+\tfrac{1}{2}\eta)^2/(1-\eta)^4, \\ \gamma &= \tfrac{1}{2}\eta\alpha, \\ \eta &= \tfrac{1}{6}\pi n d^3, \end{aligned} \tag{22}$$

and d is the hard-core diameter; this gives

$$\xi^2 = nAa(0)d^2 \tag{23}$$

for ξ. We use the thermodynamic expression (18) for $a(0)$ because the Percus-Yevick theory[31(c)] does not include the electron-gas contribution to the compressibility. However, the geometric constraints introduced by the pairwise interatomic interaction are incorporated in the factor nAd^2, and these are presumably well estimated by the

TABLE I. Correlation length in expanded liquid Hg ($\sigma = 2.76$ Å).

T °K	P atm	ρ g/cm^{-3}	$\frac{\partial P}{\partial \rho}$ atm g^{-1}cm^3	η	$f(\eta)$	ξ (Å)	r_s (Å)	$ƛ_F = k_F^{-1}$
473	2000	13.3	12 500	0.44	1.60	0.45	1.81	0.721
673	2000	12.8	12 500	0.42	1.54	0.63	1.85	0.735
873	2000	12.3	10 000	0.40	1.31	0.73	1.88	0.750
1173	2000	11.6	6700	0.35	1.23	0.97	1.51	0.763
1273	2000	11.3	6000	0.38	1.08	1.00	1.93	0.770
1373	2000	11.0	4000	0.36	1.06	1.16	1.94	0.773
1473	2000	10.7	3500	0.35	0.90	1.28	1.96	0.781
1573	2000	10.3	2200	0.34	1.36	2.03	1.98	0.789
1673	2000	9.7	1000	0.32	1.04	2.54	2.02	0.801
1773	2000	8.5	400	0.28	0.61	2.96	2.10	0.836
1823	2000	6.3	120	0.21	0.46	4.10	2.33	0.930
1473	1000	10.3	2000	0.34	1.36	1.98	1.98	0.791
1573	1000	9.6	700	0.32	1.04	2.93	2.03	0.807
1623	1200	9.2	600	0.30	0.93	2.95	2.05	0.816
1673	1300	8.8	600	0.29	0.67	2.52	2.08	0.824
1723	1500	8.2	300	0.27	0.57	3.23	2.13	0.849
1773	1800	7.1	77	0.23	0.52	5.65	2.24	0.891

Percus-Yevick theory, judging from the goodness of the fit to the radial distribution functions.

The structure of Hg at room temperature and pressure can be fitted[31(a)] by a value of 0.45 for η. This corresponds to a value of $d = 2.76$ Å. Values of η for other densities can be obtained by linear scaling with density. Finally, values of kT/κ_T can be obtained from the density data of Hensel.[6] In this way, we obtain numerical estimates of the decay length ξ for the various conditions of interest. These are given in Table I. It appears that ξ is less than the interatomic separation $2r_s$ for all densities and temperatures except for those in the last line of Table I.

The next feature of $G(R)$ is that its asymptotic exponential decay stops roughly at a value b of R, the Debye short correlation length.[28] Inside b, $G(R)$ shows oscillations inside a smoothly varying envelope. These detailed oscillations are of no interest to us. It is always possible to define a smoothed local density $n(\vec{r})$ through

$$n(\vec{r}) = \int \hat{n}(\vec{r}\,')f(|\vec{r} - \vec{r}\,'|)\,d\vec{r}\,', \tag{24}$$

where

$$f(|\vec{r} - \vec{r}\,'|) \geq 0$$

and

$$\int d\vec{r} f(r) = 1 .$$

Suppose that b is several interatomic separations $2r_s$ in size. The smoothing function[25] $f(|\vec{r} - \vec{r}\,'|)$ can then have a range λ which is large enough so that $n(\vec{r})$ is smoothly varying on an atomic scale but which is smaller than b,

$$2r_s < \lambda < b . \tag{25}$$

We can now define a correlation function $\mathcal{G}(R)$ for the local density $n(\vec{r})$,

$$\mathcal{G}(R) = \langle n(\vec{r})n(\vec{r} + \vec{R})\rangle - \langle n(\vec{r})\rangle\langle n(\vec{r} + \vec{R})\rangle . \tag{26}$$

$\mathcal{G}(R)$ will have the same asymptotic behavior as

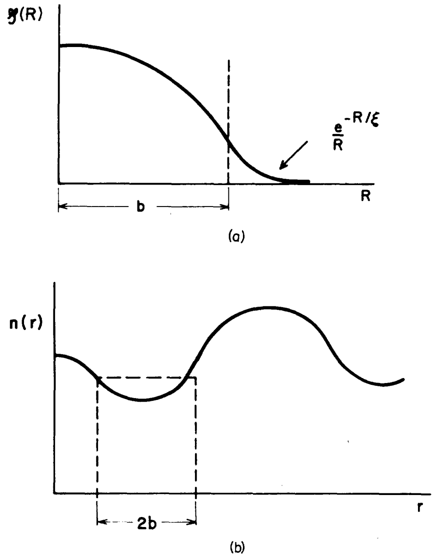

FIG. 1. Schematic representation of some features of the autocorrelation function for the local density: (a) correlation function [Eq. (26)] for the smoothed local density and (b) local density at high temperatures.

$G(R)$ [Eq. (16)], since $\lambda < b < R$ in the asymptotic region. Inside b, however, $\mathcal{G}(R)$ will be smooth, as sketched in Fig. 1(a) and not oscillatory as is $G(r)$. A step-function approximation can be taken as a first guess for $\mathcal{G}(R)$, in which $\mathcal{G}(R) = \text{const}$, $R < b$, and zero, $R > b$.

From this behavior of $\mathcal{G}(R)$ we can infer a typical variation of the local density $n(\vec{r})$ itself in space. It will vary slowly over distances of order b. Since we have assumed that b is larger than the interatomic separation $2r_s$ and have found that ξ is smaller than $2r_s$, we have that $b > \xi$. Thus the decaying tails of $\mathcal{G}(R)$ can be ignored outside b. Local-density values at separations larger than $2b$ can be considered as fluctuating independently. The behavior of $n(\vec{r})$ is that sketched in Fig. 1(b). The local density can be regarded, in first approximation as roughly constant at its mean value within a set of regions of radius b filling space, as also indicated in Fig. 1(b). We have no basis for a theoretical estimate of b. Its value will be determined below through an analysis of the transport data using the model of liquid Hg we are now developing. It is essential for the internal consistency of our analysis that b so determined indeed turns out to be larger than ξ and $2r_s$.

Because $b > \xi$ holds, fluctuations decay rapidly beyond b. Thus regions of the material of volume $v = \frac{4}{3}\pi b^3$ and separated by $2b$ fluctuate independently of one another. The probability distribution of fluctuations in mass density ρ away from the mean mass density $\bar{\rho}$ in the sampling volume v is given by

$$\begin{aligned} &P(\gamma) = (2\pi\xi^2)^{-1/2} e^{-\gamma^2/2\xi^2}, \\ &\xi^2 = \bar{\gamma}^2 = N^{-1} kT \left(\frac{\partial p}{\partial \bar{\rho}}\right)^{-1}, \\ &\gamma = (\rho - \bar{\rho})/\bar{\rho}, \\ &N = \bar{\rho} v / M = 4\pi\bar{\rho} b^3/3M, \end{aligned} \tag{27}$$

where $\bar{\rho}$ now replaces ρ as the mean mass density and M is the atomic weight. The probability that the local mass density exceeds some particular value ρ_g can be expressed in terms of the quantities defined through Eq. (27):

$$\begin{aligned} &W(\gamma_g) = \int_{\gamma_g}^{\infty} P(\gamma)\, d\gamma, \\ &\gamma_g = (\rho_g - \bar{\rho})/\bar{\rho} \end{aligned} \tag{28}$$

$$\begin{aligned} &W(\gamma_g) = \tfrac{1}{2} + \tfrac{1}{2}\,\text{erf}(-\chi_g), \quad \chi_g < 0, \\ &W(\gamma_g) = \tfrac{1}{2} - \tfrac{1}{2}\,\text{erf}(\chi_g), \quad \chi_g > 0, \\ &\chi_g = \gamma_g / \sqrt{2}\,\xi. \end{aligned} \tag{29}$$

$W(\gamma_g)$ will turn out to be the quantity of physical interest for the transport properties. We now go on to explore the consequence of the microscopic inhomogeneities described above for the transport properties.

