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Diffusion, percolation, and trapping in the Lorentz gas via variational kinetic theory

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A recently developed variational principle is applied to the solution of a self-consistent repeated-ring kinetic theory of the Lorentz gas in one, two, and three dimensions. Calculated values of the diffusion constant D, are in excellent agreement with molecular-dynamics simulation results for $d=2$ and 3. The theory predicts the existence of "critical scatterer densities," ρ_c^*, above which $D=0$; for $d=1-3$, $\rho_c^*=0$, π^{-1}, and $3/2\pi$, respectively. The theory behaves well above ρ_c^*. The behavior of D near ρ_c^* is examined, as is the "long-time tail" at densities close to ρ_c^*, and a comparison of the results to those of other authors is given.

I. INTRODUCTION

The Lorentz gas (LG) is a relatively simple but very nontrivial model for tagged-particle motion; a point particle moves through a universe of fixed spherical elastic scatterers. In the most tractable version, which we discuss, the scatterers are allowed to overlap. In this model, under certain circumstances, the diffusion constant D vanishes. For overlapping discs in two dimensions, a "continuum percolation problem" is defined; above a critical density $\rho_p^* \simeq 0.37$ ($\rho^* = \rho a^d$, a is scatterer radius, d is dimension), an infinite, connected cluster of discs exists.[1(a)] Since free space must then come in islands,[1(b)] the particle is trapped for $\rho^* > \rho_p^*$, and D equals zero. It appears possible that the density where D vanishes, defined as ρ_c^*, is less than ρ_p^*; all we can say for sure is $\rho_c^* \leq \rho_p^*$. From here on, "critical density" refers to ρ_c^*. The computer simulation of Alder and Alley[1(c)] shows $0.34 \lesssim \rho_c^* \lesssim 0.37$.

In three dimensions, the percolation density for overlapping spheres is $\rho_p^* = 0.084$,[1(a)] but there is no reason to expect that formation of an infinite cluster of spheres will divide space into islands and trap the particle. A very recent computer[1(b)] study of static percolation for free space found no infinite cluster of free space to exist above $\rho^* \cong 0.81$, so we expect $\rho_c^* \leq 0.81$. Moleclar-dynamics results only exist for $\rho^* \leq 0.4$,[9] and calculations at higher density are needed to probe the critical region. In one dimension, the particle is trapped at all densities and $\rho_c^* = 0$. Of course, the vanishing of D has nothing to do with the formation of an infinite cluster of rods. The one-dimensional behavior is obvious. It is not trivial, however, to construct an approximate kinetic theory which reproduces this behavior, so performance in $d=1$ constitutes a valuable test for a proposed theory.

A good kinetic theory of the LG at low scatterer density clearly involves (except for $d=1$) no more than a solution of the Lorentz-Boltzmann equation. On the other hand, construction of a theory which shows trapping, i.e., the existence of a critical density, is difficult. It would seem that trapping in the LG is an even stronger localization than the crucially important "cage effect" for real liquids. Thus, understanding of the dense LG is a stepping stone to an understanding of tagged-particle motion in dense real fluids. In some binary mixtures (H_2-Kr), the LG is actually a realistic model for the light component. Of course, the motion of a particle moving through a random medium is of great inherent interest.

Theories of the dense LG have been given based upon mode coupling,[2] and moderate density theories have been derived from kinetic theory;[3] it is possible, as we shall show, to relate these seemingly different approaches. Two of the mode-coupling theories show critical densities. The key element, in any case, is inclusion of "recollisions," where the tagged particle collides with a scatterer which it previously encountered; such events are absent from the Lorentz-Boltzmann equation. Theories in which tagged-particle propagation between recollisions is given by a low-density theory do not show critical densities, while theories where the intermediate propagation is given by the "true" dynamics do show do show critical densities. On the other hand, the former type of theory can be derived semirigorously for moderate densities[4] while the latter is rather *ad hoc*, if intuitively appealing.

Non-self-consistent theories have been given,

based upon the both the ring and repeated-ring kinetic equation[3]; these theories give reasonable results for moderate reduced densities. Until recently, the repeated-ring results have been uncertain because of the approximations which has to be made to solve the complicated kinetic equations. However we have given a variational principle for the repeated-ring equation,[5] based on the developed by Cercignani *et al.*,[6] which appears to produce solutions of great accuracy. The non-self-consistent variational calculations of the velocity correlation function are accurate up to $\rho^*=0.2$ in three dimensions, where ρ^* is the reduced number density of the scatterers. These calculations show no critical densities.

Self-consistent mode coupling was applied to the Lorentz gas by Masters and Madden (MM).[2(a)] They found a critical density of $\rho_c^*=3/2\pi$ in three dimensions. They also concluded that the solutions of their equations became unphysical above ρ_c^*. In fact, as we point out later on, their equations do correctly describe the high-density regime. As we also show, the MM mode coupling is very closely related to repeated-ring kinetic theory.

Götze, Leutheusser, and Yip[2(b)] (GLY) gave a comprehensive self-consistent mode-coupling theory; their theory is related to ring kinetic theory. Not only did they find critical densities, $\rho_c^*=2/\pi$ in two dimensions and $9/4\pi$ in three, but they gave the behavior of D near ρ_c^* in two and three dimensions, and they studied the LG, for the first time, at $\rho^*>\rho_c^*$. In addition, their theory, although not a kinetic theory gave an extermely accurate value for the first density correction to the low density D; they discussed several other features of the LG as well.

All the above suggests that a self-consistent version of the variational repeated-ring theory would be of interest. In previous treatments of inherently high-density phenomena, the repeated-ring equation has proven far superior to the ring equation. For example, the repeated-ring equation gives the Stokes-Einstein law for self-diffusion at low Knudsen number,[7] while the ring equation gives unphysical results.[8] Thus, one might guess that a repeated-ring theory is indicated for a study of the dense LG. Also, self-consistent kinetic theory is automatically correct at short times and distances, and at low densities, something which is often a problem in mode coupling.

In this article, we present several results of the variational self-consistent repeated-ring theory for the overlapping Lorentz gas. The theory appears to be remarkably successful.

