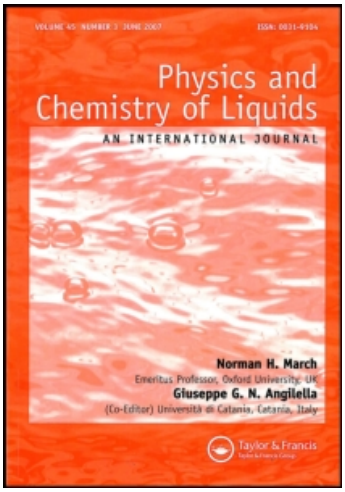

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Binary Collision Effects in Lorentz Gases

S. Ranganathan[a]; K. C. Sharma[b]
[a] Department of Mathematics and Computer Science, Royal Military College of Canada, Kingston, Ontario, Canada [b] Department of Physics, Chemical Pradesh University, Simla, India

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Binary Collision Effects in Lorentz Gases

S. RANGANATHAN

Department of Mathematics and Computer Science,
Royal Military College of Canada,
Kingston, Ontario, Canada K7K 5L0.

and

K. C. SHARMA

Department of Physics, Himachal Pradesh University, Simla, India 171005.

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The role of binary collisions in Lorentz Gases is investigated through a dynamical theory which incorporates exactly all the effects of a single collision between a pair of particles interacting with a Lennard-Jones potential. The comparison of our results with those of molecular dynamics thus yields a quantitative estimate of the effect and indicates that our simple but very physical model is able to account for a significant portion of the decay of the density fluctuation correlation function, for the wave numbers considered.

Key Words: Lorentz gas, binary collision, incoherent scattering function, molecular dynamics.

It has been realized that the Lorentz Gas model, in which classical light particles without mutual interaction move in a random array of stationary scatterers, exhibits a number of features relevant to the understanding of the dynamics in classical fluids.[1,2] Molecular dynamics computer simulation (MD) studies have been carried out for hard spheres[3,4] and very recently for Lennard-Jones potential.[5] The latter study was motivated by a neutron-scattering experiment of dilute Hydrogen in dense Argon,[6] a system which is a good realization of a Lorentz Gas model.

However a full theoretical understanding of such a simple-statistical mechanical model is still lacking. For a hard-sphere potential system,

theoretical calculations have been performed within the repeated ring collision approximation[7] and using mode coupling theories.[8] However very little progress has been made using a realistic potential.

In this paper, a dynamical theory of a Lorentz Gas System which incorporates exactly all the effects of a single binary collision is being studied. The intermolecular potential is assumed to be the Lennard-Jones potential. Such a Binary Collision Expansion[9] (BCE), when applied to classical fluids[10–12] is able to account for a significant portion of the density correlation function over a wide range of densities and wave numbers. Such a study gives us an understanding of the role the binary collisions play in the dynamical processes that occur in a fluid. Here, we have used this theory to calculate the incoherent scattering function $S_s(q, \omega)$ and its intermediate scattering function $F_s(q, t)$ of a Lorentz Gas System in which the stationary scatterers are Argon atoms in an *equilibrium* configuration and not in a random configuration and the light particle is the Hydrogen molecule. We have chosen such a system in order that the results can be compared with those of MD simulation.[5] The MD results have already been compared[5] with the experimental data.[6]

For practical calculations, the BCE is generally restricted to just the first two terms of the expansion—the first term representing the free particle contribution and the second term representing exactly all the contribution of a single binary collision between a pair of particles, interacting with any given two-body potential. The second term involves the dynamics of a two-particle system with the initial position determined by the equilibrium pair distribution function $g(r)$ and the initial velocity given by the Maxwellian distribution. The difference between the experimental or MD results and the binary collision theory can then be directly and solely attributed to third and higher order particle dynamics. An important feature of this formalism is that there are no arbitrary parameters. The only inputs required are $g(r)$ and the interatomic potential $u(r)$. As is to be expected, the results of this theory will show increased derivation from MD results for longer times, and for higher densities where the effects of higher order collisions become significant.

