The result of the present one-dimensional treatment, in spite of its limited applicability, qualitatively explains the line structure of the saturation spectra obtained in ionospheric experiments at Arecibo.[7] A fully quantitative theory would have to be three-dimensional and would have to take into account Earth's magnetic field and the inhomogeneity of the medium.

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# Logarithmic Terms in the Diffusion Coefficient for the Lorentz Gas

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By means of a computer experiment, using the method of molecular dynamics, evidence has been obtained for logarithmic terms in the density expansion of the diffusion coefficient for the two-dimensional Lorentz gas.

The possibility of a power-series expansion in the density for transport coefficients was criticized some time ago[1-3] because of the appearance of divergencies in the formal expressions for the expansion coefficients beyond a certain order. The removal of the divergencies led to the conclusion that transport coefficients should have logarithmic terms in their density expansion.

So far no experimental confirmation of the existence of logarithmic terms could be obtained. The reason is that for real systems the values of the coefficients of the logarithmic terms are unknown, and so one has to obtain evidence from least-squares fits to low-density data comparing polynomials and polynomials with logarithmic terms added. Kestin, Paykoc, and Sengers[4] performed such an analysis for the shear viscosity and concluded that the logarithmic terms are too small compared to the regular terms to be detectable from their experiments.

The presence of the logarithmic terms can in principle also be confirmed by means of a computer experiment. This is an attractive approach since one can perform it on simplified models for which the coefficients of the logarithmic terms have been calculated explicitly. One candidate would be the two-dimensional, hard-disks system, for which the coefficient of the first logarithmic term in the density expansion of the shear viscosity has indeed been determined theoretically.[5,6] However, the computer experiment carried out on this system[7] has permitted neither confirmation nor rejection of the logarithmic term. Another candidate is the Lorentz gas, for which the coefficient of the first logarithmic term in the density expansion of the diffusion coefficient has been computed both in two and three dimensions.[8,9] Fortunately, in the two-dimensional case the first logarithmic term is found to be large compared to the regular term in the same order, and therefore a computer experiment was performed on this system.

The particular case of the Lorentz gas adopted here is an assembly of $N$ random point scatterers with density $n$ in which a hard disk of radius $\sigma$ moves. The absolute value $v$ of the velocity is a constant of motion. The relevant density expansion for $N \to \infty$ is

$$v\sigma/D = c_1 n^* + c_2' n^{*2} \ln n^* + c_2 n^{*2} + c_3'' n^{*3} (\ln n^*)^2 + \cdots, \quad (1)$$

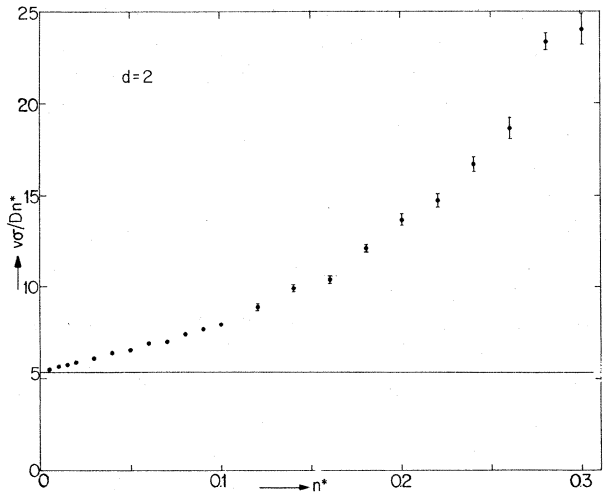


FIG. 1. The "experimental" diffusion coefficient, inverted, reduced, and divided by the density (closed circles), in comparison with the Boltzmann term $c_1 = \frac{16}{3}$ (solid line).