II. EQUATIONS AND SOLUTIONS

A. The self-consistent repeated-ring equation

In our recent paper,[5] we wrote down the repeated-ring equations in the form

$$[z-\rho\lambda_D(\vec{v}_1)]\vec{\Phi}(\vec{v}_1,z) = \rho\int \vec{d}r_{12}\bar{T}(12)\vec{\theta}(\vec{v}_1,\vec{r}_{12},z)+\vec{v}_1\phi_0(\vec{v}_1)\,, \tag{1}$$

and

$$[z+\vec{v}_1\cdot\vec{\nabla}-\rho\lambda_D(\vec{v}_1)-\bar{T}(12)]\vec{\theta}(\vec{v}_1,\vec{r}_{12},z) = T(12)\vec{\Phi}(\vec{v}_1,z)\,, \tag{2}$$

where $T(12)$ and $\bar{T}(12)$ are binary-collision operators, $\vec{r}_{12}$ is the displacement vector between the tagged particle and scatterer number 2, $\vec{v}_1$ is the velocity of the tagged particle, $\phi_0(\vec{v}_1)$ is the microcanonical velocity distribution function which means the particle has always a constant speed v_0, z is the frequency Laplace-transform variable, ρ is the number density of the scatterers, and $\lambda_D(\vec{v}_1)$ is the Lorentz-Boltzmann operator. For a three-dimensional Lorentz gas, the action of $\lambda_D(\vec{v}_1)$ on a function of velocity $f(\vec{v}_1)$ is given by

$$\rho\lambda_D(\vec{v}_1)f(\vec{v}_1)=-\nu_B\left[f(\vec{v}_1)-\phi_0(\vec{v}_1)\times\int d\vec{v}f(\vec{v})\right], \tag{3}$$

where $\nu_B=\pi\rho a^2/v_0$, the Boltzmann friction coefficient, and a is the collision radius of the tagged particle.

In order to calculate the z-dependent diffusion constant $D(z)$, defined in d dimensions by $(1/d)$ times the Laplace-transformed velocity-time correlation function, we must solve the above equations for $\vec{\phi}(\vec{v}_1,z)$, and use

$$D(z)=\frac{1}{d}\int d\vec{v}_1\vec{\Phi}(\vec{v}_1,z)\cdot\vec{v}_1\,. \tag{4}$$

Equations (1) and (2) clearly only give an approximation to the true $\vec{\Phi}(\vec{v}_1,z)$ which would give the exact value of $D(z)$ through the above equation. Let us write the true equation of motion of $\vec{\Phi}(\vec{v}_1,z)$ in the form

$$[z-\rho\hat{B}(\vec{v}_1,z)]\vec{\Phi}(\vec{v}_1,z)=\vec{v}_1\phi_0(\vec{v}_1)\,, \tag{5}$$

where $\hat{B}(\vec{v}_1,z)$ is the exact kinetic operator which gives the equation of motion of any function of the tagged particle's velocity. If we further write $D(z)$ in the form

$$D(z)=\frac{v_0^2}{d}\frac{1}{z+\nu(z)}\ , \tag{6}$$

where $\nu(z)$ is the exact frequency-dependent friction coefficient, we have the results

$$\rho\hat{B}(\vec{v}_1,z)\phi_0(v_1)=0 \tag{7a}$$

and

$$\rho\hat{B}(\vec{v}_1,z)\vec{v}_1\phi_0(\vec{v}_1)=-\nu(z)\vec{v}_1\phi_0(\vec{v}_1)\ . \tag{7b}$$

The first equality arises because the number density of the tagged particle is a conserved variable, the second arises from Eqs. (4)—(6) and from noticing that in a microcanonical ensemble $\vec{\Phi}(\vec{v}_1,z)\propto\vec{v}_1\phi_0(\vec{v}_1)$.

We now consider the first two equations of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy for $\vec{\Phi}(\vec{v},z)$. The first equation is identical to that given by Eq. (1). The second is written in the form

$$[z+\vec{v}_1\cdot\vec{\nabla}-\rho\hat{C}(\vec{v}_1,\vec{r}_{12},z)-\bar{T}(12)]\vec{\theta}(\vec{v}_1,\vec{r}_{12},z)=T(12)\vec{\phi}(\vec{v}_1,z)\ . \tag{8}$$

The operator $\hat{C}(\vec{v}_1,\vec{r}_{12},z)$ is an exact kinetic operator, involving extremely complicated integral operators. The approximation that we propose in this paper is to replace $\hat{C}(\vec{v}_1,\vec{r}_{12},z)$ by $\hat{B}(\vec{v}_1,z)$. Thus we have the approximate equation

$$[z+\vec{v}_1\cdot\vec{\nabla}-\rho\hat{B}(\vec{v}_1,z)-\bar{T}(12)]\vec{\theta}(\vec{v}_1,\vec{r}_{12},z)-T(12)\vec{\Phi}(\vec{v}_1,z)=0\ . \tag{9}$$

Equations (1), (5), and (9) may now in principle be solved to yield an approximate value of $\vec{\Phi}(\vec{v}_1,z)$ and hence $D(z)$. The approximation involves assuming that functions of the velocity of the tagged particle decay on a much faster time scale than functions of its position. It is clearly a somewhat drastic step which cannot be strictly justified, but we hope to show in the remainder of this section that it is quite a plausible approximation both at a low density of scatterers and at those higher densities for which the diffusion constant becomes small.

Firstly, we consider the collision sequences that Eqs. (1) and (9) take into account. If Eq. (9) is formally solved for $\vec{\theta}(\vec{v}_1,\vec{r}_{12},z)$ and this is then substituted into Eq. (1), we obtain the result

$$\{[z-\rho\lambda_D(\vec{v}_1)]-\rho\int d\vec{r}_{12}\bar{T}(12)[z+\vec{v}_1\cdot\vec{\nabla}-\rho\hat{B}(\vec{v}_1,z)-\bar{T}(12)]^{-1}T(12)\}\vec{\Phi}_D(\vec{v}_1,z)=\vec{v}_1\phi_0(\vec{v}_1)\ . \tag{10}$$

A comparison of this equation with Eq. (5) yields an equation for the operator $\hat{B}(\vec{v}_1,z)$ in the form

$$\hat{B}(\vec{v},z)=\lambda_D(\vec{v}_1)+\int d\vec{r}_2\bar{T}(12)[z+\vec{v}_1\cdot\vec{\nabla}-\rho\hat{B}(\vec{v}_1,z)-\bar{T}(12)]^{-1}T(12)\ . \tag{11}$$

We may obtain a density expansion for the operator $\hat{B}(\vec{v}_1,z)$ in the form $\sum_{l=0}^{\infty}\rho^l\hat{B}_l(\vec{v}_1,z)$ by expanding the inverse operator in Eq. (11) about the free-streaming term, and we may compare the results with the density expansion of the true kinetic operator, as given by Van Leeuwen and Weyland.[3(a)] To lowest order, we find $\hat{B}_0(\vec{v}_1,z)$ is given by the Lorentz-Boltzman operator, which is the exact result. The first-order correction is given by

$$\hat{B}_1(\vec{v}_1,z)=\int d\vec{r}_2 d\vec{r}_3\bar{T}(12)G_0\bar{T}(13)G_0T(12)\ , \tag{12}$$

where $G_0=(z+\vec{v}_1\cdot\vec{\nabla})^{-1}$. This is the three-body ring term which is by far the dominant contributor to the leading density correction to ν [$\nu=\nu(z=0)$] in three dimensions.[3(a),5] Thus our approximate theory, just like the repeated-ring equations, yields the first term in the density expansion of ν exactly and gives a good approximation to the leading correction.

