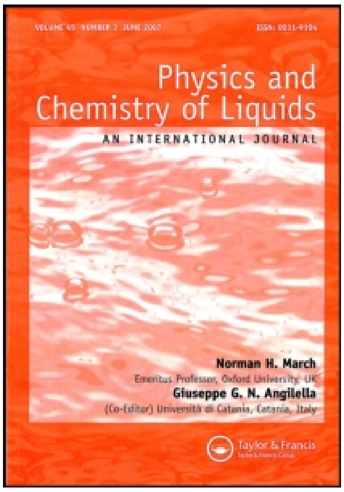

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TRANSPORT PROPERTIES FROM THE EQUATION OF STATE BY MEANS OF ENSKOG THEORY FOR *d*-DIMENSIONAL HARD SPHERES

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In this work we have used Enskog theory to evaluate transport properties in d-dimensional hard spheres. In order to carry out this study we have made use of the relation between the compressibility factor Z and the ratio X_E/X_0, where X_E is the Enskog value for a transport property and X_0 is that corresponding to a dilute gas. From the available numerical data for Z in simulation experiences, we have calculated the aforementioned ratio for the diffusion coefficient D, the shear viscosity coefficient η, the bulk viscosity coefficient Φ and the thermal conductivity coefficient λ. This calculation has been extended to hard disks ($d = 2$), hard spheres ($d = 3$) and hard hyperspheres ($d = 4,5$) in the maximum allowable range of densities. We have also tested the suitability of some algebraic equations of state proposed for such bodies by comparing their respective values for X_E/X_0. Finally, we have obtained numerical values for the ratio D/D_E in the cases $d = 4,5$. The behavior is similar to that of hard spheres.

KEY WORDS: Transport properties, Enskog's theory, hard spheres, compressibility factor.

I INTRODUCTION

The significant progress that has been made in the knowledge of the equilibrium properties is due mainly to the existence of a virial expansion for the equation of state (EOS). Unfortunately, the same thing cannot be done in the case of the transport properties. On the basis of the work of Bogoliubov[1] and Uhlenbeck, quoted by Cohen[2], the impossibility of such an expansion was recognized by the mid 1960's. However, the coefficient of the logarithmic term, which impedes the expansion of transport coefficients in power series of the density, is sometimes very small[3], which has originated some ambiguity.

The Enskog theory arises from the Boltzmann equation by taking into consideration two main features: a) the frequency of collisions in a dense system is greater than in a dilute gas; b) collisional transfer of flux can be more important than molecular transfer. However, the Enskog theory is not completely rigorous because the presence of correlations is not considered. In spite of this limitation, the Enskog theory is the best description in the context of the kinetic theory of dense gases and its final formulation is very simple. Furthermore, this is the only theory, except for some others clearly inspired by it[4,5], which establishes a reciprocal relation between transport and equilibrium properties in the framework of hard spheres. This feature makes it possible to use the abundant information concerning these properties. The present work has been performed with this purpose in mind.

At present, simulation methods provide an alternative procedure for determining the transport properties. This procedure can be used to test the Enskog theory by evaluating the relation X/X_E at all possible densities. The diffusion coefficient is the most frequently used quantity for very good reasons[6,7] but there are also good motives for employing the other properties[8,9].

The rest of the paper is organized as follows. Section II summarizes the Enskog theory for hard-sphere systems and provides numerical results for X_E/X_0 calculated from the compressibility factor Z by using the simulation values and those from an analytical equation of state. In Section III, we have tackled the case of four- and five-dimensional hard hyperspheres, calculating the ratio D/D_E from the few simulation data available. Finally, we have discussed the variation of D/D_E with the numerical density.