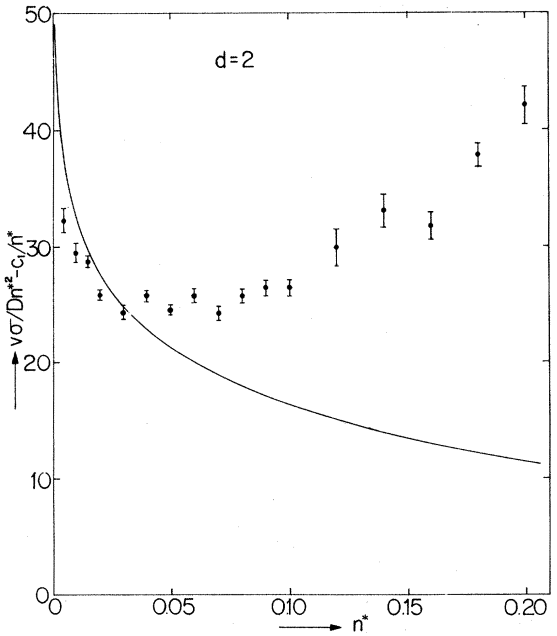


FIG. 2. The difference between $v\sigma/D$ and the Boltzmann term divided by $n^{*2}$ (closed circles) compared to the most important logarithmic term $-\frac{64}{9}\ln n^*$ (solid line).

where $D$ is the diffusion coefficient and $n^* = n\sigma^d$ the reduced density of the scatterers, the dimensionality being given by $d = 2$. The coefficient $c_1 = \frac{16}{3}$ follows from the Boltzmann equation. The coefficient $c_2' = \frac{64}{9}$ has been computed by Weijland and van Leeuwen,[9] and $c_2 = -4.68$ and $c_3'' = 24.10$ have been computed for this experiment by the same type of diagram analysis which led to the value of $c_2'$.

In the computer experiment the positions of the $N$ scatterers are chosen at random in a square box on which periodic boundary conditions are imposed. The initial position of the moving particle and the initial direction of its velocity are also random. The numerical solution of the equation of motion yields the dynamical variables of the moving particle as a function of time. From this information the velocity autocorrelation function can be calculated, which reads in its reduced form

$$\varphi(t^+) = \langle \vec{v}(0) \cdot \vec{v}(t^+) \rangle / v^2, \tag{2}$$

where $t^+ = t/\tau$ is reduced time with $\tau = \sigma/2n^*v$ being the mean free time. The averaging procedure consists of taking an average over a number of different random configurations of $N$ scatterers and a time average for each configuration. The reduced diffusion coefficient can be expressed as an integral over the velocity autocorrelation function

$$D/v\sigma = (1/2dn^*)\int_0^\infty dt^+ \, \varphi(t^+). \tag{3}$$

In the numerical calculations the integral is cut off at a time beyond which contributions are negligible (see below).

In Fig. 1 the "experimental" values obtained for $v\sigma/D$ divided by $n^*$ are plotted against the density; for low densities the data converge perfectly to the Boltzmann result $c_1$. Next, the Boltzmann contribution is subtracted from $v\sigma/D$ and the difference is divided by the density squared in order to compare the resulting data with the first logarithmic term as shown in Fig. 2. For low densities the data are not only of the same order of magnitude as the logarithmic term but also the density dependence, for $n^* < 0.03$, is strikingly similar. The computations carried out at these densities were designed so as to yield statistical errors (of a 68% confidence level) smaller than half the differences of the corresponding points and their neighbors on the logarithm. This required long runs on the computer since on this scale the statistical error of the data is inversely proportional to the density for given accuracy of $\varphi(t^+)$. For $n^* > 0.03$ the data in Fig. 2 lie systematically above $c' \ln n^*$ and it is concluded that the contribution of higher-order terms is growing fast.

It has been verified whether a power series could fit the data and, given the accuracy of the data, it is not easy to distinguish unambiguously between the predicted expansion and a power ser-

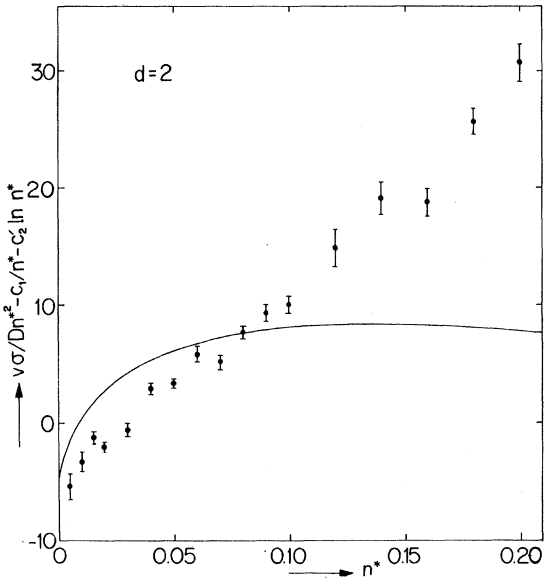


FIG. 3. The closed circles show the data after subtraction of the first logarithmic term: $v\sigma/Dn^{*2}-16/3n^{*}+\frac{64}{9}\ln n^{*}$. For comparison the sum of the other known terms, $-4.68+24.10n^{*}(\ln n^{*})^{2}$, is shown by the solid line.