IV. MICROSCOPIC CONDUCTIVITY

Linear-response theory states that in a microscopically inhomogeneous medium there is a nonlocal conductivity tensor relating the microscopic current density to the microscopic electric field

$$\vec{j}(\vec{r}) = \int \vec{\sigma}(\vec{r}, \vec{r}\,') \cdot \vec{E}(\vec{r}\,')\, d\vec{r}\,'. \tag{30}$$

The range of $\vec{\sigma}(\vec{r}, \vec{r}\,')$ in $|\vec{r} - \vec{r}\,'|$ over which it is nonlocal is the phase coherence length l. On the other hand, the variation $\sigma(\vec{r}, \vec{r}\,')$ with mean position $\frac{1}{2}(\vec{r} + \vec{r}\,')$ is on the distance scale of b, if both the Fermi wavelength and l are smaller than b. The Fermi wavelength is definitely smaller than b under our assumption that b exceeds $2r_s$ in liquid Hg at the densities of interest to us, cf., Table I. Moreover, in the density range 9.2–11 g cm^{-3} the diffusion regime holds, from which we may infer that l is substantially shorter than the Fermi wavelength, i.e.,

$$b \gg l. \tag{31}$$

Examination of Eq. (30) and the inverse relation for $\vec{E}(\vec{r})$ shows that both $\vec{j}(\vec{r})$ and $\vec{E}(\vec{r})$ vary on the scale of b. Thus, the integration over $\vec{r}\,'$ in Eq. (30) can be carried out by setting $\vec{E}(\vec{r}\,')$ equal to $\vec{E}(\vec{r})$ and taking the latter outside the integral,

$$\begin{aligned} &\vec{j}(\vec{r}) = \vec{\sigma}(\vec{r}) \cdot \vec{E}(\vec{r}), \\ &\vec{\sigma}(\vec{r}) = \int \vec{\sigma}(\vec{r}, \vec{r}\,')\, d\vec{r}\,'. \end{aligned} \tag{32}$$

As a further approximation, we shall ignore any tensorial character in $\vec{\sigma}(\vec{r})$ except when it is induced by a magnetic field, $\vec{\sigma}(\vec{r}) \to \sigma(\vec{r})$.

The position dependence of $\sigma(\vec{r})$ is analogous to that of $n(\vec{r})$ in Fig. 1(b). We can make the corresponding approximation of replacing $\sigma(\vec{r})$ by a set of constant values within a set of space-filling spheres of radius b. Of course, the Debye short correlation length for $\sigma(\vec{r})$ need not be precisely the same as that for $n(\vec{r})$, but after the many stages of simplification carried out here, there is little point in maintaining the distinction.

Finally, we note that it is the variation in local density which ultimately gives rise to the variation in local conductivity $\sigma(\vec{r})$. As all the other lengths in the problem are shorter than b, it is a good approximation simply to put

$$\sigma(\vec{r}) = \sigma(\rho(\vec{r})). \tag{33}$$

Values of $\sigma(\vec{r})$ at points separated by more than $2b$ are statistically independent. The probability distribution of the values $\sigma(\vec{r})$ at any one point $\vec{r}$ can be obtained from that of the values of $\rho(\vec{r})$ once the functional relationship (33) is known explicitly.

We now address the problem of calculating the transport properties of a material with nonuniform local transport coefficients.

V. EFFECTIVE-MEDIUM THEORY

We are concerned with a material which behaves like a random macroscopic medium with regions of randomly varying transport coefficients. Within each region of radius b the transport coefficients are constant. Their values in different regions are statistically independent. Our problem is to calculate the macroscopic transport coefficients of such a medium and in particular, the macroscopic conductivity σ.

Kirkpatrick has shown[23] that the effective-medium theory[24] is remarkably accurate for a simple cubic array of resistors which randomly take on one of two values providing the conductance ratio is greater than about 10^{-2}. Even when the ratio vanishes, the worst possible case, the theory is in error only in the range of fraction of resistors present between the percolation threshold and 0.4. We assume here that this range of accuracy of the effective-medium theory is more general than the simple system for which it was found and go on to develop and use an effective-medium theory appropriate to the system we are considering.

In the presence of a magnetic field the local conductivity becomes a tensor of the form[32]

$$\overleftrightarrow{\sigma}' = \sigma_d' \overleftrightarrow{I} + \overleftrightarrow{\sigma}_A', \tag{34}$$

where σ_d' is independent of magnetic field $\vec{H}$ and $\overleftrightarrow{\sigma}_A'$ is antisymmetric and such that

$$\begin{aligned} \overleftrightarrow{\sigma}_A' \cdot \vec{B} &= \alpha \vec{H} \times \vec{B}, \\ \vec{B} \cdot \overleftrightarrow{\sigma}_A' &= \alpha \vec{B} \times \vec{H}, \end{aligned} \tag{35}$$

all to first order in $\vec{H}$. Here $\vec{B}$ is any arbitrary vector and α is a constant.

We have carried out an effective-medium theory for the full magnetoconductivity tensor for arbitrary distribution of conductivity components. Here we give the essential results; a derivation and detailed discussion will be published separately.[32] The effective medium condition for determining the macroscopic zero-field conductivity is

$$\langle (\sigma' - \sigma)/(\sigma' + 2\sigma) \rangle = 0 \tag{36}$$

where σ' is the random value of the local conductivity. The averaging process in (36) is defined by

$$\langle f(\sigma') \rangle = \int d\sigma' P(\sigma') f(\sigma'), \tag{37}$$

where $P(\sigma')$ is the probability distribution of values of σ' and $f(\sigma')$ is any function of σ'. Correspondingly, the effective-medium condition for the full magnetoconductivity tensor is

$$\langle (\overleftrightarrow{\sigma}' - \overleftrightarrow{\sigma}) \cdot (\sigma_d \overleftrightarrow{I} - \tfrac{1}{3}\overleftrightarrow{\sigma} + \tfrac{1}{3}\overleftrightarrow{\sigma}')^{-1} \rangle = 0, \tag{38}$$

where the average is over the joint probability distribution of all the components of $\overleftrightarrow{\sigma}'$. Equation (38) can be solved to first order in $\vec{H}$ for $\overleftrightarrow{\sigma}_A$ by expanding and inserting (36). We get

$$\overleftrightarrow{\sigma}_A = \left\langle \frac{\overleftrightarrow{\sigma}_A'}{(\sigma' + 2\sigma)^2} \right\rangle \Big/ \langle (\sigma' + 2\sigma)^{-2} \rangle . \tag{39}$$

We are concerned here with a metal-to-semiconductor transition in the density range 7.8–9.2 g cm^3. We therefore expect that density fluctuations give rise to a range of values for σ' and $\overleftrightarrow{\sigma}_A'$ embracing at least that range observed for σ and $\overleftrightarrow{\sigma}_A$ over that density region. Accordingly at one end of the range, the values for σ' will be semiconducting in their magnitude and temperature dependence. At the other end, they will be metallic. We can select some intermediate value of σ', σ_g, corresponding to some particular value of local density [according to (33)], which separates the "semiconducting" values of σ from the "metallic" ones. For a purely mathematical analysis or for a quantitative analysis of the data, it is not necessary to specify a value of σ_g, only to state that it exists. However, if seems to us that there is only one natural choice of σ_g and ρ_g. Eq. (33) is equivalent to the statement that a local electronic structure exists because of the phase incoherence of the wave functions important in transport. Our interpretation of the metal semiconductor transition is that an energy gap opens locally via Mott's s-p overlap mechanism[15-19] at a local density ρ_g. σ_g is then that value of the conductivity which corresponds to just vanishing local band gap. Since the conductivity is nearly local and insensitive to the distant structure of the material, we may regard $\sigma(\vec{r})$ as the conductivity in a material artificially constrained to be uniform at the local density $\rho(\vec{r})$. Thus σ_g is the conductivity of a fictitious homogeneous material of density ρ_g in which the band gap just vanishes.

The expression (36) can now be simplified considerably in form with the aid of the mean-value theorem

$$C\left(\frac{\sigma_0 - \sigma}{\sigma_0 - 2\sigma}\right) + (1 - C)\left(\frac{\sigma_1 - \sigma}{\sigma_1 + 2\sigma}\right) = 0, \tag{40}$$

where

$$C=\int_{\sigma_g}^{\infty}P(\sigma')\,d\sigma', \tag{41}$$

$$\frac{\sigma_0-\sigma}{\sigma_0+2\sigma}=C^{-1}\int_{\sigma_g}^{\infty}P(\sigma')\left(\frac{\sigma'-\sigma}{\sigma'+2\sigma}\right)d\sigma', \tag{42}$$

$$\frac{\sigma_1-\sigma}{\sigma_1+2\sigma}=(1-C)^{-1}\int_0^{\sigma_g}P(\sigma')\left(\frac{\sigma'-\sigma}{\sigma'+2\sigma}\right)d\sigma'. \tag{43}$$

Equations (42) and (43) define mean metallic and mean semiconducting conductivities σ_0 and σ_1, respectively. C is the probability that the local conductivity is metallic in character, and $1-C$ is the probability that it is semiconducting. Thus, C is the volume fraction of metallic material. Making use of the connection between σ' and $\rho(\vec{r})$, Eq. (33), and the definition of ρ_g, we can also write

$$C=\int_{\gamma_g}^{\infty}P(\gamma)\,d\gamma\equiv W(\gamma_g), \tag{44}$$

$$\gamma_g=(\rho_g-\bar{\rho})/\bar{\rho}$$

according to (28). The explicit functional form of $W(\gamma_g)$ is contained in (29).