II HARD SPHERES

The Enskog theory expresses the values of the four basic transport properties with respect to those of the dilute gas[10,11] in the form:

$$D_E/D_0 = 1/g(\sigma) \tag{1}$$

$$\eta_E/\eta_0 = (1/g(\sigma)) + 0.8(b/V) + 0.761g(\sigma)(b/V)^2 \tag{2}$$

$$\Phi_E/\eta_0 = 1.002g(\sigma)(b/V)^2 \tag{3}$$

$$\lambda_E/\lambda_0 = (1/g(\sigma)) + 1.2(b/V) + 0.755g(\sigma)(b/V)^2 \tag{4}$$

where $g(\sigma)$, b and V are the radial distribution function, the covolume and the volume, respectively.

Introducing the numerical density of particles n, the hard sphere diameter σ, the reduced density $n^* = n\sigma^3$ and the compressibility factor Z, one finds

$$D_E/D_0 = 2\pi n^*/3(Z-1) \tag{5}$$

$$\eta_E/\eta_0 = (2\pi/3)n^*((1/Z-1) + 0.8 + 0.761(Z-1)) \tag{6}$$

$$\Phi_E/\eta_0 = (2\pi/3)n^* 1.002(Z-1) \tag{7}$$

$$\lambda_E/\lambda_0 = (2\pi/3)n^*((1/Z-1) + 1.2 + 0.755(Z-1)) \tag{8}$$

The derivation is omitted because these results are included in standard texts on statistical mechanics[12]. For this reason, we do not present a table with detailed data.

A commonly used procedure consists in comparing the results of a proposed EOS with the simulation predictions for the compressibility factor Z. In the context of hard spheres, such predictions were pioneered by Alder and Wainwright[13]. This method has now been extended to systems with thousands of particles for the stable fluid region[14], and even to the metastable fluid and glassy regions[15], although with fewer statistics.

Alternatively, many attempts have been made to obtain an analytical EOS for hard spheres. Unquestionably, the Carnahan–Starling equation[16] is the best known. In an earlier work[17], we proposed a semiempirical EOS and tested it against the simulation data. The agreement was found to be very good. As is usual, the parameter chosen for the comparison was the compressibility factor Z. However, since Z is always greater than one, the comparison can be made more instructive by introducing a function of the parameter $Z - 1$. This provides a more severe test in the range where Z approaches unity (i.e. in the low-density range).

The results obtained have been completely gratifying in the whole range of the stable and metastable fluid. In fact, the quantitative agreement remains good well into the glassy region in spite of the fact that there are no conceptual grounds for applying an EOS for the fluid state to the amorphous state. For example, the relative deviation of the four transport properties is still less than 30% when $n^* = 1.16$, which corresponds to more than half of the glassy region.

III HARD DISKS

The formulation of the problem needs only slight modifications with respect to the preceding case. The theory has been developed by Alder and Wainwright[18] and in greater depth by Gass[19]. Their analytical form is:

$$D_E/D_0 = 1/g(\sigma) \tag{9}$$

$$\eta_E/\eta_0 = (1/g(\sigma)) + (b/A) + 0.8729 g(\sigma)(b/A)^2 \tag{10}$$

$$\Phi_E/\eta_0 = 1.246 g(\sigma)(b/A)^2 \tag{11}$$

$$\lambda_E/\lambda_0 = (1/g(\sigma)) + (3/2)(b/A) + 0.8718 g(\sigma)(b/A)^2 \tag{12}$$

where D_0, η_0 and λ_0 are again the quantities corresponding to the dilute gas. Here

$$b = (1/2)N\pi\sigma^2; \qquad b/A = (\pi/2)n\sigma^2 = (\pi/2)n^* \tag{13}$$

with $n^* = n\sigma^2$, the reduced density.