ies proper. However, upon performing a least-squares fit of the second-order polynomial $a_0+a_1n^{*}+a_2n^{*2}$, which contains as many adjustable coefficients as Eq. (1) after subtraction of the Boltzmann term, to the seven data points with $n^{*}\leq 0.05$ (as given in Fig. 2) unacceptable coefficients are found: $a_0=34.4$, $a_1=-524$, and $a_2=6763$. In view also of the value of the Boltzmann coefficient, $c_1=\frac{16}{3}$, the coefficients would increase by about a factor of 10 with each order. This is all the more improbable since in three dimensions[8] the first two regular terms differ only by a factor of 2. On the other hand reasonable values for $c_1'$, $c_2$, and $c_3''$ have been obtained from a least-squares fit of the predicted expansion to the same data: $c_2'=-8.7$, $c_2=-18.9$, and $c_3''=38.2$.

In Fig. 3 the difference between the data and the first logarithmic term is compared with the remaining known terms $c_2+c_3''n^{*}(\ln n^{*})^{2}$. At most densities these two terms give a correction into the right direction. At the three lowest densities the increase with the density runs parallel to that of the data, but higher-order terms cannot be neglected even at these densities.

The evidence for logarithmic terms depends heavily on the data at the four lowest densities and therefore the cutoff of $\varphi(t^{+})$ is discussed explicitly for these densities. In Fig. 4 the difference of $\varphi(t^{+})$ and the Boltzmann result $\varphi_B(t^{+})=\exp(-4t^{+}/3)$ is shown; for $t^{+}>6$ it is given on an enlarged scale. Within the statistical error, which is shown for a number of points, $\varphi(t^{+})$ can be considered to be zero for $t^{+}>9$. Thus a cutoff at $t^{+}=10$ is justified. For higher densities cutoffs at larger values of $t^{+}$ were necessary, since higher densities favor a negative velocity autocorrelation also at larger times.

Apart from the statistical error, computed from the standard deviation of subaverages, and a systematic error in the diffusion coefficient due to the cutoff of $\varphi(t^{+})$, attention should be given to the systematic error due to the deviation of a periodic system of $N$ scatterers from an infinite system which is required to be smaller than the statistical error. Computations on the $N$ depen-

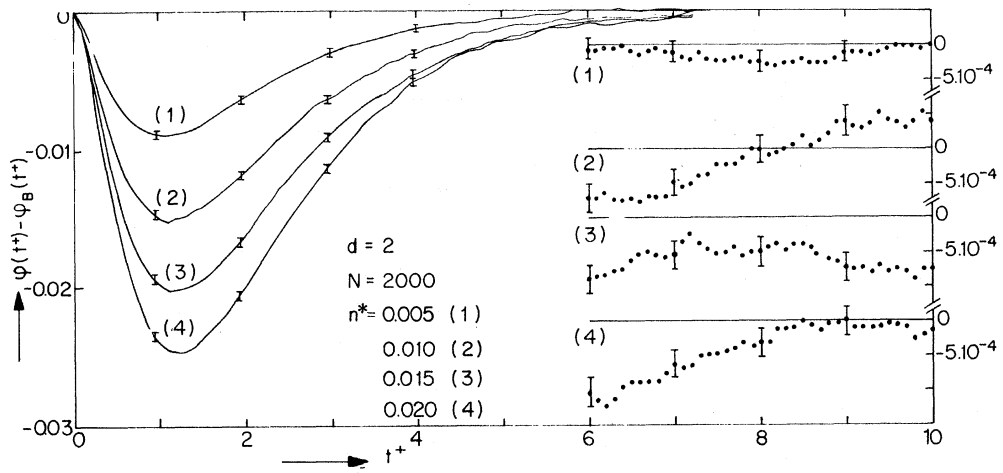


FIG. 4. The quantity $\varphi(t^{+})-\varphi_B(t^{+})$ for the four most accurate points and lowest densities. The lines are drawn through the data points, which were obtained at time intervals of 0.1; at several points the error bars are given. The tails for $t^{+}>6$ are given on a 5-times enlarged scale (closed circles).