The tagged-particle intermediate scattering function is defined as

$$\begin{aligned} F_s(q, t) &= \langle \rho_{-q}(0)\rho_q(t) \rangle \\ &= \langle \rho_{-q}(0) e^{iLt} \rho_q(0) \end{aligned} \tag{1}$$

where $\rho_q = e^{i\mathbf{q}\cdot\mathbf{R}}$ is the tagged particle density and $L = L_0 + \sum_{jk} L_{jk}$ is the complete Liouville operator. Here L_0 is the kinetic contribution and

L_{jk} is the two-body potential contribution to L. $\langle\cdots\rangle$ denotes an equilibrium ensemble average. The basic formula of BCE is[9]

$$\frac{1}{z - iL} = \frac{1}{z - iL_0} + \sum_{j,k}\left[\frac{1}{z - iL_0 - iL_{jk}} - \frac{1}{z - iL_0}\right] + \cdots \tag{2}$$

where z is the Laplace transform variable of t. The first term involves no collisions while the second term involves just one collision between the pair of particles j and k which in our case refer to the Hydrogen and the stationary Argon atoms. Inserting (2) into (1), we can write

$$F_s(q, t) = F_s^0(q, t) + nF_s^1(q, t) \tag{3}$$

where

$$F_s^0(q, t) = \exp[-q^2u_0^2t^2/4]$$

is the ideal gas contribution and, after some algebra,

$$F_s^1(q, t) = \int d\mathbf{R}g(R)\left[\int d\mathbf{V}\phi(V)\exp(\mathbf{iq}\cdot[\mathbf{R} - \mathbf{R}(t)]) - F_s^0(q, t)\right] \tag{4}$$

Here n is the density of the Argon scatterers and $u_0^2 = 2k_BT/m$ with m being the mass of the Hydrogen atom. $\mathbf{R}(t)$, the position of the Hydrogen atom at time t is determined through two-particle dynamics. $g(R)$ is the Hydrogen–Argon pair distribution function and $\phi(V)$ is the Maxwellian distribution of velocities of Hydrogen atoms.

The potential that determines the two-particle dynamics is taken to be the Lennard-Jones potential and $g(R)$ is calculated through the mean spherical model equation[13]

$$g(R) \equiv g_{HA}(R) = \frac{\sigma_H g_{AA}(R) + \sigma_A g_{HH}(R)}{\sigma_H + \sigma_A} \tag{5}$$

where the subscripts A and H stand for Argon and Hydrogen respectively. σ is the Lennard-Jones potential length parameter. g_{AA} and g_{HH} are computed for L-J potential using the optimized cluster theory[14] at a temperature of 298 K and at an Argon density of 10.45×10^{21} particles per c.c. ($n^* \equiv n\sigma^3 = 0.41$) and a Hydrogen density of 0.54×10^{21} ($n^* \sim 0.01$), as used in the experiment.[6] The Hydrogen behaves essentially as an ideal gas at this density. The density of the scatterers is quite high (about half the triple point density) and thus the system qualifies as a dense gas and hence dilute gas theories like the Boltzmann equation will not be applicable.

The multi-dimensional integral occurring in (4) is performed through an importance sampling Monte Carlo integration methods.[15] $\mathbf{R}(t)$ is

evaluated through the Verlet algorithm.[16] A typical number of initial configurations taken to compute the integral is 60,000 and the R-integration is cut off around $R = 2.25\sigma_A$. It is estimated that the errors involved in the numerical integration is no more than a few percent. The incoherent scattering function $S_s(q, \omega)$ is then obtained from

$$S_s(q, \omega) = \frac{1}{\pi} \int_0^\infty F_s(q, t) \cos(\omega t) dt \tag{6}$$

To get an overall view of the effect of the binary collision, we have plotted in Figure 1, the half-width of $S_s(q, \omega)$ as a function of the wave number q. The triangles are the results of our calculations and the circles are the MD results. It is seen that our results are in very good agreement with MD values at larger values of q and, as is to be expected, our model does show increased deviation from MD as the wave number is reduced, when the contributions from higher order collisions become quite significant. But even at $q = 2.82$ Å^{-1}, the ideal gas behaviour is far from being approached. Our results are higher than the MD value by less than 4% but the ideal gas half width is higher by more than 18% at this value of q. Again, even at the lowest value of q ($=0.87$ Å^{-1}) considered, a reasonable portion of the spectrum can be explained by a single binary collision between the Hydrogen atom and