The problem is now reduced in form to the case of only two possible values of σ'. The standard results for σ for that case can be put in the form[23,24,32]

$$\begin{aligned}&\sigma=f\sigma_0,\\&f=a+(a^2+\tfrac{1}{2}x)^{1/2},\\&a=\tfrac{1}{2}[(\tfrac{3}{2}C-\tfrac{1}{2})(1-x)+\tfrac{1}{2}x],\\&x=\sigma_1/\sigma_0.\end{aligned} \tag{45}$$

The corresponding analysis of $\overleftrightarrow{\sigma}_A$ is subtler. We note that because we have assumed that the local-conductivity tensor depends only on local density, Eq. (33), $\overleftrightarrow{\sigma}'_A$ is a function of σ' only. Thus Eq. (39) becomes

$$\overleftrightarrow{\sigma}_A=\int P(\sigma')\frac{\overleftrightarrow{\sigma}'_A(\sigma')}{(\sigma'+2\sigma)^2}\,d\sigma'\Big/\int\frac{P(\sigma')\,d\sigma'}{(\sigma'+2\sigma)^2}\,. \tag{46}$$

Use of the mean-value theorem gives

$$\overleftrightarrow{\sigma}_A=\frac{C[\overleftrightarrow{\sigma}^0_A/(\sigma_{0\alpha}+\sigma)^2]+(1-C)[\overleftrightarrow{\sigma}^1_A/(\sigma_{1\alpha}+\sigma)^2]}{C(\sigma_{0\alpha}+\sigma)^{-2}+(1-C)(\sigma_{1\alpha}+\sigma)^{-2}}\,, \tag{47}$$

where

$$\begin{aligned}&C(\sigma_{0\alpha}+2\sigma)^{-2}=\int_{\sigma_g}^{\infty}P(\sigma')(\sigma'+2\sigma)^{-2}\,d\sigma',\\&(1-C)(\sigma_{1\alpha}+2\sigma)^{-2}=\int_0^{\sigma_g}P(\sigma')(\sigma'+2\sigma)^{-2}\,d\sigma',\\&C\overleftrightarrow{\sigma}^0_A(\sigma_{0\alpha}+2\sigma)^{-2}=\int_{\sigma_g}^{\infty}P(\sigma')\overleftrightarrow{\sigma}'_A(\sigma')\\&\qquad\times(\sigma'+2\sigma)^{-2}\,d\sigma',\\&(1-C)\overleftrightarrow{\sigma}^{(1)}_A(\sigma_{1\alpha}+2\sigma)^{-2}=\int_0^{\sigma_g}P(\sigma')\overleftrightarrow{\sigma}'_A(\sigma')\\&\qquad\times(\sigma'+2\sigma)^{-2}\,d\sigma'.\end{aligned} \tag{48}$$

Equation (46) is now of the two-component form and can be analyzed accordingly. Unfortunately, for the continuous distributions of values of σ' which we have, different mean values of metallic or semiconducting σ emerge for different transport properties, namely $\sigma_{0\alpha}$ in the magnetoconductivity versus σ_0 in the conductivity. We shall suppose that we can ignore this variability of mean conductivity and replace $\sigma_{0\alpha}$ by σ_0 and similarly for $\sigma_{1\alpha}$. The results can be written in the convenient form[32]

$$\begin{aligned}&g=\frac{\mu}{\mu_0}=f^{-1}\left(1-\frac{(2f+1)^2(1-C)(1-xy)}{(2f+1)^2(1-C)+(2f+x)^2C}\right),\\&h=R/R_0=g/f,\\&y=\mu/\mu_0.\end{aligned} \tag{49}$$

Here μ is the Hall mobility and R the Hall constant corresponding to the macroscopic magnetoconductivity $\overleftrightarrow{\sigma}_A$. μ_0 and R_0 correspond to $\overleftrightarrow{\sigma}^0_A$ and μ_1 to $\overleftrightarrow{\sigma}^{(1)}_A$.

From Kirkpatrick's results,[23] we infer that for $x\sim10^{-2}$–10^{-1} the effective-medium theory for σ

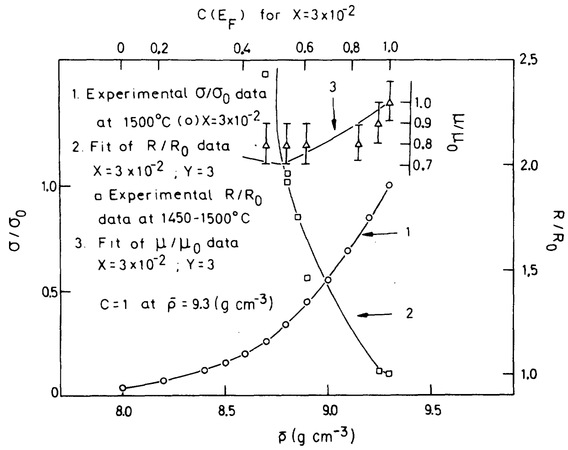

FIG. 2. Analysis of the electrical transport properties of expanded liquid Hg in the inhomogeneous transport regime $8.0<\bar{\rho}<9.3$ g cm^{-3} in terms of the effective-medium theory. The experimental conductivity data (Refs. 3–6) were utilized to establish the relation between $C(E_F)$ and $\bar{\rho}$, which was subsequently applied to account for the density dependence of R and μ (Refs. 8, 9, and 27) in the pseudometallic regime.

is valid for the whole range of C, and a similar behavior is expected for R and μ. We are interested in such moderately large x values (10^{-2}–10^{-1}) and thus expect Eqs. (47) and (49) to hold for all C.

Equations (47) and (49) constitute a complete, if approximate, theory of the low-field magnetoconductivity tensor of the kinds of materials under consideration. Fitting the theory to actual data requires establishing values of the parameters x, y, and R_0 (or μ_0) and a connection between C and observables.

From the mean-value theorem we have

$$\sigma_g < \sigma_0 < \infty \tag{50a}$$

and

$$0 < \sigma_1 < \sigma_g , \tag{50b}$$

and, in principle, σ_0 and σ_1 depend on C. As a further approximation we shall set these conductivities and the conductivity tensors $\overleftrightarrow{\sigma}_A^{(0)}$ and $\overleftrightarrow{\sigma}_A^{(1)}$ to be constants, independent of C. We next approximate the values of $\overleftrightarrow{\sigma}_0$ and $\overleftrightarrow{\sigma}_1$ [cf. Eq. (34)] by the values of the conductivity tensors at the metallic and nonmetallic ends of the inhomogeneous regions, respectively. Thus, σ_0 is taken as equal to the value of the observed conductivity at the lower limit of the diffusion region (mean density $\bar{\rho} = 9.3$ g cm^{-3}, while σ_1 is chosen to be equal to the conductivity at $\bar{\rho} = 8.0$ g cm^{-3} (see Sec. VII). This highly approximate procedure is followed in order to minimize the number of parameters in the theory without loss of physical content. In Sec. VI, we utilize effective-medium theory, [Eqs. (45) and (49)], to fit the conductivity and Hall data, obtaining *inter alia*, C vs $\bar{\rho}$.

VI. DETAILED ANALYSIS OF TRANSPORT PROPERTIES

Effective-medium theory will now be applied to account for the electrical transport properties in the inhomogeneous transport regime. In Fig. 2 we display the experimental conductivity,[3-6] Hall-coefficient, and Hall-mobility[8,9] data for Hg in the density range which is assigned by us to the inhomogeneous transport regime. Three parameters, x, y, and $\bar{\rho}$ corresponding to $C = 1$, enter into our transport theory [Eqs. (45) and (49)] and should be chosen to yield the relation between C and $\bar{\rho}$ that gives the best fit to the density dependence of σ/σ_0 and R/R_0 (or μ/μ_0). However, inaccuracies in available Hall-effect data[8,9] prohibit such a detailed analysis, and at present we have to rely on semiquantitative estimates of the relevant parameters. On the basis of the analysis of the transport data presented in Sec. II we expect that the effective onset of the inhomogeneous regime occurs at $\bar{\rho} \simeq \rho_F = 9.2$ g cm^{-3}, and we have accordingly chosen $C(\bar{\rho}) = 1.0$ at $\bar{\rho}_0 = 9.3$ g cm^{-3}. The conductivity ratio x Eq. (45), for a high-temperature material such as expanded Hg is expected to be appreciable, being of the order $x \sim e^{-\Delta E/kT}$ where the mean mobility gap $\Delta E = E_c - E_F$ in the semiconducting regime takes the value $\Delta E \sim (2-4)kT$, so that $x \sim 0.02$–0.10. We have chosen $x = 3 \times 10^{-2}$ which according to Hensel's data[6] corresponds to $C = 0$ at $\bar{\rho} = 8.0$ g cm^{-3}. The electrical conductivity data[6] were then utilized to establish the relation between C and $\bar{\rho}$. The more significant values of $C(\bar{\rho})$ obtained from Eq. (45) (see Fig. 3) are listed in Table II. The Hall-effect and Hall-mobility data, Fig. 2, available only in the range $0.5 < C < 1$ are properly accounted for by Eq. (49) with the physically reasonable value of the Hall-mobility ratio $y = 1$–3. The fit to $y = 3$ is somewhat better; see Fig. 2. However, the accuracy of the experimental results is still insufficient for a more accurate determination of y. The Hall mobilities in the metallic regions and above the mobility edge in the semiconducting regions are both dominated by diffusion-type transport,[14] and thus we expect the Hall-mobility ratio to be close to unity. It is of importance to notice that the observed weak density dependence of the Hall mobility and

TABLE II. Features of the transition.