The next-order term in the density expansion is given by

$$\begin{aligned}\hat{B}_2(\vec{v}_1,z)=\int d\vec{r}_2 d\vec{r}_3 d\vec{r}_4[&\bar{T}(12)G_0\bar{T}(13)G_0\bar{T}(14)G_0T(12)+\bar{T}(12)G_0\bar{T}(13)G_0\bar{T}(12)G_0\bar{T}(14)G_0T(12)\\&+\bar{T}(12)G_0\bar{T}(13)G_0\bar{T}(14)G_0\bar{T}(13)G_0T(12)]\ .\end{aligned} \tag{13}$$

The first term is the four-particle ring term, the second is a repeated ring, and the third is a term not present in the repeated-ring equations, but which was shown by Van Leeuwen and Weyland[3] to contribute to the leading-logarithmic divergence in the density expansion of ν in three dimensions.

The higher-order terms may also be obtained in a similar way, but the number of collision sequences

in each term increases rapidly. These terms will not only contain all the rings and repeated rings, but also repeated rings within repeated rings and many other sequences. We note, though, that the operator $\hat{B}_N$, which contains collision sequences involving $(1+N)$ scatterers, does not include, for example, those sequences in which the tagged particle hits each of the $(1+N)$ scatterers two or more times. Thus our approximate $\hat{B}_1$ does not contain the sequence

$$\bar{T}(12)G_0\bar{T}(13)G_0\bar{T}(12)G_0\bar{T}(13)G_0T(12) .$$

Similarly the true $\hat{B}_2$ will contain a sequence such as

$$\bar{T}(12)G_0\bar{T}(13)G_0\bar{T}(14)G_0\bar{T}(12)G_0\bar{T}(13) \times G_0\bar{T}(14)G_0T(12) ,$$

which describes the tagged particle rattling around twice in a triangle of scatterers. As discussed previously,[3(a),5] including this extra term in the $\hat{B}_1$ operator only makes about 15% difference to the coefficient of the leading density correction to the diffusion constant in three dimensions. The ring term, given by Eq. (12) is the most important term in $\hat{B}_1$. It is our hope, therefore, that a similar situtation prevails for all other operators $\hat{B}_N$, though of course this is by no means certain. As we said in the Introduction, this procedure is somewhat *ad hoc*. We offer no fundamental justification for retaining some collision sequences and disregarding others, though below we offer some plausibility arguments to indicate the theory may be a good approximation at densities near the critical density.

We now consider the behavior of Eqs. (1) and (9) at a high density of scatterers, such that $\nu(z)$ is very large. In that case $\vec{\theta}(\vec{v}_1,\vec{r}_{12},z)$ is given by its hydrodynamic form

$$\vec{\theta}(\vec{v}_1,\vec{r}_{12},z) = \phi_0(\vec{v}_1)W(r_{12})\{1-[1/\nu(z)]\vec{v}_1\cdot\vec{\nabla}\} \times\vec{M}(\vec{r}_{12},z) , \quad (14)$$

where $\vec{M}(\vec{r}_{12},z)$ satisfies the diffusion equation

$$[z-D(z)\nabla^2]\vec{M}(\vec{r}_{12},z)=0, \quad |\vec{r}_{12}|>a \quad (15)$$

and is continuous at $|\vec{r}_{12}|=a$. $W(r)$ is the unit step function, defined by $W(r)=1$, $r\geq a$, and $W(r)=0$, $r<a$. These results were obtained by the normal Chapman-Enskog procedure where we treated $\vec{z}+\vec{v}_1\cdot\vec{\nabla}$ as a perturbation to $\rho\hat{B}(\vec{v}_1,z)$ and made use of Eqs. (7a) and (7b). The next term in the equation for $\vec{\theta}(\vec{v}_1,\vec{r}_{12},z)$ is smaller by a factor of $av_0/\nu(z)$. Furthermore, as discussed previously,[5] this hydrodynamic form also satisifes the boundary conditions on the surface of the scatterer, given by $T(12)[\Phi(\vec{v}_1,z)+\theta(\vec{v}_1,\vec{r}_{12},z)]=0$, both to zeroth- and first-order in $av_0/\nu(z)$. Thus this hydrodynamic solution is the true solution of our kinetic equations to first order in $av_0/\nu(z)$, the kinetic boundary layer yielding only higher-order corrections. The hydrodynamic solution will give a value for $D(z)$, valid for $z\ll\nu(z)$, with a fractional error of order $av_0/\nu(z)$. For a detailed discussion of hydrodynamic solutions and boundary layer effects, we refer the reader to Ref. 7(b). The explicit results of these calculations are given in the next section.

We note, however, that Eqs. (14) and (15) are just the equations that one would expect the *exact* function $\vec{\theta}(\vec{v}_1,\vec{r}_{12},z)$, as given by Eqs. (1) and (8), to obey for $|\vec{r}_{12}|\gg a$ in this hydrodynamic limit. Mode-coupling techniques give a more formal justification for this intuitively obvious result, which simply states that far from a given scatterer, the particle diffuses with its full diffusion constant, the perturbation due to the presence of the scatterer being negligible. Furthermore, it is clear from Eq. (8) that the boundary conditions at $|\vec{r}_{12}|=a$ are identical to those given by our approximate theory. Nearby the scatterer, however, there will exist a boundary layer over and above that allowed for by the approximate theory, due to the collision sequences that we have ignored. Mode-coupling approximations and our approximate kinetic theory assume that this extra boundary layer effect is small and does not contribute to zeroth or first order in $av_0/\nu(z)$. In conclusion then, our kinetic theory gives what we believe to be an exact equation, in this hydrodynamic limit, both far from and right at the scattering surface, and thus leads us to believe that the theory might be quite a reasonable approximation.