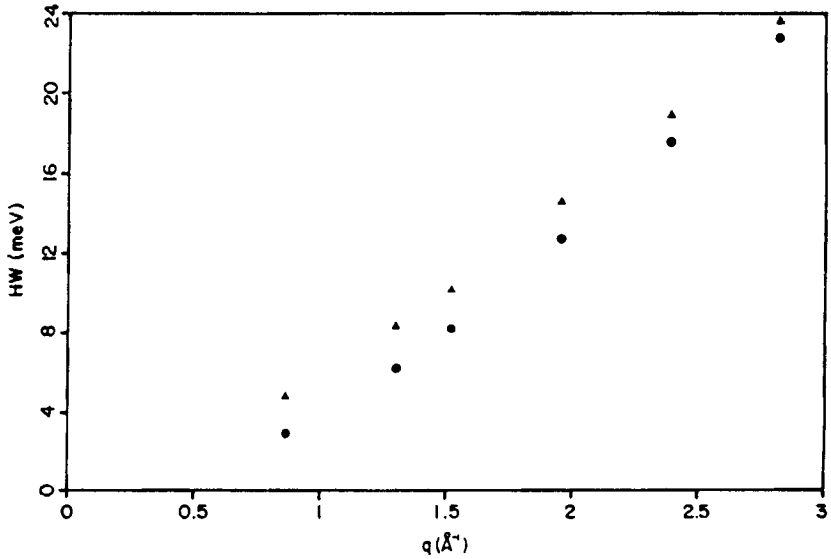

Figure 1 Half-width (meV) of $S_s(q, \omega)$ vs. q (Å^{-1}) of Lorentz Gas. The circles represent MD results while the triangles represent our results.

the stationary Argon atom. More importantly, the difference between our results and those of MD can be attributed solely to three and higher-order particle dynamics.

A look at the time domain will provide a more critical test of the validity of the BCE method. In Figure 2, we have plotted $F_s(q, t)$, the intermediate scattering function, as a function of time for a relatively low value of $q = 1.30\ \text{Å}^{-1}$, for which we expect multiple collisions contribution to be significant. The solid line represents our results while the dashed curve is for MD and the curve with dots on them is for the ideal gas. The difference between our results and that of ideal gas is solely due to the effect of a single binary collision and that between our and MD results is solely due to the multiple collisions. It is seen that the BCE theory is able to account for the decay of the correlation function to about 0.15 p sec, by which time it has decayed to nearly one-quarter of its initial value. Thus it is the last 25% of the decay, for this value of q, which is influenced by higher order dynamics. In order to fully describe the decay at longer times, we need a theory which takes into account such events. By contrast, the system behaves like an ideal gas only up to the time the correlation function has decayed to 75% of its initial value.

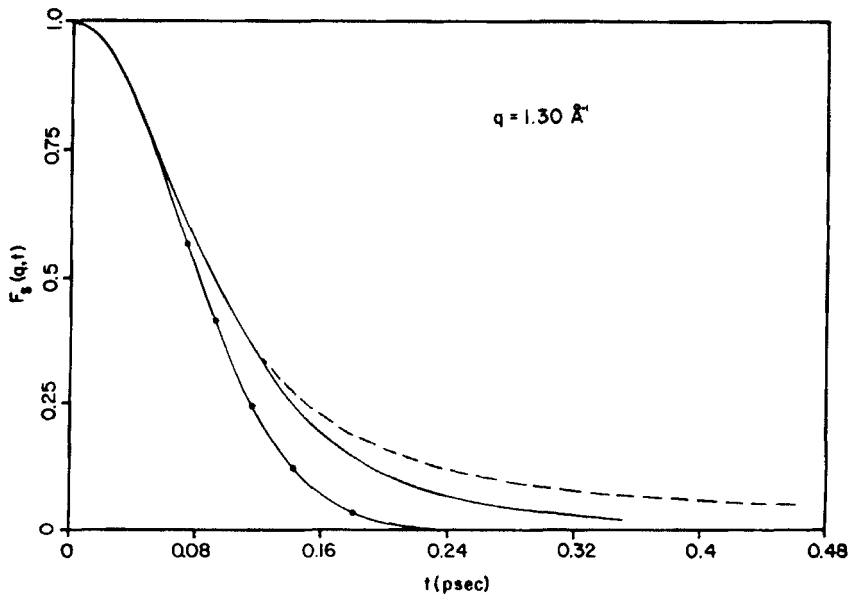

Figure 2 Intermediate scattering function $F_s(q, t)$ vs. t (p sec) for $q = 1.30\ \text{Å}^{-1}$. The solid line represents our results. The dashed line represents MD results and the curve with dots represents the ideal gas results.

As we go to higher values of q, the agreement becomes better and for example at $q = 2.82\ \text{Å}^{-1}$, most of the decay of $F_s(q, t)$ can be accounted for by a binary collision.

We have presented a dynamical theory with realistic potential in which we have investigated the role a binary collision plays in the evolution of the density correlation function of a Lorentz Gas. One would expect our approximation to be valid only for short times and at low densities. However, the analysis shows that it is able to account for a significant portion of the observed spectrum. Our analysis has also provided a quantitative estimate of the effect.

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