

Free energy and transport properties of the Gaussian overlap model: Variational approach

Jorge Orozco and Rolando Castillo

Instituto de Física, Universidad Nacional Autónoma de México, P.O. Box 20-364, 01000 México, Distrito Federal, México

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The purpose of this paper is to find a method for calculating the free energy and the transport properties of a fluid made up of nonspherical nonpolar molecules in the dense regime. The model potential used was the Gaussian overlap model with constant ϵ . Our procedure relies on the assumption that at high densities the behavior of a molecular fluid is dominated by the harsh repulsive forces. Hence, the properties of the fluid can be given in terms of an effective hard core fluid. Thus, the free energy was obtained through a variational method with the aid of a nonspherical reference potential. The results were compared with molecular dynamics calculations and with calculations using a perturbation method. These results are in a close agreement with simulation data. In a further level of approximation the transport properties, thermal conductivity and shear viscosity, can be estimated with an extension of the effective-diameter hard-sphere theory. The results of our calculations for transport properties were compared with experimental data, and with calculations using the effective-diameter hard-sphere theory, but with effective diameters coming from perturbation theory. In particular, for the case of shear viscosity the results were excellent. For thermal conductivity the results are not that good, however, the sources of discrepancy are discussed.

I. INTRODUCTION

The development of fundamental microscopic theories devised to understand the features of thermodynamic and transport properties (TP's) of molecular fluids (MF's), has proven to be very difficult. This aim has been pursued for a long time. Therefore, alternative routes that can deal with realistic intermolecular potentials making our estimations little dependent on measurements are useful, if they allow us to make explicit calculations, even when neither the model potential nor the theory are exact.

A considerable effort has been devoted to the study of thermodynamic properties of MF's, and a relatively important progress has been acquired in the last years,¹ mainly due to the help provided by Monte Carlo and by molecular dynamics simulations. For the case of TP's of MF's the situation is very different. Our capability for estimating these properties based on realistic physical models is very limited.

In order to calculate thermodynamic properties of MF's, two approaches have been used. These are based on perturbation or variational methods. These methods are a logical extension of the work for atomic fluids developed by Weeks, Chandler, and Andersen² (WCA) for the case of perturbation methods, and of the work developed by Mansoori and Canfield,³ and by Rasaiah and Stell,⁴ for the case of variational methods. In the perturbation method, the free energy can be given as an expansion in terms of a reference potential (RP); here several techniques have been developed.¹ The first step was to take as the RP, a potential with a spherical symmetry.⁵ Of course, it was proven that is more convenient to take a nonspherical hard body (HB) as the RP, since it can mimic, in a better way, the angular dependence of the model potential. This kind

of RP was considered by Mo and Gubbins⁶ in their generalization of the WCA method. In the same way, when variational theory is used similar facts can be found. Here, the free energy of the MF is bounded by the free energy of a RP plus a correction term. Thus, the first step was addressed to use a RP which does not include angular dependence.⁷⁻⁹ The use of a nonspherical RP has not been explored yet.

As mentioned earlier, the study of TP's of MF's is quite undeveloped. Their study began with the pioneering work of Curtiss and co-workers,¹⁰⁻¹² who found a generalized Boltzmann equation for dilute gases in order to include contributions to free streaming and collisions. Since there, several routes have been devised mainly for hard-convex-body (HCB) fluids. These routes follow quite different lines: (1) derivation of kinetic equations for the phase space density,^{13,14} with solutions obtained through the Grad's moment method; (2) the use of time correlation functions in conjunction with the method of Ernst to transform the time correlation functions into distribution functions;¹⁵ (3) the use of a Mori-generalized Langevin equation method;¹⁶ (4) the use of first order perturbation theory, through the expansion of all terms in the time correlation functions including the propagator.^{17,18} In spite of these quite formal results, an explicit evaluation of these methods has not been reported.