We now turn our attention to how one can obtain a value for $D(z)$ from the self-consistent repeated-ring equation for all values of ρ and z. This may be done analytically for low density and for densities where $\nu(z)$ is large, but in between we need to introduce a simplifying approximation for the operator $\hat{B}(\vec{v}_1,z)$. We follow GLY,[2(b)] and write

$$\rho\hat{B}(\vec{v}_1,z)f(\vec{v}_1) \simeq -\nu(z)\left[f(\vec{v}_1)-\phi_0(\vec{v}_1)\int d\vec{v}f(\vec{v})\right] , \quad (16)$$

a Bhatnager-Gross-Krook (BGK) approximation that retains the properties of the exact operator given by Eqs. (7a) and (7b). We note that if this ap-

proximation is substituted into Eq. (9) and if the term $\overline{T}(12)\vec{\theta}(\vec{v}_1,\vec{r}_{12},z)$ is dropped, we would then have exactly the same self-consistent equation considered by GLY — a form of ring kinetic theory. Again we cannot strictly justify this approximation for these intermediate densities, but we can make some plausibility arguments. Firstly, we consider the low-density limit. As discussed previously the true operator $\hat{B}$ should reduce to the Lorentz-Boltzmann operator λ_D in this limit. The low-density limit of the BGK approximation for $\hat{B}$ is obtained by replacing $\nu(z)$ in Eq. (16) by the Boltzmann friction coefficient ν_B. In three dimensions, therefore, the right-hand side (RHS) of Eq. (16) does indeed reduce to the exact Lorentz-Boltzmann operator, given by Eq. (3). The BGK approximation does not affect the first two coefficients in the density expansion of ν. In two dimensions, however, this is no longer true. The exact Lorentz-Boltzmann operator is not of the form given in Eq. (3). Thus, the true low-density expansion for ν in two dimensions is given by[3(a)]

$$\nu=8\rho^*/3-(32/9)\rho^{*2}\log_{10}\rho^*+\cdots , \tag{17}$$

whereas Eq. (16) yields the same result found by GLY[2(b)]

$$\nu=8\rho^*/3-(32/9)(8/3\pi)\rho^{*2}\log_{10}\rho^*+\cdots , \tag{18}$$

so that Eq. (16) predicts the coefficient of the leading density correction to be a factor of $(8/3\pi)\approx 0.85$ times smaller than the true value. Thus, at low density, we expect Eq. (16) to become exact for the three-dimensional gas, and to give a fair result for the two-dimensional case. At densities close to the percolation threshold, we expect the solution of the equations to be given by the hydrodynamic form discussed previously. This hydrodynamic solution, though, will be the same whether one uses the exact $\hat{B}$ or the BGK approximation, and as we show later, the hydrodynamic solution alone is sufficient to calculate the percolation threshold density, the form of the approach of the diffusion constant to zero from below the threshold and the small z form of $D(z)$ just above the threshold. Thus the BGK approximation will give identical results to the exact operator in this high-density limit for the above properties in all dimensions. Hence we believe that as the BGK approximation is good both at low density (especially in three dimensions) and at or above the critical density, it might be a reasonable approximation at all densities. This could be checked, in principle, by modeling the operator to give the memory functions of both $\langle\vec{v}(z)\cdot\vec{v}\rangle$ and $\langle(\vec{v}\vec{v}-\frac{1}{3}v^2\vec{1})(z)(\vec{v}\vec{v}-\frac{1}{3}v^2\vec{1})\rangle$ correctly, solving the resulting coupled equations for these memory functions, and then seeing whether the results for D are significantly changed, but we have not so far carried out this procedure.

With this extra BGK approximation we can now obtain numerical results for $D(z)$ for all densities using the variational method we used previously, and also obtain analytical results for the behavior of $D(z)$ near ρ_c^*. For further convenience, from now on we work in dimensionless units, measuring lengths in units of a, and measuring times in units of a/v_0.

B. The variational method revisited

For details of the variational solution to the repeated-ring equation denoted VRRA (variational, repeated-ring approximation) the reader is referred to our recent paper.[5] We found in three dimensions that

$$\nu(z)=\nu_B+\rho^*(\nu_B/4\pi^2)(\vec{g},\vec{s}) , \tag{19}$$

where $(\vec{g},\vec{s})$ denotes the integral of $\vec{g}\cdot\vec{s}$ over all space exterior to the scatterer. The function $\vec{g}$ is a solution of the equation

$$\vec{g}=\hat{A}\vec{g}-\vec{s} ,$$

where $\hat{A}$ is an integral operator and $\vec{s}$ a source. In the VRRA, $\hat{A}$ contained ν_B, while the self-consistent theory is simply obtained by replacing ν_B by $\nu(z)$. Upon writing

$$\vec{\tilde{g}}=\vec{g}+\delta\vec{g} , \tag{20}$$

where $\vec{g}$ is a trial function, Eqs. (19) and (20) yield

$$(\vec{g},\vec{s})=(\vec{\tilde{g}},\vec{\tilde{g}}-\hat{A}\vec{\tilde{g}}+2\vec{s})-(\delta\vec{g},\delta\vec{g}-\hat{A}\delta\vec{g}) , \tag{21}$$

given that $\hat{A}$ is symmetric. So Eq. (21) is just the statement that $\vec{g}=\vec{\tilde{g}}$ is a stationary value of the functional J

$$j(\vec{\tilde{g}})=(\vec{\tilde{g}},\vec{\tilde{g}}-\hat{A}\vec{\tilde{g}}+2\vec{s}) . \tag{22}$$

The working equation of the variational method follows,

$$\nu(z)=\nu_B+\rho^*[\nu(z)/4\pi^2]\,\mathrm{Stat}\,J . \tag{23}$$

In the VRRA we used, as we do here, a "hydrodynamic" trial function

$$\vec{g}=\alpha\hat{r}h_1(i\delta r)\ , \tag{24}$$

where

$$\delta=[z/D(z)]^{1/2}\ ,$$

h_1 is a spherical Hankel function, and α is the parameter to be determined. For $\rho^*\to\rho_c^*$, $\nu(z=0)\to\infty$, corresponding to the vanishing of D. Then, the value of α in the optimized $\vec{g}$ can be shown to be $-2\pi\nu(z)/[i\delta h_1'(i\delta)]$ for small z, where $h_1'(x)=dh_1(x)/dx$. The resulting function is denoted $g_{\rm Hy}$, and is correct to $O(\nu)$, with an error of $O(\nu^{-1})$. The theory obtained by using $g_{\rm Hy}$ in Eq. (23) is equivalent to that obtained by simply projecting the original repeated-ring equations onto their hydrodynamic modes. Consequently, we have

$$\text{Stat}\,J=\text{Stat}J_{\rm Hy}+O(\nu^{-2})\ , \tag{25}$$

and the error is obtained by using Stat $J_{\rm Hy}$ in Eq. (7) is $O(\nu^{-2})$; the term $O(\nu^{-1})$ is obtained correctly. It is possible to obtain Stat $J_{\rm Hy}$ analytically for large $\nu(z)$, and, consequently, we can find an analytic expression, correct to $O(\nu^{-1})$ from Eq. (23). This point is essential to our detailed treatment of the critical region.