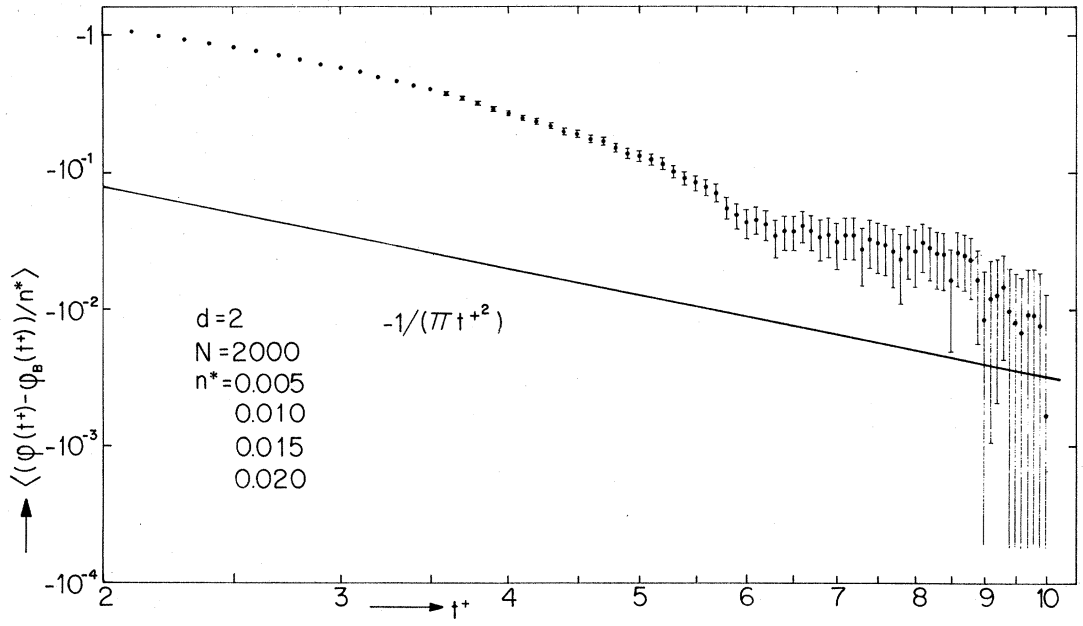


FIG. 5. The quantity $\varphi(t^+) - \varphi_B(t^+)$ averaged over the four lowest densities with weight factor $1/n^*$, plotted on a log-log scale (closed circles). The straight line represents the corresponding asymptotic expression $-1/\pi(t^+)^2$.

dence, the detailed results of which will be published elsewhere,[10] have shown that for $n^* = 0.01$, within the required accuracy $N = 100$ is probably too small but $N = 500$ is sufficiently large. For $n^* = 0.1$ it was found that $N = 25$ is already large enough. These numbers confirm what one would expect qualitatively from a comparison of the mean free path and the size of the periodic square box: For lower densities one needs larger systems to get comparable deviations. For all densities, provided they are not too high, small $N$ resulted in a long positive tail for $\varphi(t^+)$. The diffusion coefficient was thus too high.

For the data presented $N = 2000$ was used for $n^* \leq 0.1$ and $N = 500$ for $n^* > 0.1$. The only density which is not covered by the computations on the $N$ dependence is $n^* = 0.005$. However, since $N = 500$ is large enough for $n^* = 0.01$ it can be safely assumed that $N = 2000$ is large enough for $n^* = 0.005$. This is also confirmed by the structure of $\varphi(t^+)$, which at this density shows no positive tail.

In addition we will pay some attention to the asymptotic behavior of the velocity autocorrelation function. Ernst and Weyland[11] derived expressions for the Lorentz gas in the ring approximation from a kinetic argument and their result reads in two dimensions, for one value of $v$,

$$\varphi(t^+) - \varphi_B(t^+) = -n^*/\pi(t^+)^2. \quad (4)$$

This equation only holds in the limit of low densities and of long times where it is a very small effect. In order to improve statistics the function $\varphi(t^+) - \varphi_B(t^+)$ was averaged over the four lowest, and most accurate, densities with a weight factor $1/n^*$. From Fig. 5 it follows that for $t^+ < 9$ the asymptotic behavior is still not dominant and for larger times the data have error bars too large to be conclusive, though $\varphi(t^+)$ has been determined for each of these densities with a better statistical accuracy than $2 \times 10^{-4}$.