The EOS is[20]

$$P/nkT = 1 + (1/2)\pi\sigma^2 n g(\sigma) \tag{14}$$

Now the radial distribution function is:

$$g(\sigma) = (2/\pi\sigma^2 n)((P/nkT) - 1) = (2/\pi n^*)(Z - 1) \tag{15}$$

So then

$$D_E/D_0 = \pi n^*/2(Z-1) \tag{16}$$

$$\eta_E/\eta_0 = (\pi/2)n^*((1/Z-1)+1+0.8729(Z-1)) \tag{17}$$

$$\Phi_E/\eta_0 = (\pi/2)n^*1.246(Z-1) \tag{18}$$

$$\lambda_E/\lambda_0 = (\pi/2)n^*((1/Z-1)+3/2+0.8718(Z-1)) \tag{19}$$

In this dimensionality, the Enskog theory has additional importance because the transport coefficients are self-contradictory[21,22]. Therefore, some authors[18,23] have adopted the Enskog value as the representative result.

The values of Z have been obtained from the simulation data of Erpenbeck and Luban[24]. Alternatively, values have been used that were obtained from the EOS which we proposed in an earlier work[17]. In this case, only values from the stable fluid region were employed. The agreement between the two values is excellent, as one can see in Table 1.

IV FOUR AND FIVE-DIMENSIONAL HARD HYPERSPHERES

To our knowledge, the Enskog theory has not been developed for a dimensionality greater than three. Erpenbeck and Wood[25] attempted to generalize the theory for arbitrary dimensionality but their development was limited to two cases ($d = 2,3$) and to the diffusion coefficient. Recently, Bishop, Michels and de Schepper[26] applied the formalism to other dimensionalities in order to describe the short-time behavior of the velocity autocorrelation function. From these findings and the structure of the Enskog theory itself, it seems very reasonable to suggest that the expressions (1) and (9) can be extrapolated to any dimensionality. Based on this assumption, we have developed the relationship with the compressibility factor Z.

Table 1 Ratio of the Enskog theory values to dilute gas values (X_E/X_0) with the reduced density n^* for the following transport properties of a hard disk fluid: a) the diffusion coefficient D; b) the shear viscosity η; c) the bulk viscosity Φ and d) the thermal conductivity λ. The subscripts sim. and calc. indicate whether the compressibility factor values are from simulation data or calculated from an analytical equation of state.

n^*	0.0385	0.0574	0.1155	0.2309	0.3849	0.5774	0.6415	0.7217	0.7698	0.8248
$(D_E/D_0)_{\text{sim.}}$	0.9541	0.9261	0.8611	0.7279	0.5613	0.3177	0.3177	0.2521	0.2156	0.1773
$(D_E/D_0)_{\text{calc.}}$	0.9541	0.9261	0.8611	0.7277	0.5612	0.3739	0.3176	0.2522	0.2159	0.1772
$(\eta_E/\eta_0)_{\text{sim.}}$	1.018	1.024	1.076	1.248	1.734	3.200	4.115	5.838	7.344	9.735
$(\eta_E/\eta_0)_{\text{calc.}}$	1.018	1.024	1.076	1.248	1.734	3.201	4.116	5.833	7.337	9.741
$(\Phi_E/\eta_0)_{\text{sim.}}$	0.0048	0.0110	0.0476	0.2252	0.8114	2.740	3.982	6.351	8.449	11.79
$(\Phi_E/\eta_0)_{\text{cal.}}$	0.0048	0.0110	0.0476	0.2252	0.8116	2.741	3.983	6.348	8.438	11.80
$(\lambda_E/\lambda_0)_{\text{sim.}}$	1.048	1.069	1.167	1.429	2.036	3.651	4.615	6.396	7.941	10.37
$(\lambda_E/\lambda_0)_{\text{calc.}}$	1.048	1.069	1.167	1.429	2.036	3.652	4.616	6.394	7.934	10.38