III. THREE DIMENSIONS

A. Numerical calculations

We solved the combined Eqs. (23) and (24) numerically for $z=0$ and $0.4>\rho^*>0$, the range of densities studied in the molecular-dynamics simulation of Bruin.[9] Our results for D/D_B (D_B is the Boltzmann diffusion constant), and those of the simulation, are plotted versus ρ^* in Fig. 1. Agreement between theory and experiment is very good, although the theoretical points fall somewhat below the simulation as $\rho^*\to 0.4$. Of course, the simulation becomes difficult at these densities. It must be stressed that the theory is working well at densities where the Lorentz-Boltzmann equation is hopeless, and where the non-self-consistent theory, also shown in the figure, has substantially broken down.

B. Approach to the critical density

As ρ_c^* is approached (assuming the theory has a ρ_c^*), ν must become infinite. It is possible to evaluate the first terms of an expansion of Stat $J_{\rm Hy}$ in ν^{-1}, which should then be rapidly convergent. We find

$$\nu=\nu_B+\frac{2\pi}{3}\rho^*\nu\left[1-\frac{3}{2\nu}+\frac{18}{5\nu^2}\right]+O(\nu^{-2}) \tag{26}$$

and, since $\nu_B=\pi\rho^*$,

$$\nu=\frac{2\pi}{3}\rho^*\nu\left[1+\frac{18}{5\nu^2}\right]+O(\nu^{-2})\ . \tag{27}$$

As discussed in VRRA, the explicit cancellation of ν_B just demonstrated for large ν is an important feature of the correct solution of a repeated-ring theory. Many previous papers, including GLY, found that the zero density ν_B (or D_B in a theory for D) still contributes to ν at large ρ^* or ν. We believe that the cancellation is correct; an empirical argument is that it is needed to produce the Stokes-Einstein law for the motion of a large tagged particle.

Canceling a factor of ν, we have

$$1=\frac{2\pi}{3}\rho^*\left[1+\frac{18}{5\nu^2}\right]\ ; \tag{28}$$

thus, a critical density exists,

$$\rho_c^*=\frac{3}{2\pi} \tag{29}$$

and we have included the point ($D=0$, $\rho^*=\rho_c^*$) in the figure. For large but noninfinite ν, using $D=1/3\nu$, Eqs. (28) and (29) yield

$$D=\frac{1}{9}(\tfrac{5}{2})^{1/2}\epsilon^{1/2},\quad \rho^*\to\rho_c^* \tag{30}$$

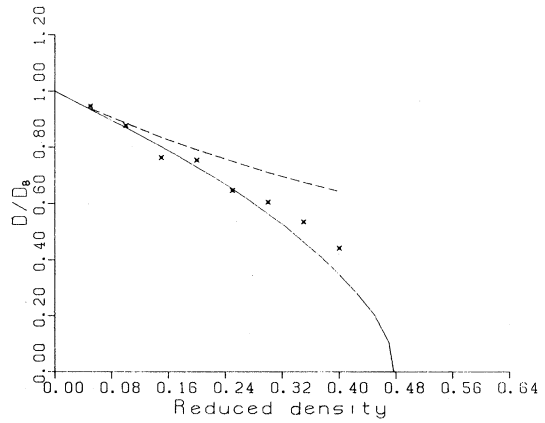

FIG. 1. The density dependence of the diffusion constants in three dimensions. The crosses show the molecular-dynamics results of Bruin, the dashed line shows the results of the RRA and the full line shows the results of the self-consistent approximation.

where

$$\epsilon=(\rho_c^*-\rho^*)/\rho_c^* .$$

Defining the critical exponent β,

$$D\propto\epsilon^{\beta},\ \rho^*\to\rho_c^* \tag{31}$$

we obtain $\beta=\frac{1}{2}$.

C. High density

Above the threshold, we expect $D=0$, $\nu=\infty$. However, this does not mean $\nu(z)=\infty$, only that $\lim_{z\to 0}$ only that $\lim_{z\to 0}\nu(z)=\infty$. Thus, following GLY, we look for a solution to our z-dependent equations with $\nu(z)\propto z^{-1}$ as $z\to 0$; the hope, of course, is that this solution exists only for $\rho^*>\rho_c^*$. The expansion of Stat$J(z)$ yields the equation

$$\nu(z)=\rho^*\nu(z)\left[\frac{4\pi}{3}\frac{(1-\delta)}{(2+2\delta+\delta^2)}+O(\nu^{-1})\right], \tag{32}$$

where

$$\delta=[3z\nu(z)]^{1/2} ; \tag{33}$$

under our hypothesis, δ is $O(1)$. Equation (32) yields

$$\delta^2-2\delta\left[1-\frac{2\pi\rho^*}{3}\right]+2\left[1-\frac{2\pi\rho^*}{3}\right]=0$$

or

$$\delta=\epsilon\pm(\epsilon^2-2\epsilon)^{1/2} . \tag{34}$$

Now, δ must be real, so

$$(\epsilon-1)^2\geq 1 ; \tag{35}$$

thus, we require $\epsilon\geq 2$ or $\epsilon\leq 0$. A negative density is needed for $\epsilon\geq 2$, so $\epsilon\leq 0$, or $\rho^*\geq\rho_c^*$. Also, δ is positive, so

$$\delta=\epsilon+(\epsilon^2-2\epsilon)^{1/2}\underset{\epsilon\to 0}{\to}(2\,|\,\epsilon\,|\,)^{1/2} . \tag{36}$$

It follows from Eq. (31) that

$$\nu(z)=2\,|\,\epsilon\,|\,/3z,\ \epsilon\to 0 . \tag{37}$$

Our equations do, then, have a solution with $\nu(z)\propto z^{-1}$, or $D(z)\propto z$, for $\rho^*>\rho_c^*$; this solution describes the high-density LG, where $D(z)=0$ due to trapping of the tagged particle. Equation (37) suggests that we define a characteristic frequency z_c by the relation

$$\nu(z)=\tfrac{2}{3}\omega\left[\frac{z_c}{z}\right],$$

where ω has no critical anomaly. Then,

$$z_c\propto|\,\epsilon\,|\ \epsilon\to 0^-$$

and z_c is the frequency below which the effect of trapping appears in the tagged-particle motion.