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# Pressure-Induced Electronic Collapse and Semiconductor-to-Metal Transition in EuO

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Pressure-volume data for EuO to 400 kbar are presented. An electronic collapse in the Eu ion involving the promotion of a $4f$ electron to the $5d$ state occurs near 300 kbar at room temperature. The structure remains NaCl type in this transformation. The transition appears to be first order and is from semiconductor to the metallic state. The collapsed NaCl phase undergoes a phase change to the CsCl-type structure near 400 kbar.

We have investigated the pressure-volume relationship in EuO to 400 kbar at room temperature, with a view to finding out if a pressure-induced electronic collapse due to the promotion of a $4f$ electron to the $5d$ state occurs in the Eu ion. Such a transition does not seem to take place in EuTe,[1] EuSe, and EuS[2] at pressures up to 300 kbar. In EuO we have found strong evidence for such an electronic transition near 300 kbar. The transition is isostructural (NaCl type to NaCl′) but the lattice parameter contracts rapidly near this pressure. The high-pressure phase exhibits a *silvery luster* indicating that it is metallic in nature and hence the transition is from semiconductor to metal. This is the first time a $4f$-$5d$ electronic collapse has been observed in a europium chalcogenide and the finding has interesting consequences.

Pressure-volume data to 400 kbar were obtained using a high-pressure diamond-anvil x-ray camera,[3,4] with Ag as the internal standard. Pressures were computed from the recent data of Liu and Bassett[5] for silver. The latter have compared Ag with NaCl up to 300 kbar. The bulk modulus $B_0$ and its pressure derivative $B_0'$ obtained by Liu and Bassett were used in the Birch equation of state to extrapolate the pressure scale above 300 kbar. The pressures are believed to be true within ± 20 kbar in the higher pressure range and ± 10 kbar below 300 kbar.

In Fig. 1 the pressure-volume data for EuO are presented. In a previous study McWhan, Souers, and Jura,[6] have obtained $P$-$V$ data on EuO to 80 kbar and fitted their experimental points to a curve calculated with $B_0 = 1170$ and $B_0' = 4$ in the Birch equation of state. Subsequently McWhan revised the value of $B_0$ to 1130 kbar.[7] In Fig. 1 the solid curve represents the calculated $P$-$V$ relationship using $B_0 = 1130$ kbar and a $B_0'$ of 3.75, in the Birch equation of state. The present data, which extend to very much higher pressures than those of Ref. 6, give a better fit with a $B_0'$ of 3.75. Up to about 280 kbar our experimental points follow the calculated curve closely. Within a narrow pressure interval the volume drops rather abruptly by about 4%. However, there is no change in the structure; the NaCl-type structure remains NaCl. The lattice-parameter contraction suggests that the atomic volume of one of the ions decreases. We ascribe this rather rapid volume decrease without change of structure to a change in the valence state of the Eu ion from divalent to trivalent due to $4f \rightarrow 5d$ electron promotion. Figure 1 also shows a further abrupt decrease in volume near 400 kbar. This volume decrease is associated with the transition of the collapsed

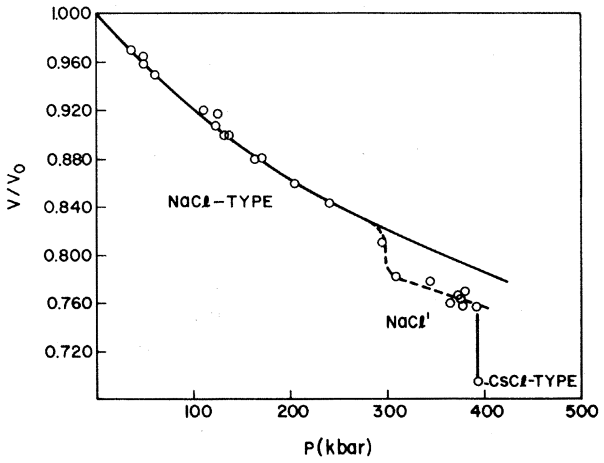


FIG. 1. Pressure-volume relationship for EuO.