Feature	$\bar{\rho}$ (g cm^{-3})	$C(E_F)$
Onset of inhomogeneous transport	$\rho_0 = 9.3$	1.0
Friedman theory fails	$\rho_F = 9.2$	0.9
Opening of local gap	$\rho_g = 8.8$	0.5
Opening of pseudogap	$\rho_{pg} = 8.2$	0.2
Termination of inhomogeneous transport	$P_1 = 8.0$	0
Semiconductor-like transport ($E_g > 4kT$ in 80% of the material)	$\rho_s = 7.8$	

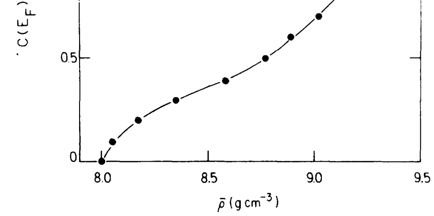

FIG. 3. Density dependence of $C(E_F)$ in the inhomogeneous regime as obtained from the fit of the conductivity data (-●-).

the strong variation of σ and R in the density region 9.3–8.7 g cm^{-3} follow from our picture.

Further information can be obtained from the temperature and the volume coefficients of the electron conductivity, determined by Hensel and Schmutzler,[6] which exhibit a sharp increase in the density range 9.0–8.0 g cm^{-3}. This behavior is consistent with the features of the inhomogeneous transport regime. The volume dependence of the electrical conductivity at constant temperatures is attributed to the density dependence of C. From Eq. (45) we have

$$-\left(\frac{\partial \ln f}{\partial \ln V}\right)_T=\left(\frac{\partial \ln f}{\partial \ln \bar{\rho}}\right)_T=\frac{\bar{\rho}}{f}\left(\frac{\partial f}{\partial C}\right)_x\left(\frac{\partial C}{\partial \bar{\rho}}\right)_T$$
$$=\frac{3\bar{\rho}}{4(f-a)}\left(\frac{\partial C}{\partial \bar{\rho}}\right)_T . \tag{51}$$

The density dependence of C is obtained from Fig. 3. From Eq. (51) we assert (see Fig. 4) that $f^{-1}(\partial f/\partial C)$ exhibits a maximum at $C\simeq 0.3$; however, in the present system this maximum is washed out in $\partial \ln f/\partial\bar{\rho}$ owing to the increase of $\partial C/\partial\bar{\rho}$ with increasing $\bar{\rho}$ in the range $C>0.2$. The resulting density dependence of the normalized electrical conductivity (Fig. 4) exhibits an increase for $C<1.0$ with a shoulder at $C\sim 0.2$. This behavior is quite consistent with the experimental data evaluated from Hensel's isotherm[6] at 1500 °C.

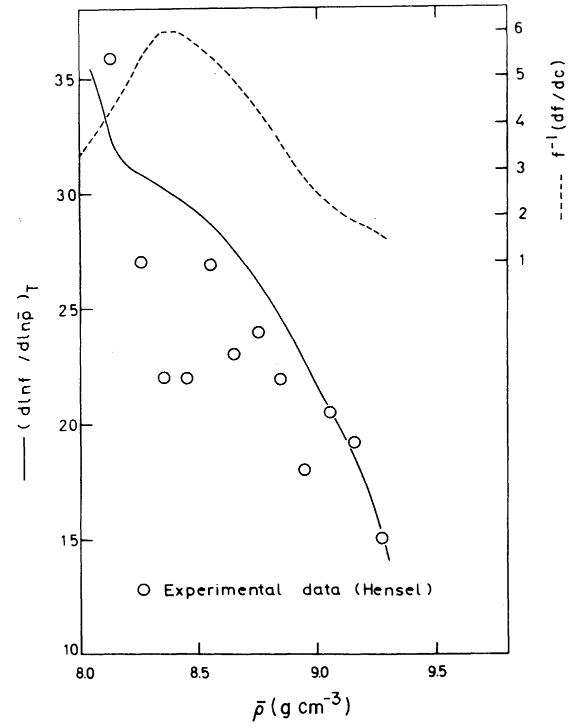

FIG. 4. Density dependence of $\partial \ln f/\partial C$ and of $\partial \ln f/\partial \ln\bar{\rho}$ [Eq. (51)]. The latter curve exhibits a sharp rise in the inhomogeneous region which is consistent with Hensel's experimental data (Ref. 6), represented by open circles.

The temperature dependence of the electrical conductivity at constant density

$$\left(\frac{\partial \ln\sigma}{\partial T}\right)_{\bar{\rho}}=\left(\frac{\partial \ln f}{\partial T}\right)_{\bar{\rho}}+\left(\frac{\partial \ln\sigma_0}{\partial T}\right)_{\bar{\rho}} \tag{52}$$

is assigned to the temperature dependence of x and of C. Using Eq. (45) for the evaluation of the derivatives with respect to these parameters we get

$$\left(\frac{\partial \ln f}{\partial T}\right)_{\bar{\rho}}=\left(\frac{\partial \ln f}{\partial x}\right)_C\left(\frac{dx}{dT}\right)_{\bar{\rho}}+\left(\frac{\partial \ln f}{\partial C}\right)_x\left(\frac{dC}{dT}\right)_{\bar{\rho}}$$
$$=\frac{f+1}{4f(f-a)}\left(\frac{dx}{dT}\right)_{\bar{\rho}}+\frac{3}{4(f-a)}\left(\frac{dC}{dT}\right)_{\bar{\rho}} . \tag{53}$$

The temperature coefficient of C can be estimated utilizing the statistical theory of Sec. II. Neglecting the temperature dependence of $\partial p/\partial\bar{\rho}$ we estimate from Eqs. (27), (29), and (44)

$$\frac{dC}{dT}=\frac{|\chi_g|}{2(\sqrt{\pi})T}e^{-\chi_g^2}\simeq 2\times 10^{-4}|\chi_g|e^{-\chi_g^2}\ {}^\circ\mathrm{K}^{-1} \tag{54}$$

which depends on C (or on $\bar{\rho}$). The temperature coefficient of the conductivity ratio is approximately given by

$$\frac{dx}{dT}=\frac{x\Delta E}{kT^2}\simeq 10^{-4}\ {}^\circ\mathrm{K}^{-1}, \tag{55}$$

which is $\bar{\rho}$ independent. The major contribution to the temperature coefficient for $C<0.5$ (i.e., $\bar{\rho}<8.77$ g cm^{-3}) comes from the first term on the right-hand side (rhs) of Eq. (52), which exhibits a sharp rise (see Fig. 5) in this density region. The estimated temperature coefficient (taking

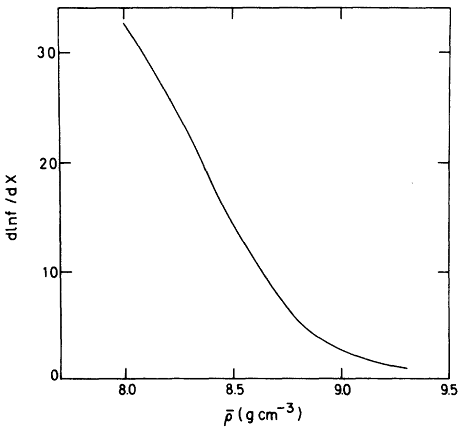

FIG. 5. Density dependence of $(\partial \ln f/\partial x)_C$ in the inhomogeneous region.

$dx/dT \simeq 10^{-4}$ °K^{-1} is $(\partial \ln f/\partial T)_{\bar{\rho}} = 3.3\times 10^{-3}$ °K^{-1} at $\bar{\rho} = 8.0$ g cm^{-3}, is not inconsistent with the experimental value[6] $(\partial \ln f/\partial T)_{\bar{\rho}} = (10 \pm 5)\times 10^{-3}$ °K^{-1} at this density.

The inaccuracies in the experimental density and electronic transport data are such as to make a more detailed analysis premature; more accurate measurements are under way. The present analysis of the available experimental data provides a coherent picture of the electrical conductivity, the Hall coefficient, the Hall mobility, and the temperature and volume coefficients of the transport properties of expanded liquid Hg in the intermediate microscopically inhomogeneous regime.

VII. AVERAGE LENGTH FOR DENSITY FLUCTUATIONS

We have demonstrated that the concept of a microscopically inhomogeneous medium advanced by us provides a complete semiquantitative interpretation of the electronic transport data in the density range 9.3–8.0 g cm^{-3}. The next cardinal question we have to address for Hg is whether the dependence of C on $\bar{\rho}$, obtained from the analysis of the transport data is consistent with the density-fluctuation picture underlying it. To provide a direct test of our fluctuation picture, the values of C vs $\bar{\rho}$ (see Fig. 3) extracted from the conductivity data, by means of the effective-medium theory will be interpreted in terms of our statistical theory. Utilizing Eqs. (27)–(29) and (44) we obtain the density dependence of χ_g which yields $\xi(\bar{\rho})$. These values together with the result (see Fig. 3) $\rho_g = 8.77$ g cm^{-3} and the experimental compressibility data[6] were used to derive the density dependence of N. The average number of atoms, N, within a density fluctuation is plotted in Fig. 6 and varies from 420 ± 80 at $\bar{\rho} = 9.3$ g cm^{-3} to $N = 360 \pm 80$ at $\bar{\rho} = 8.2$ g cm^{-3}. Thus, within the experimental uncertainty the value of N is practically constant over this density range. This analysis results in the value of $b = (3NM/4\pi\bar{\rho})^{1/3} = 15$ Å for the Debye short correlation length, which corresponds to the average range of density fluctuations. b is practically density independent. This value of the Debye short correlation length is characterized by the following features (see Table I): (i) it spans several interatomic separations ($2r_s < 4.5$ Å in the inhomogeneous regime); (ii) it considerably exceeds the decay length ξ ($\xi < 3.2$ Å in the inhomogeneous regime); and (iii) it is considerably larger than the phase-coherence length, l, of the electron wave function in the diffusion regime ($l < 0.9$ Å in the inhomogeneous regime). Thus, the requirements for internal consistency of our picture are well met.