The compressibility factor and the radial distribution function are related through the half volume of the d-dimensional sphere. Then, for the four-dimensional hard hypersphere:

$$Z = P/nkT = 1 + (\pi^2/4)\sigma^4 ng(\sigma); \qquad n^* = n\sigma^4; \qquad g(\sigma) = (4/\pi^2 n^*)(Z - 1) \quad (20)$$

$$D_E/D_0 = \pi^2 n^*/4(Z - 1) \quad (21)$$

and for the five-dimensional hard hypersphere:

$$Z = P/nkT = 1 + (4\pi^2/15)n\sigma^5 g(\sigma); \qquad n^* = n\sigma^5; \qquad g(\sigma) = (15/4\pi^2 n)(Z - 1) \quad (22)$$

$$D_E/D_0 = 4\pi^2 n^*/15(Z - 1) \quad (23)$$

The variation with $Z - 1$ can be seen, which is characteristic of Enskog theory. Here the values of Z have been obtained from the simulation data of Michels and Trappeniers[27] and from an EOS suggested by us[28]. Again the agreement is very good as is shown in Table 2.

Since the pioneering work of Alder, Gass and Wainwright[29] in three dimensions, the determination of the transport properties by means of molecular dynamics simulation has become widespread. The available data have been used to test the Enskog theory by means of the relation X/X_E. Particularly, major efforts have been addressed to the diffusion coefficient.

At low densities, the computed value of D is higher than prediction whereas at high densities, it is lower because of the existence of the backscattering effect[30].

The variation of the ratio D/D_E in three dimensions with the reduced density n^* has been studied exhaustively in the literature. A recent data compilation has been published by Speedy[31].

Surprisingly, we have not found any information on this quantity in other

Table 2 As in Table 1 for four- and five-dimensional hard hypersphere fluid but only for the diffusion coefficient.

n^*	$d = 4$							
	0.20	0.40	0.60	0.80	0.90	0.95	1.00	
$(D_E/D_0)_{sim.}$	0.7747	0.5910	0.4439	0.3269	0.2792	0.2563	0.2359	
$(D_E/D_0)_{calc.}$	0.7747	0.5921	0.4443	0.3284	0.2792	0.2567	0.2355	
	$d = 5$							
n^*	0.20	0.40	0.60	0.80	1.00	1.10	1.15	1.18
$(D_E/D_0)_{sim.}$	0.8061	0.6482	0.5250	0.4214	0.3397	0.3040	0.2858	0.2769
$(D_E/D_0)_{calc.}$	0.8061	0.6507	0.5246	0.4223	0.3389	0.3032	0.2866	0.2771

Table 3 Variation in the ratio D/D_E, the diffusion coefficient given by molecular dynamics simulation over that corresponding to the Enskog theory, for four- and five-dimensional hard hyperspheres with the reduced density n^*.

	$d = 4$							
n^*	0.20	0.40	0.60	0.80	0.90	0.95	1.00	
D/D_E	1.0638	1.1382	1.1590	1.0111	0.8851	0.8133	0.7080	
	$d = 5$							
n^*	0.20	0.40	0.60	0.80	1.00	1.10	1.15	1.18
D/D_E	1.0478	1.0855	1.1065	1.0533	0.9197	0.8038	0.7289	0.6961

dimensionalities in spite of the fact that some authors[26,27] have the suitable means available. Consequently, we have calculated the quotient D/D_E versus the reduced density n^* for $d = 4{,}5$. Previously, we checked the reliability of the method by comparing it with the considerable predictions available for $d = 3$.

The simultaneous consideration of values corresponding to $d = 3{,}4{,}5$ makes it possible to observe how the dimensionality affects D/D_E (Table 3). The ratio D/D_E rises at low reduced densities for all dimensionalities, but this effect is minimized as the dimensionality increases. This is probably due to variation in the degree of packing with dimensionality. In fact, compact close packing is reached for $n^* = 2/(3)^{1/2}$, $2^{1/2}$, 2 and $2(2)^{1/2}$ when $d = 2{,}3{,}4{,}5$ respectively. In other words, for the same value of n^*, the overcrowding is greater at low dimensionalities.

In addition, the observed decrease of D/D_E at high reduced density is smoother for the higher dimensionalities. This behavior can also be explained in terms of packing effects.

At higher densities, the particles surrounding any one particle are more densely packed. The major effect of these neighbors is to reflect the particles, leading to the negative contribution discussed in terms of backscattering[32].

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