D. Discussion of $d=3$ results

Our result $\rho_c^*=3/2\pi\simeq 0.477$, was found by Masters and Madden[2(a)]; GLY found $\rho_c^*=9/4\pi\simeq 0.716$. The true critical density for the LG in $d=3$ is unknown, although it is surely plausible that the free-space percolation threshold, $\rho^*=0.81$, is a good approximation to ρ_c^*. This number, and also a linear extrapolation of the molecular-dynamics results for D/D_B, would favor the higher GLY value of ρ_c^*, while our theory predicts that D/D_B should bend down sharply below the linear extrapolation for $\rho^*>0.4$. A simulation at higher density would be most valuable.

It is of interest that the mode-coupling approach of Masters and Madden gives the same critical density as the repeated-ring theory. Their theory includes effects usually ignored in mode coupling; in particular, they treat ("$k'\neq k''$"), or intermediate wave vector mixing, terms. As MM showed, these terms are necessary if mode coupling is to produce the correct coefficient (4π) in the Stokes-Einstein law.[10] A related fact is that they are needed to prevent the bath fluid from unphysically penetrating the large tagged particle. In kinetic theory, the collision events needed to produce the above desirable features are the repeated rings.

In short, the MM mode-coupling theory bears a striking similarity to repeated-ring kinetic theory. We suggest that the theories are equivalent. The GLY theory appears related to a "ring" kinetic theory.

Our value for β ($\beta=\frac{1}{2}$) differs from the result of GLY, $\beta=1$. This difference is a consequence of the perfect cancellation of ν_B by a term in Stat$J_{\rm Hy}$ which occurred in Eq. (26); as we stated there, the cancellation is an essential feature of the repeated rings. Without the cancellation, assuming ρ_c^* still existed, $\beta=1$ would be obtained. The cancellation is absent from ring theories, so we expect $\beta=1$ for such theories.

The behavior which we found above ρ_c^* has identical ϵ dependence to that found by GLY, although some coefficients differ. Note that, since $\nu(z)\to\infty$ as $z\to 0$ for all $\rho^*>\rho_c^*$, the results in Sec. III C hold for small z at all $\rho^*>\rho_c^*$, not just for the critical region.

E. The long-time tails for $d=3$

At low density, Ernst and Weyland[3(c)] showed that the velocity correlation function (VCF) exhibited a negative $t^{-5/2}$ long-time tail. Thus

$$\langle \vec{v}_1(t)\cdot\vec{v}_1\rangle = -(6\pi D_B^2/\rho^*)(4\pi D_B t)^{-5/2}\,, \quad t\to\infty \quad (38)$$

where D_B is the Boltzmann diffusion constant. This an exact result, the tail arising from ring-collision sequences. If the effects of repeated rings are also taken into account, as in Eqs. (1) and (2), it is fairly straightforward to show that the coefficient of the long-time tail in Eq. (38) is multiplied by a factor of $[1+(4\pi\rho^*/3)(D_R/D_B)]^2$, where D_R is the diffusion constant obtained from solving the repeated-ring equations.[5(b)] At low density, $D_R=D_B$, and the result becomes the same as that obtained by Keyes and Mercer,[3(c)] and the low-density result of GLY.[2(b)] We make no claim, though, that these results yield the true first-order density corrections to the long-time tail coefficient.

Unfortunately, however, we have not so far been able to explicitly extract the long-time tail coefficient at all densities from the self-consistent equations (1), (5), and (9). The reason for this failure is that because the operator $\hat{B}(\vec{v}_1,z)$ has eigenvalues that are nonanalytic in z, the long-time behavior of the VCF does not simply arise from the hydrodynamic modes, as is the case in normal ring or repeated-ring theories and this complicates the analysis severely. It is possible, though, to calculate the long-time behavior from the self-consistent theory in certain limits. Firstly, it is clear that as the operator $\hat{B}$ reduces to the Lorentz-Boltzmann operator λ_D at low densities, the self-consistent theory yields the same low-density coefficient for the tail as given in Eq. (38). At higher densities where $\nu(z)\gg 1$, the form of the long-time behavior may be extracted by making use of the BGK approximation Eq. (16), and Eqs. (23)–(25) for finite z. These equations yield the result

$$\nu^2(z)=\frac{18}{5}\rho^*\frac{(1-\delta^2/2+\delta^3/2)}{(\rho_c^*-\rho^*+\rho^*\delta^2/2-\rho^*\delta^3/2)}\,, \quad (39)$$

valid for $\rho^*\le\rho_c^*$ and z, $\delta\ll 1\ll\nu(z)$. For $\rho^*<\rho_c^*$, we may expand the denominator in inverse powers of $(\rho_c^*-\rho^*)$, which yields eventually an expansion for $\nu(z)$ and hence $\langle\vec{v}_1(z)\cdot\vec{v}\rangle$ in powers of z. This result may then be inverse Laplace transformed to yield

$$\langle \vec{v}_1(t)\cdot\vec{v}_1\rangle = -\frac{9}{4\pi}\frac{\rho_c^*}{D(\rho_c^*-\rho^*)}t^{-5/2}\,, \quad t\to\infty \quad (40)$$

where D is given by Eq. (30). Thus, as $\rho^*\to\rho_c^*$ from below, there still exists a negative $t^{-5/2}$ tail with a coefficient that becomes very large near the critical density. The conditions on the magnitude of z in order for the expansion of Eq. (39) to be valid, show that this long-time tail will only be observed at times t, such that $t\gg 1/\epsilon^{3/2}$, where ϵ is defined after Eq. (30). This result is qualitatively in agreement with that obtained by GLY.