VIII. PHYSICAL INTERPRETATION OF C

We have demonstrated that a complete, self-consistent physical picture for electronic transport in liquid Hg can be constructed by interposing the inhomogeneous transport regime between the conventional metallic diffusion and the semiconducting regimes. The inhomogeneous transport regime occurs in a disordered material provided that two sets of necessary conditions on the magnitude of the Debye correlation length are obeyed. First, the basic structural requirements $b > 2r_s$ and $b > \xi$ imply the existence of structural fluctuations which are independent when separated by more than twice the correlation radius. Second, a short phase-coherence length satisfying Eq. (31) provides the physical basis for the validity of the concepts of local electronic structure and local response functions and consequently for the applicability of the effective-medium theory. As is evident from the analysis of Sec. VII, expanded liquid Hg in the density range 9.3–8.0 g cm^{-3} is characterized by a sufficiently large correlation length, b, for density fluctuations to satisfy the necessary conditions of our model.

We now examine the consequences of this picture of liquid Hg for some of the details of its electronic structure. These are contained in the one-electron Green's function $\hat{G}(\vec{r}, \vec{r}\,')$. Just as we considered the nuclear density smoothed over a smoothing radius in Sec. III, cf. Eq. (24), here we consider the correspondingly smoothed one-electron Green's function

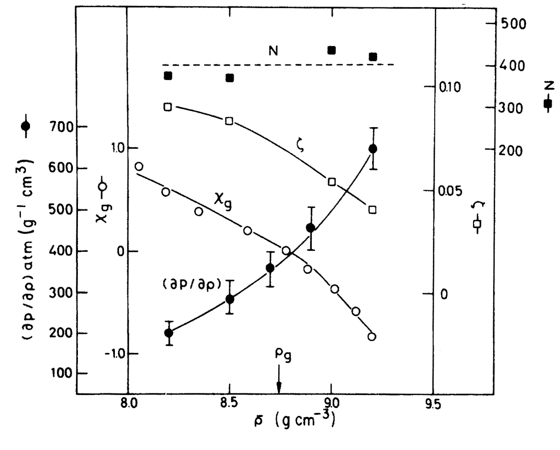

FIG. 6. Analysis of the density dependence of $C(E_F)$ in terms of the thermodynamic fluctuation theory. The results of Fig. 3 together with Eq. (29) were utilized to obtain the density dependence of χ_g, which in turn yields ξ vs $\bar{\rho}$. The experimental compressibility data (Ref. 6) were subsequently applied to calculate the average number of atoms, N, within a density fluctuation at several densities.

$$G(\vec{r},\vec{r}\,')=\int d^3R\,G(\vec{R}+\tfrac{1}{2}(\vec{r}-\vec{r}\,'),\vec{R}-\tfrac{1}{2}(\vec{r}-\vec{r}\,'))\times f(|\tfrac{1}{2}(\vec{r}+\vec{r}\,')-\vec{R}|)\,. \tag{56}$$

As λ is significantly greater than l, $G(\vec{r},\vec{r}\,')$ decays in $|\vec{r}-\vec{r}\,'|$ over a distance of order l, the phase-coherence length. In other words, $G(\vec{r},\vec{r}\,')$ is certainly local on a distance scale of b in $\frac{1}{2}(\vec{r}+\vec{r}\,')$. We expect that the characteristic distance of variation of $G(\vec{r},\vec{r}\,')$ in $\frac{1}{2}(\vec{r}+\vec{r}\,')$ is not less than b, the distance over which the smoothed potential varies. In liquid Hg, where the kinetic energy is high and both the wavelength and phase-coherence length are short, it is likely that b is that characteristic distance. This permits us to define a local density of states

$$n(E;\,\vec{r})=\frac{1}{\pi}\,\mathrm{Im}G(\vec{r},\vec{r};\,E), \tag{57}$$

which is approximately constant within b.

From the local density of states we can extract a local gap. At this point we run into the problem of confusion between a pseudogap and a real energy gap, and all we can do now is to take a band edge as an energy where the density of states falls below some small unspecified value. For simplicity, we take this to be zero. This band gap is presumably the gap between the top of the s band and the bottom of the p band, as proposed by Mott.[15-19] The above constitutes a more detailed justification of the statement of Sec. V that σ_g and $\rho_g = 8.77$ g cm^{-3} correspond to vanishing local band gap.

The physical picture of Sec. V in which conductivity varies randomly within the material, remaining approximately constant within domains of radius b, is now seen to correspond to one in which there is a randomly varying energy gap. The density ρ_g divides the material into regions of finite energy gap at the Fermi energy, the semiconducting regions, and regions of finite s-band–p-band overlap, the metallic regions. C is the volume fraction of the material in which the local density exceeds ρ_g and therefore that volume fraction in which there is no energy gap at the Fermi energy.

Having defined a local energy gap, we now enquire after its density dependence. Below the density $\bar{\rho}=\rho_s = 7.8$ g cm^{-3}, the material exhibits semiconductor transport properties. For this to occur, the semiconducting regions having a local gap greater than $4kT$ cannot be "shorted out" by regions having a local gap less than $4kT$. The volume fraction of the latter must therefore be less than the percolation threshold, 0.2. In other words, 80% of the material is occupied by regions having a local gap greater than $4kT$. Let ρ_{4kT} be the local density corresponding to a local gap of $4kT$, and γ_{4kT} and χ_{4kT} the corresponding values of γ and χ (cf. Sec. III). Let $W(\gamma_{4kT})$ be the probability that γ is greater than γ_{4kT}; its numerical value is 0.2 according to the above arguments. Equations (28) and (29) for W permit us to write

$$\begin{aligned}\rho_{4kT}&=\rho_s[1+(\sqrt{2}\,)\zeta(\rho_s)\,\mathrm{erf}^{-1}(1-2W(\gamma_{4kT}))]\\&=\rho_s[1+0.84\zeta(\rho_s)]\,.\end{aligned} \tag{58}$$

The value of $\zeta(\rho_s)$ is about 0.09, extrapolating from the values of ζ in Fig. 6. Thus ρ_{4kT} is 8.4 g cm^{-3}. Since ρ_g is 8.8 g cm^{-3} and $4kT = 0.5$ eV, the local deformation potential is $8.8\times0.5/0.4 = 11$ eV. Ignoring the inhomogeneity of the semiconducting material at a mean density of 7.8 g cm^{-3} would be equivalent to setting $\rho_{4kT} = 7.8$ g cm^{-3}. That would give a lower limit of 4 eV to the deformation potential. Both estimates, of 11 eV for the deformation potential itself and of 4 eV for its lower limit, are reasonable values and support the analysis of the preceding sections.

The extent of the smallest region in which an energy gap occurs is $2b$. If tunneling across such a region were unimportant and if quantum-kinetic energy corrections within the metallic regions were also unimportant, the semiclassical picture would apply to the motion of electrons at the Fermi energy in liquid Hg. We shall proceed by assuming tunneling and kinetic-energy corrections unimportant and justify that assumption subsequently. C then becomes identical to $C(E_F)$ the volume fraction of material allowed semiclassically to an electron at the Fermi energy.

The inhomogeneous transport regime in liquid Hg can be subdivided into two parts[29]: (a) pseudometallic regime $(1 > C > C^*)$ where continuous metallic paths extend through the material, and (b) pseudosemiconducting regime $(0 < C < C^*)$, where only local metallic domains exist. The identification of C with the semiclassically allowed volume fraction $C(E_F)$ permits us to say that a mobility gap opens up just at Fermi energy at $\rho_{pg} = 8.2$ g cm^{-3}. For lower densities $8.0 < \rho < 8.2$ g cm^{-3}, there is a mobility gap within which the Fermi energy lies. The localized states in that mobility gap are confined to the metallic regions, the volume fraction of which $C(E_F) < C^* = 0.2$.

There is clearly a metal-semiconductor transition taking place continuously within the density range 8.0–9.3 g cm^{-3}. The electrons at the Fermi energy are confined to an increasingly smaller region of the material until at $\rho_{pg} = 8.2$ g cm^{-3}, $C(E_F) = C^* = 0.2$, metallic conduction without intermediation by semiconducting regions ceases. At that point, the wave functions at the Fermi energy become localized, and in a sense a metal-nonmetal transition occurs. It would be artificial to select $\bar{\rho}_{pg}$ as the density of the metal-nonmetal transition, however, because at these high temperatures thermal excitation within semiconducting regions and hopping conduction occur.

The consequences of this interpretation of C as the allowed volume fraction $C(E_F)$ are also displayed in Table II.

To complete the argument that liquid Hg satisfies the necessary validity conditions for the applicability of the semiclassical picture in the density range 9.3–8.0 g cm^{-3}, we estimate the magnitude and relative importance of tunneling and kinetic-energy effects.

Obviously, if tunneling between metallic regions is important, it will be effective in erasing classical inhomogeneities in electronic structure and transport properties. The estimate of the contribution of tunneling across the semiconducting regions to the transport properties is crucial to assessing the validity of the semiclassical physical picture advanced by us.

Since the most probable energy gap in the pseudometallic regime above $\bar{\rho} = \rho_g = 8.8$ g cm^{-3} is zero and small for densities below but near to $\bar{\rho} = \rho_g$, the accuracy of the approach which neglects tunneling across the semiconducting regions is questionable. However, we have seen that the properties of the system are practically independent of x for $C \gtrsim 0.5$, and ignoring tunneling amounts roughly to underestimating x. Therefore we are concerned primarily with tunneling effects for $C < 0.5$. The conductance G through a unit area of a semiconducting region of length L contains contributions from tunneling across it, $G_0 |T|^2$, and from thermally activated carriers within it, σ_0/L:

$$G = G_0 |T^2| + \sigma_1/L . \tag{59}$$

For the tunneling amplitude T we take the approximate expression

$$T = \exp[-(2m\tfrac{1}{2}E_g)^{1/2} L/\hbar] , \tag{60}$$

where E_g is the local energy gap and L is the width of the semiconducting region. The latter corresponds to a multiple of $2b$, $2bn$ with the probability[25]

$$P_n = C(1-C)^{n-1} . \tag{61}$$

For E_g we use a deformation-potential approximation

$$E_g \simeq -D(\rho - \rho_g)/\bar{\rho}, \quad \rho < \rho_g \tag{62}$$

where ρ is the local density. The deformation potential D has been estimated in Sec. VII to be $D > 4$ eV, $D \sim 11$ eV. Equation (62) can be rewritten using (27) and (28) as

$$E_g = -D(\gamma - \gamma_g), \quad \gamma < \gamma_g . \tag{63}$$

The preexponential G_0 can be conveniently expressed in terms of a length l_G,

$$G_0 = \sigma_0 / l_G . \tag{64}$$

The condition for tunneling to be negligible in (59) is that

$$\langle (L/l_G) |T|^2 \rangle \ll x , \tag{65}$$

where the averaging is taken independently over length L and local gaps E_g.

Tunneling over the distance $L = 2bn$ results in the following contribution:

$$T^2(n) = \prod_{i=1}^{n} \exp\left(\frac{-2(E_g^i m)^{1/2}(2b)}{\hbar} \right), \tag{66}$$

where the values of E_g^i in each segment are independent. Averaging over E_g values we utilize Eq. (63) to obtain

$$\langle T^2(n) \rangle_\gamma = t(\gamma_g)^n , \tag{67}$$

where

$$t(\gamma_g) = \int_{-\infty}^{\gamma_g} d\gamma\, P(\gamma) \exp\left(-4(mD)^{1/2} \frac{b}{\hbar} (\gamma_g - \gamma)^{1/2} \right) \tag{68}$$

and

$$P(\gamma) = \frac{\exp(-\gamma^2/2\zeta^2)}{(2\pi\zeta^2)^{1/2}[1 - C(E_F)]} . \tag{69}$$

Making use of Eq. (61), we get

$$\langle n T^2 \rangle = \sum_n n\, p_n \langle T^2(n) \rangle_\gamma , \tag{70}$$

which, together with Eqs. (67) and (68), yields

$$\langle n T^2 \rangle = \frac{C(E_F) + (\gamma_g)}{\{1 - [1 - C(E_F)] + (\gamma_g)\}^2} . \tag{71}$$

We can obtain a crude estimate of the integral in (68) as follows. The exponential factor

$$\tau(\gamma) = \exp\left(-4(mD)^{1/2} \frac{b}{\hbar} (\gamma_g - \gamma)^{1/2} \right) \tag{72}$$

in Eq. (68) is equal to unity at $\gamma = \gamma_g$ and decreases very fast for $\gamma < \gamma_g$ (see Fig. 7). We can thus take for the slowly varying function $P(\gamma)$ its value at $P(\gamma_g)$.

Correspondingly, we have

$$t(\gamma_g) = \frac{\exp(-\gamma_g{}^2/2\zeta^2)}{(2\pi\zeta^2)^{1/2}[1 - C(E_F)]} \frac{\hbar^2}{8mb^2 D} \tag{73}$$

for the mean tunneling probability across a semiconducting region of the minimal width $2b$. Using the free-electron value for the mass m, 5 eV for D, and 0.07 for ζ, we obtain from Eq. (73), $t(\gamma_g)$

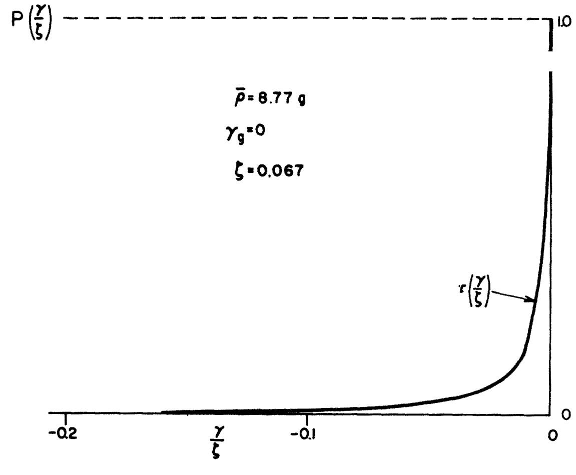

FIG. 7. Dependence of the tunneling function $\tau(\gamma)$ (solid curve) and the relative probability distribution $P(\gamma)$ (dashed curve) on the local density for $\bar{\rho} = \rho_g$.

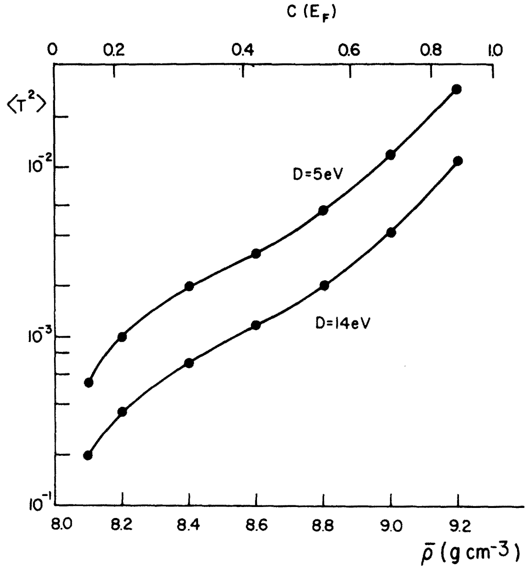

FIG. 8. Density dependence of the mean-square tunneling amplitude across semiconducting regions. Calculations were performed for two values of the deformation potential, which correspond to slightly above the lower limit ($D = 5$ eV) and above our "best" estimate ($D = 11$ eV).

$=8.4\times10^{-3}$ at $C=0.5$. For a value of $t(\gamma_g)$ as small as 10^{-2}, the denominator in (71) may be replaced by unity, which implies that only minimal length regions ($n=1$) need be considered. Equation (65) thus simplifies to

$$(2b/l_G)\langle |T|^2\rangle \ll x \tag{74}$$

with

$$\langle |T|^2\rangle = C(E_F)\, t(\gamma_g)\ . \tag{75}$$

The results of numerical integration of (68) for $\langle T^2\rangle$ are shown in Fig. 8.

Before we can use (74) to establish whether tunneling is negligible, we need a theory of l_G. We now construct one based on a simple tunneling Hamiltonian formalism and an analysis of the metallic conductivity, both for the diffusion regime. We consider two metallic regions, each of cross-sectional area A and volume Ω separated by a semiconducting region of width L. The conductance of Eq. (59) can be readily expressed as

$$G = \frac{I}{A}\,\frac{\partial I}{\partial V} = \frac{2\pi e^2}{\hbar A}\, W^2\Omega^2[n(E_F)]^2 \tag{76}$$

via the tunneling Hamiltonian method. In (76), W is the rms transfer matrix of the tunneling Hamiltonian which can be estimated to be

$$W = l_d\, T\, \tfrac{1}{2} E_g (A l^2)^{1/2}/\Omega\ . \tag{77}$$

In (77), l_d is the decay length inside the barrier,

$$l_d^2 = \frac{\hbar^2}{2m\frac{1}{2}E_g} \tag{78}$$

and T is the tunneling amplitude, Eq. (60). The first three factors in (77) would give the magnitude of W if it were not for the fact that the phases of the wave functions are random in the metallic regions. Thus we have A/l^2 contributions of magnitude l^2 and of random phase to the transverse integration, where l is the phase coherence length. The rms value of transverse integration is therefore $(A/l^2)^{1/2}\, l^2$, as given in (77). Inserting (77) and (78) into (76) gives

$$G = \tfrac{1}{2}\pi e^2(\hbar/m)E_g[l\, T n(E_F)]^2\ . \tag{79}$$

The metallic conductivity may conveniently be written as

$$\sigma_0 = n(E_F)e^2(\tfrac{1}{6}\nu l^2) \tag{80}$$

in the diffusion regime. Here ν is roughly the reciprocal of the time it takes an electron at the Fermi energy to cross the phase coherence length. Comparing (79), (80), and (64), gives

$$l_G = \tfrac{1}{3} m\nu/\hbar n(E_F)E_g \tag{81}$$

for l_G. We can obtain a lower limit for ν in the following way. The density 11 g cm^{-3} is the lower limit of the propagation regime. Consequently

$$\sigma_{11} = \tfrac{1}{3} n_{11}(E_F)e^2\hbar k_F l/m$$

holds but with $k_F l$ about 2, or

$$\sigma_{11} = \tfrac{2}{3} n_{11}(E_F)e^2\hbar/m\ . \tag{82}$$

The conductivity at 9.3 g cm^{-3}, the lower limit of the homogeneous metallic regime is given by (80),

$$\sigma_{9.3} = \tfrac{1}{6} n_{9.3}(E_F)e^2\nu l^2\ . \tag{83}$$

The experimental ratio of σ_{11} to $\sigma_{9.3}$ is about 9. Dividing (82) by (83) gives an expression for the value of ν entering (81),

$$\nu=\frac{4}{9}\frac{n_{11}(E_F)}{n_{9.3}(E_F)}\frac{\hbar}{ml^2}. \qquad (84)$$