We may also examine the long-time behavior for $\rho^*=\rho_c^*$. In this limit, it is clear from the definition of δ and from Eq. (37) that $\delta\to 0$ as $z\to 0$, whether ρ_c^* is approached from above or from below. Thus the conditions for the validity of Eq. (39) still hold for sufficiently small z, and it can then easily be shown that for small z

$$\langle \vec{v}(z)\cdot\vec{v}\rangle=(5/12)^{1/3}z^{1/3},\quad \rho^*=\rho_c^*\,. \quad (41)$$

This leads to a negative $t^{-4/3}$ long-time tail in the VCF, a result that differs from the negative $t^{-3/2}$ tail obtained by GLY. The reason for this difference is again associated with the perfect cancellation of the Boltzmann friction coefficient ν_B in Eq. (26) in the hydrodynamic limit of a repeated-ring-like theory, a cancellation not present in ring theories.

In conclusion, therefore, our self-consistent theory predicts a negative $t^{-5/2}$ asymptotic long-time tail for densities less than the critical density. As the density nears ρ_c^*, the long-time tail sets in only at increasingly longer times. At earlier times there will be a negative, preasymptotic $t^{-4/3}$ tail. Eventually, for $\rho^c=\rho_c^*$, this $t^{-4/3}$ tail persists indefinitely. Finally for $\rho^*>\rho_c^*$ the theory predicts no long-time tail whatsoever—a result also found by GLY.

IV. TWO DIMENSIONS

Two dimensions currently provides the best test for a theory of trapping in the LG. The percolation density ρ_p^*, is known (~ 0.37), and the computer simulation of Alder and Alley[1(c)] makes it clear that $0.37>\rho_c^*>0.33$. Despite the difficulty in precisely pinning down ρ_c^*, the combined simulations of Bruin and Alder and Alley make $d=2$ the best-characterized case for the LG. The predictions of the theory, and the data from the simulations, are plotted in Fig. 2; agreement is even better than in

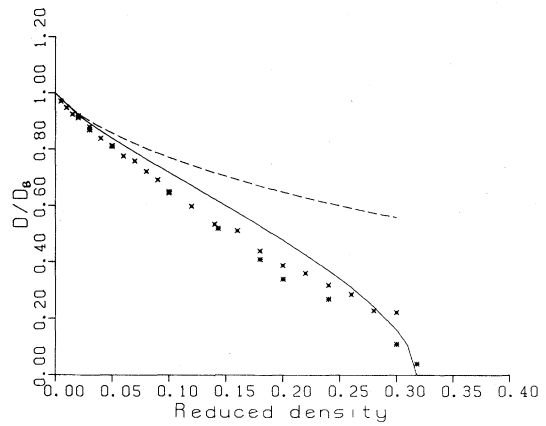

FIG. 2. The density dependence of the diffusion constant in two dimensions. The crosses show the molecular-dynamics results of Bruin, the stars the molecular-dynamics results of Alder and Alley, the dashed line the RRA, and the full line the self-consistent theory. Alder and Alley also reported a value for D/D_B of -0.04 at $\rho^*=0.37$, but this point is not shown on the figure.

$d=3$, while the test of the theory is more rigorous as the simulations run all the way up to the critical region in $d=2$.

The theoretical points in Fig. 2 were obtained numerically from the two-dimensional version of Eq. (23). In this case the hydrodynamic trial function $\vec{g}$, is of the form $\alpha\hat{r}K_1(\delta r)$, where K_1 is a modified Bessel function and, as before, α is the parameter to be determined from the variational principle. The definition of δ is the same as that given after Eq. (24). The methods of Sec. III B then predict a critical density $\rho_c^*=\pi^{-1}\sim 0.32$ and show that as $\rho^*\to\rho_c^*$ from below, $D=(1/8)^{1/2}\epsilon^{1/2}$, where ϵ is given after Eq. (30). Thus, as in three dimensions, we find that $\beta=\frac{1}{2}$. The theory of GLY gave $\rho_c^*=2/\pi\sim 0.64$ and $\beta=1$.

For $\rho^*>\rho_c^*$, the methods of Sec. III C again may be applied. Thus we find in this limit that

$$\nu(z)=\rho^*\nu(z)\left[-\frac{\pi K_1(\delta)}{K_1'(\delta)}+O(\nu^{-1}(z))\right], \quad (42)$$

where $K_1'(x)=\dfrac{dK_1(x)}{dx}$. A property of the K's is

$$\delta K_1'(\delta)=-K_0(\delta)-K_1(\delta)\,. \quad (43)$$

Hence, if $\nu\to\infty$ as $z\to 0$, Eq. (42) becomes

$$1=\frac{\pi\rho^*K_1(\delta)}{K_1(\delta)+K_0(\delta)} \quad (44)$$

or

$$\frac{K_0(\delta)}{K_1(\delta)+K_0(\delta)}=\frac{1}{\pi\rho^*}(\pi\rho^*-1)\,. \quad (45)$$

Now, $\delta\geq 0$, and consequently, $K_0(\delta)$, $K_1(\delta)\geq 0$, and

$$\frac{1}{\pi\rho^*}(\pi\rho^*-1)\geq 0\,; \quad (46)$$

thus, as before

$$\rho^*\geq 1/\pi=\rho_c^*,\ (d=2)\,. \quad (47)$$

In other words, only for $\rho^*\geq 1/\pi$ does a $\nu(z)$ exist which diverges as $z\to 0$. The resulting $\nu(z)$ is just $\delta^2/2z$ with δ obtained by solution of Eq. (44). Hence, as in three dimensions, the theory predicts a zero diffusion constant for $\rho>\rho_c^*$.

Finally, we use the methods of Sec. III E to investigate the long-time behavior of the VCF in two dimensions. This has been extensively investigated in the simulation work of Alder and Alley. At low density, Ernst and Weyland[3(c)] showed that there was a negative t^{-2} tail. Thus

$$\langle\vec{v}_1(t)\cdot\vec{v}_1\rangle=-(1/4\pi\rho^*)t^{-2},\ t\to\infty\,. \quad (48)$$

The repeated-ring equations may be shown to modify the above result by multiplying it by a factor of $(1+\pi\rho^*D_R/D_B)^2$, where D_R and D_B are the repeated ring and Boltzmann diffusion constant, respectively. The self-consistent theory reproduces Eq. (48) at low density. As $\rho^*\to\rho_c^*$ from below, it predicts that

$$\langle\vec{v}(t)\cdot\vec{v}\rangle=-\epsilon^{-1}t^{-2},\ t\to\infty\,. \quad (49)$$

For $\rho^*=\rho_c^*$, the theory yields

$$\langle\vec{v}_1(z)\cdot\vec{v}_1\rangle=-(1/3)^{1/3}(z\ln z)^{1/3} \quad (50)$$

for small z, which leads to a negative $t^{-4/3}(\ln)^{1/3}$ long-time tail.