Because $k_F l<1$ at 9.3 g cm^{-3}, $l<0.9$ Å. Moreover, $n_{11}(E_F)>n_{9.3}(E_F)$ because of the incipient metal-semiconductor transition. We arrive at $\nu \gtrsim 10^{16}$ sec^{-1}. We use an upper limit of $4\ kT\cong 0.1$ eV for E_g and of the free-particle density of states for $n_{9.3}(E_F)$. These give $l_G>1000$ Å when inserted into (81).

We note parenthetically that $l_d<2b$ for (77), and the tunneling Hamiltonian formalism, to be valid. That requires $E_g>0.006$ eV, which defines the lower limit of the local gap for which the material can be considered locally semiconducting. This is sufficiently small so as not to affect our previous consideration in which we chose zero for the lower limit. Moreover, since l_G is explicitly dependent on E_g, it should have been included explicitly in the averaging over local densities carried out in (67). There the exponential dependence of T^2 on E_g dominates all other dependence and a mean-value argument for the E_g dependence of l_G, as implied above, is sufficient.

Returning now to (74) and inserting $x=3\times10^{-2}$ and $2b/l_G<3\times10^{-2}$, we find that

$$\langle T^2\rangle <1 \qquad (85)$$

is the condition for tunneling to be unimportant in conduction. Comparing (85) with Fig. 8, we see that it is well satisfied for all values of C. In general, tunneling corrections are unimportant when x is relatively large, as is the case for high-temperature materials such as liquid Hg. However, tunneling may also be unimportant in small-x systems for large enough barrier potentials and values of b, as in metal-ammonia solutions.

Having shown that we can ignore tunneling we now make a rough estimate of the kinetic-energy effects associated with the finite size of the metallic regions. These will be largest for the smallest possible metallic region, containing N atoms, with $N\simeq 400$ and b in radius. The effect of finite size will be to split the levels at the Fermi energy into a set of discrete levels with mean spacing δ given by

$$\delta=\frac{1}{D_N(E_F)}=\frac{3}{2}\left(\frac{Nz}{E_F}\right)^{-1}, \qquad (86)$$

according to Kubo.[33] Here $D_N(E_F)$ is the density of states at the Fermi energy E_F of a small metallic particle containing N atoms of valence z. We have invoked the randomness in shape of the metallic regions in using (86). This discreteness of the levels is important only if δ becomes comparable to kT. For $N=400$ and $T=1500$°K, $\delta/kT=0.03$. Such quantum effects are therefore quite unimportant in liquid Hg. This result implies that our treatment of tunneling, which ignores problems of energy conservation, for the tunneling conductivity is, in fact, reasonably accurate.

In summary, we conclude that an interpretation of the values of C taken from the transport data as values of $C(E_F)$, the semiclassically allowed volume fraction for an electron at the Fermi energy, is justified as consistent with values of D and b taken from the transport data.

IX. DISCUSSION

We have proposed that a metal-nonmetal transition can proceed continuously in disordered materials via the interposition of an inhomogeneous regime between essentially homogeneous metallic and semiconducting regimes. We have developed this idea in the present paper to provide an explanation for the curious transport properties of expanded liquid Hg in the density range 9.3–7.8 g cm^{-3}. We argued that below a density of 7.8 g cm^{-3} the material is semiconducting because of a gap exceeding $4kT$ between the filled s band and the empty p band as proposed by Mott.[15-19] The metallic behavior between 9.3 and 11.0 g cm^{-3} is of a diffusion type and can be described by Friedman's theory.[14] We observed that there is therefore great sensitivity of the electronic structure to density in the range of transition. Consequently we proposed that density fluctuations were sufficient to cause inhomogeneities in electron structure and transport in that density range. To explore the consequences of this idea we introduced the Debye short correlation length b to specify the spatial extent of fluctuations in a smoothed local density. We then assumed that b was several interatomic separations in size and consequently larger both than the Ornstein-Zernike decay length and the phase-coherence length of the conduction electrons. This permitted us to state that the microscopic conductivity was local and roughly constant within b. Regions separated by more than b have statistically independent values of local conductivity. To solve the resulting transport problem we utilized a general version of effective-medium theory. The latter was cast into a form equivalent to that of a two-component system by defining a conductivity separating the semiconducting from metallic values of the local conductivity. This allowed us to introduce a metallic volume fraction C and mean transport coefficients for the metallic and semiconducting regions. For simplicity and to avoid proliferations of parameters, these were given values equal to the values of the transport coefficients at the limits of the inhomogeneous regime. It was found that a self-consistent interpretation of data on resistivity, Hall-coefficient, and volume and temperature dependence of the resistivity could be carried out via the resulting theory. The density dependence of C and a rough estimate of the deformation potential were obtained. A value of $b = 15$ Å was then inferred from a statistical analysis of density fluctuations and turned out to satisfy the consistency requirements of the physical picture. The concept of a local-energy gap was then introduced and used to construct a semiclassical picture in which electrons at the Fermi energy are confined only to metallic regions. An estimate was made of the mean tunneling probability through forbidden regions which showed that tunneling was unimportant in the transport properties. The mean level splitting in isolated allowed regions was found to be much smaller than kT. Thus quantum corrections to the semiclassical picture turned out to be unimportant for expanded liquid Hg. This allowed us to identify the metallic volume fraction extracted from the transport data with the allowed volume fraction for electrons at the Fermi energy and made possible the application of semiclassical percolation concepts to liquid Hg. From the analysis of the transport data we obtained $\rho_g = 8.77$ g cm^{-3} for the local density corresponding to the opening of the gap and $\rho_{pg} = 8.2$ g cm^{-3} for the mean density where $C = C^* = 0.2$ which may be taken to characterize a pseudometal to pseudo-semiconductor transition. We note a difference between our value of $\rho_{pg} = 8.2$ g cm^{-3} and Hensel's extrapolation of the optical data[7] in the vapor to give a vanishing optical gap at 5.5 g cm^{-3}. This is a serious discrepancy and may arise from the extrapolation used.[7] It is most unlikely that our estimate of ρ_{pg} can be off enough to eliminate the discrepancy. What is needed is a series of optical measurements in the liquid from the critical density up.

Despite the internal consistency and quantitative success of the description of the data so developed, the picture proposed is complex. Many approximations and simplifications were introduced in order to make theoretical analysis tractable. It is therefore important to consider the question of the uniqueness of our picture. Several alternative models either come to mind or have already been proposed. We review these critically below.

Kirkpatrick[34] has also suggested that an inhomogeneous transport regime exists in liquid Hg in which percolation through classically allowed regions plays a crucial role. His interpretation is based on the relations

$$R_{\mathrm{fe}}/R = P(C(E_F)), \tag{87}$$

$$\sigma \propto [\tfrac{3}{2}C(E_F) - \tfrac{1}{2}], \quad C(E_F) > 0.4 \tag{88}$$

$$\sigma \propto [C(E_F) - C^*]^{1.6}, \quad C(E_F) < 0.4. \tag{89}$$

Kirkpatrick's conjecture concerning the dependence of the Hall coefficient on the percolation probability $P(C(E_F))$, Eq. (87), is incompatible with the results[32] of the effective-medium theory for the Hall effect. Eqs. (88) and (89) for the conductivity have to be modified to include the conductivity ratio x. He apparently assumed that $C(E_F) \propto \bar{\rho}$ and fitted the conductivity data over the density range 11.0–8.7 g cm^{-3} to (89). The percolation threshold obtained in this way coincides with the density at which R_{fe}/R tends to zero when extrapolated from above $\bar{\rho} = 8.7$ g cm^{-3}. Since the region over which R/R_{fe} deviates from unity starts at $\bar{\rho} = 11$ g cm^{-3}, Kirkpatrick's interpretation[34] of the data implies that the inhomogeneous regime starts there as well. This is the most extreme possible interpretation based on inhomogeneity. We have three objections to this assignment of density to the inhomogeneous regime: (i) the quantitative fit of σ to the Friedman theory[14] is better[8(b)] than that to (88) and (89) in the region $9.2 < \bar{\rho} < 11$ g cm^{-3}; (ii) the variation of R and σ with density are not mutually consistent in this application of percolation theory. Because R_{fe}/R reaches unity at $\bar{\rho} = 11$ g cm^{-3}, Kirkpatrick assumes that $C(E_F) = 1$ there. On the other hand, serious deviations of σ from Eq. (89) occur when $C(E_F)$ exceeds 0.4 or 0.5. Kirkpatrick fits the data for σ with (89) also up to $\bar{\rho} = 11$ g cm^{-3}. Thus, his interpretation implies that $C(E_F)$ is simultaneously 1 and 0.5 at $\bar{\rho} = 11$ g cm^{-3}; (iii) Kirkpatrick's interpretation[34] implies that $\rho_{pg} = 8.6$ g cm^{-3}, and what we designated by ρ_F becomes 11 g cm^{-3}. Using our fluctuation theory together with these values for ρ_{pg} and ρ_F, we obtain values of 9.5 g cm^{-3} for ρ_g, $\zeta = 0.12$, and 9 for N at $\bar{\rho} = 11$ g cm^{-3}. That value of N is too low to permit the material to be considered submacroscopically inhomogeneous, as is required for the interpretation.

The opposite extreme interpretation is that the material remains homogeneous and metallic down to densities below 8.5 g cm^{-3} (where the Hall-effect data cease) but that the Friedman theory[14] goes wrong below 9.3 g cm^{-3}. However, it seems to us that there is no room for error in Friedman's argument for a single component system. Once the condition of random phases is reached, the only further change possible is nonuniformity of the wave-function amplitudes, as we have proposed. Moreover this uniform metallic picture does not explain why the temperature and volume coefficients of the conductivity start increasing below 9.0 g cm^{-3}. We are, of course, familiar with the fact that small deviations of the Hall coefficients of binary alloys in the propagation regime, e.g., 15% for Hg/In alloys,[35] are often difficult to interpret accurately because, e.g., of small uncertainties in knowledge of pseudopotentials and pair correlation functions as well as uncertainties about the organization of higher-order perturbation theory as the strong scattering limit is approached. This can by no means be used as an argument[27(b)] that the Hall effect is not suitable as a diagnostic tool for establishing transport regimes, where we are concerned with changes of 100%–1000% in this quantity. We therefore rule out the persistence of a homogeneous metallic regime down to about 8.5 g cm^{-3}.

A serious possibility is that originally proposed by Mott[15-19] and subsequently by Even and Jortner.[8(b)] The latter considered the material homogeneous and that a mobility gap opens at $\rho = 9.2$ g cm^{-3} and reaches $4kT$ at 7.8 g cm^{-3}. That corresponds to a deformation potential of $D = 0.5 \times 8.5/1.5 = 2.3$ eV. Assuming symmetric conduction and bands, the conductivity can be written[36]

$$\sigma \geq 2N(E_c)e\mu^*(E_c)\, kTe^{-(E_c - E_F)/kT}, \tag{90}$$

where $N(E_c)$ and $\mu^*(E_c)$ are the density of states and the mean mobility at or near the mobility edge E_c, respectively. The inequality arises in Eq. (75) because we have omitted contributions to the conductivity from localized states within the mobility gap. In Mott's picture of transport[15-19] in disordered materials in which $\mu(E)$ drops abruptly from the diffusion value to zero (at $T = 0$), both $N(E_c)$ and $\mu(E_c)$ are approximately density independent. In our semiclassical picture of transport near a mobility edge, $N(E_c)$ is constant but $\mu(E_c)$ will be a decreasing function of density because $\mu(E)$ goes gradually to zero as $E \to E_c$ over a range of energy increasing with decreasing density. Thus the pre-exponential in Eq. (75) is smaller than or equal to σ_M, the conductivity at 9.2 g cm^{-3}, i.e., the density at which the mobility gap first opens,

$$2N(E_c)e\mu(E_c)kT \leq \sigma_M. \tag{91}$$

Allowing the opposite inequalities in (90) and (91) to compensate, we obtain

$$\sigma/\sigma_M \simeq e^{-E_g/2kT}, \tag{92}$$

where E_g is the mobility gap in the homogeneous material. If use the above deformation potential $D = 2.8$ eV, we obtain a value of 0.14 for σ/σ_M at $\rho = 7.8$ g cm^{-3}. Experimental conductivity values[1-6] give instead $\sigma/\sigma_M = 0.02$ at 7.8 g cm^{-3} at 1500 °C. Further difficulties are encountered when using Mott's picture[15-19] for the temperature and volume dependence of conductivity. However, the rough constancy of the Hall mobility could be explained within this picture as owing to the constancy of the Hall mobility of electrons at E_c. On the other hand, if our semiclassical picture of transport near the mobility edge is used, the Hall mobility would be a decreasing function of density.

We note in passing that (92) is also applicable to our inhomogeneous model provided we replace the macroscopic conductivity σ_M by the local conductivity σ_g at local density $\rho_g = 8.77$ g cm^{-3}, so that for the local conductivity of the semiconducting regions we have $\sigma/\sigma_g = e^{-E_g/2kT}$. This implies that for the local conductivities $\sigma(4kT)/\sigma_g = 0.14$. On the other hand, for the macroscopic conductivities[6] $\sigma\,(\bar{\rho} = 7.8)/\sigma(\bar{\rho} = 8.77) = 0.07$ at 1500 °C. The discrepancy of a factor of 2 originates from the averaging process contained within the effective-medium theory.

Thus far it would appear the picture developed in the present paper offers only a quantitative improvement over Mott's idea[15-19] of a mobility gap in a microscopically homogeneous material at $\rho = 9.2$ g cm^{-3}. However, we cannot ignore the existence of density fluctuations. Making use of the deformation potential of 2.8 eV originating from Mott's model, one can estimate the inhomogeneity of the material for transport as follows. First the conductivity is taken as

$$\begin{aligned} \sigma' &= \sigma_M e^{-E_g/2kT}, \quad \rho < 9.2 \text{ g cm}^{-3} \\ \sigma' &= \sigma_M, \quad \rho > 9.2 \text{ g cm}^{-3}. \end{aligned} \tag{93}$$

This underestimates somewhat the inhomogeneity of the conductivity. Next, we set

$$E_g = D(\gamma_F - \gamma), \tag{94}$$

where

$$\gamma_F = (\rho_F - \bar{\rho})/\bar{\rho}. \tag{95}$$

The probability distribution for γ is taken from Sec. III, Eq. (27). This gives the conductivity distribution

$$\begin{aligned} P(\sigma') &= (2\pi\zeta^2)^{1/2} \left\{ \exp\left[-\left(\frac{2kT}{D} \ln\left(\frac{\sigma'}{\sigma_M}\right) + \gamma_F \right)^2 2\zeta^2 \right] \right\} \frac{2kT}{D\sigma'} \\ &\quad + \left[\tfrac{1}{2} - \tfrac{1}{2}\operatorname{erf}\left(\frac{\gamma_F}{\sqrt{2}\zeta} \right) \right] \delta(\sigma' - \sigma_M), \quad \sigma' < \sigma_M^+ \\ P(\sigma') &= 0, \quad \sigma' > \sigma_M^+. \end{aligned} \tag{96}$$

For a density $\bar{\rho}$ in the middle of the transition region, e.g., 8.5 g cm^{-3}, the weight of the δ function in Eq. (96) is negligible and it can be ignored.

The most probable conductivity is simply

$$\sigma_{\text{Mode}} = \sigma_M \, e^{-(D/2kT)\gamma_F}, \tag{97}$$

and the spread of the distribution is

$$\Delta\sigma = 2\sigma_{\text{Mode}} \sinh(D\xi/2kT). \tag{98}$$

The next question is what sampling region to consider in estimating the density fluctuations. In our previous treatment (Secs. V–VII) we have taken $\xi = 0.07$, corresponding to $N = 400$, and use this same value for N to begin the present argument. Thus from Eq. (83) we have $\Delta\sigma = 2.7\sigma_{\text{Mode}}$. The conductivity is therefore quite inhomogeneous for density fluctuations for the regions of that size. To reduce $\Delta\sigma$ to $0.5\sigma_{\text{Mode}}$ say, we would have to increase N to 7700 or b to 40 Å. Over such distances one runs into serious difficulties with inhomogeneities in the wave-function amplitude, the exponential decay of wave functions at the mobility edge in one region across a neighboring region of larger mobility gap. We conclude that inhomogeneities in transport and electronic structure are inescapably implied by the parameters obtained by fitting experimental data into Mott's picture,[15-19] and we are led back to our original approach.

Moreover, our picture of liquid Hg is essentially identical to our picture[29] of liquid Te apart from the physical basis of the microscopic inhomogeneities. In liquid Te, the behavior of σ, R, and μ is similar to that of Hg, and has received no convincing physical interpretation other than the one we have given. The same technique of analysis and physical picture are proving useful for a still more complex system, liquid metal-ammonia solutions.[29] They are promising even for solid systems such as granular metals.[37]

To conclude, we have added to earlier views on transport in expanded liquid Hg the notion that in between the metallic and the semiconducting regimes there is an intermediate regime in which density fluctuations lead to localization and percolation. Because of percolation effects in the inhomogeneous regime, the metal-nonmetal transition in this one-component system should be envisioned in terms of a continuous decrease in the conductivity in that range. We believe this picture has wide applicability for disordered systems.

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