Thus the theory predicts a negative t^{-2} tail at densities below ρ_c^*, which sets in at increasingly later times as ρ_c^* is approached. At earlier times it predicts a preasymptotic, negative $t^{-4/3}(\ln)^{1/3}$ tail, although in practice the logarithmic dependence will prove hard to detect. For $\rho^*=\rho_c^*$, the $t^{-4/3}(\ln)^{1/3}$ tail will persist for all times, and for $\rho^*>\rho_c^*$, no long-time tail is predicted, as is the case for $d=3$.

The computer simulation of Alder and Alley showed that if the VCF data was fitted to the form $\alpha t^{-\beta}$, where α and β are constants, for times between 15 and 50 mean collision times, then the value of β dropped monotonically from its initial

value of 2 down to a value of 1.34 at $\rho^*=0.37$. At still higher densities, the value of β started to increase again. GLY were able to account for the trend from their theory by arguing that because the true, asymptotic long-time tail only starts after such long times at higher densities, the observed value of β reflects some sort of average of the preasymptotic and asymptotic long-time tails. Furthermore, by numerically calculating the VCF from their theory, they were able to show quite good quantitative agreement between their theory's prediction for β and the simulation results. Unfortunately numerical difficulties have prevented us so far from obtaining accurate numerical predictions for the VCF from our theory, but if indeed the simulation is yielding an effective, preasymptotic, value for β, our theory would predict $1.33<\beta<2$, $\rho^*<\rho_c^*$, the value of β reaching 1.33 at $\rho^*=\rho_c^*$ and increasing again for $\rho^*>\rho_c^*$. Thus although we cannot as yet make any quantitative comparisons, we suspect our theory is in reasonable qualitative agreement with the simulation and our prediction for the value of β at the critical density is gratifyingly close to the observed value.

V. ONE DIMENSION

In one dimension, the methods of Sec. III C give

$$\nu(z)=\rho^*\nu(z)[\delta^{-1}+O(\nu^{-1})]\ , \tag{51}$$

where, now, $\delta=[z\nu(z)]^{1/2}$. Thus, if $\nu\to\infty$ as $z\to 0$,

$$\delta\simeq\rho^*\ ; \tag{52}$$

that is, a solution to Eq. (51) with $\nu\to\infty$, $z\to 0$, exists for all $\rho^*>0$, and

$$\rho_c^*=0,\quad (d=1)\ . \tag{53}$$

We immediately obtain

$$\nu(z)=\rho^{*2}/z,\quad (d=1) \tag{54}$$

so the characteristic frequency z_c, varies as ρ_c^{*2} [or equivalently $(\rho^*-\rho_c^*)^2$] in one dimension; Eq. (54) holds for all ρ^* as $z\to 0$. In view of these results, there is obviously no point to an analysis for $\rho^*<\rho_c^*$.

Of course, the exact percolation threshold is $\rho_c^*=0$ in one dimension, so our answer is correct. The unusual nature of percolation for $d=1$ represents a real test for approximate theories, and we are extremely encouraged by this result. We do note, though, that the usual repeated-ring equations, using the true one-dimensional Lorentz-Boltzmann operator instead of a BGK approximation, also predict a zero diffusion constant at all densities. This was shown by Weijland.[3(b)]

It is straightforward to solve for the one-dimensional VCF exactly. The tagged particle undergoes ceaseless oscillations between two scatterers, the scatterers being rods each of length two reduced units. Thus the VCF may be calculated by averaging the product $\vec{v}(t)\cdot\vec{v}$ over all starting positions between two scatterers a fixed distance apart, and then averaging over all distributions of the distance between the two scatterers, such that they do not overlap. For small z, the value of $\langle\vec{v}(z)\cdot\vec{v}\rangle$ is given by

$$\langle\vec{v}_1(z)\cdot\vec{v}\rangle=\frac{z\epsilon^{-2\rho^*}}{12\rho^{*2}}(1+2\rho^*+4\rho^{*2})\ . \tag{55}$$

Thus, the leading z dependence is the same as that predicted by Eq. (54), and the ρ^* dependence is the same in the limit of small ρ^*, though Eq. (54) is incorrect even then by a factor of 12. For a thorough account of the one-dimensional Lorentz gas, we refer to Ref. 12. The reason for the discrepancy between the self-consistent theory and the true result is evidently due to the fact that the binary collision sequences that we have taken into account allow the tagged particle to leak out from its initial cage.

Finally, we repeat that the calculated values of the critical densities in all dimensions arose from the hydrodynamic solution of our approximate Eqs. (1) and (9). The "extra" BGK approximation [Eq. (16)] was only used to obtain information about the diffusion constant at densities below ρ_c^*.

VI. SUMMARY

We have unearthed some features of the self-consistent variational repeated-ring theory in this paper. Our most important results are in Fig. 2, which shows that the theory works extremely well, from low density to the critical density in $d=2$. Two dimensions provides the best test of the theory, as only in $d=2$ do the computer studies reach the critical density. Agreement of theory and simulation is also quite good in $d=3$, where the simulations only reach $\rho^*=0.4$. The theory of GLY may be superior to ours at higher density in $d=3$, but the definitive computer study of this regime remains to be done. In one dimension, reassuringly, the theory gives the true answer, $\rho_c^*=0$. Although this result is obvious, other approximate theories, such as that of GLY, do not find it. Insofar as our theory is successful, it confirms our contention that

the repeated-ring equations, at least, are needed for dense systems. Masters and Madden did not work out all the consequences of their theory, but it is basically equivalent to ours and should give almost the same results; the exception is that without the variational principle, their theory is less able to work at intermediate and low densities.

Of course, calculation of static percolation thresholds, with no reference to dynamics, is a major problem. Our theory, that of GLY and that of MM extract thresholds from formulations which simultaneously provide a wealth of dynamical information. A related theory has been given by one of us for exciton migration in two-component crystals.[12] The exciton can only hop about the "sublattice" composed of one of the components. That sublattice is analogous to empty space in the LG, while the other sublattice is analogous to space occupied by scatterers. Systems which show both "diffusion" and "localization" phases have an extremely rich structure, and are also relatively unstudied. Application of theories to such systems provides the most rigorous test imaginable for the theories, and also provides an intriguing marriage of concepts from dynamics and phase transitions. We hope that the theory presented here represents a first step in general treatment of particle and fluid motion in random media.

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