The selection of a model potential to mimic the interaction between particles of a MF is a relevant point. Although there are several different alternatives, the model must have two basic characteristics: it must be mathematically simple, and it must not violate too strongly our sense of what is physically correct. The potentials models mainly considered in the literature for modeling these fluids are the generalized Stockmayer model,¹ the Kihara-

type models,^{1,19} the site-site models,¹ and the Gaussian overlap (GO) model.²⁰⁻²⁹ In this study, we selected the last model. In the Gaussian overlap model, a molecule is regarded as an ellipsoidal Gaussian distribution of matter density, and it is assumed that when the distributions overlap slightly, the pair potential is proportional to the overlap volume integral of the distributions. The original model was devised primarily to give a simple expression for the orientation dependence of molecular interactions, and further modified to give a realistic r dependence.²⁰ This model can describe oblate as well as prolate shapes of arbitrary anisotropy, and the shape of the molecular core is modeled correctly, at least qualitatively. The main problem of this model potential is related with the failure to yield correctly some long-range interactions, and of course the correct multipolar behavior. Some of the most important features of this model, and its relation with other models can be found in Refs. 21, 23-26, and 29. The GO potential can be expressed as

$$\Phi(r, \mathbf{u}_1, \mathbf{u}_2) = 4\epsilon(\mathbf{u}_1, \mathbf{u}_2) \{ [\sigma(\hat{\mathbf{r}}, \mathbf{u}_1, \mathbf{u}_2)/r]^{12} - [\sigma(\hat{\mathbf{r}}, \mathbf{u}_1, \mathbf{u}_2)/r]^6 \}, \quad (1a)$$

with

$$\sigma(\hat{\mathbf{r}}, \mathbf{u}_1, \mathbf{u}_2) = \sigma_0 \left[1 - \frac{1}{2} \chi \left(\frac{(\hat{\mathbf{r}} \cdot \mathbf{u}_1 + \hat{\mathbf{r}} \cdot \mathbf{u}_2)^2}{1 + \chi \mathbf{u}_1 \cdot \mathbf{u}_2} + \frac{(\hat{\mathbf{r}} \cdot \mathbf{u}_1 - \hat{\mathbf{r}} \cdot \mathbf{u}_2)^2}{1 - \chi \mathbf{u}_1 \cdot \mathbf{u}_2} \right) \right]^{-1/2}, \quad (1b)$$

and

$$\epsilon(\mathbf{u}_1, \mathbf{u}_2) = \epsilon_0 [1 - \chi^2 (\mathbf{u}_1 \cdot \mathbf{u}_2)]^{-1/2}. \quad (1c)$$

Here, $\hat{\mathbf{r}}$ is the unit vector in the r direction and \mathbf{u}_1 and \mathbf{u}_2 are unit vectors along the principal axis of the molecules. ϵ_0 , σ_0 , and χ are strength, range, and anisotropy parameters, respectively. σ_0 and χ can be written in terms of the range parameters σ_{\parallel} and σ_{\perp} characterizing each ellipsoid as

$$\sigma_0 = \sqrt{2} \sigma_{\perp},$$

and

$$\chi = [\sigma_{\parallel}^2 - \sigma_{\perp}^2] / [\sigma_{\parallel}^2 + \sigma_{\perp}^2] = [\kappa^2 - 1] / [\kappa^2 + 1]. \quad (1d)$$

Here, κ is the length to breadth ratio of the ellipsoids, such that $\kappa > 1$ for prolate, and $\kappa < 1$ for oblate molecules.

As mentioned, the shape of the anisotropic molecular core is modeled reasonably well, but this is not the case for long-range interactions. We hope this point will be of no consequence in our approach for dense nonspherical fluids. We shall assume that the repulsive forces,¹ i.e., the shape of the molecules, determine the liquid structure and intermolecular correlations in the same way as in atomic fluids.

One further advantage of the GO model is that, for that anisotropies of interest here, molecular dynamic calculations developed by Steele and his colleges²⁴ have shown that thermodynamic properties of the GO model, are almost identical to a simpler version of this model. This

is the Gaussian overlap model, but with constant ϵ . This is called the GOCE model.²⁴ The calculations with GOCE model are simpler than with the GO model.

The purpose of this paper is addressed to calculate the free energy, and TP's of a fluid made up of nonspherical nonpolar molecules in the dense regime. This fluid will be modeled with the GOCE potential. The free energy will be obtained through a variational method with the aid of a nonspherical RP. The TP's of interest here will be the thermal conductivity, and the shear viscosity. These will be estimated with an extension of the effective-diameter hard-sphere theory (EDHST).³⁰

Our procedure to calculate the free energy will be a direct generalization of the Rasaiah and Stell⁴ work for atomic fluids. The most important problems to be solved in this procedure will be the following: (a) The development of a specific procedure to obtain free energies for the nonspherical RP. In our case, we selected as the RP, the hard-Gaussian overlap (HGO) potential. This is defined as

$$\begin{aligned} \Phi(r, \mathbf{u}_1, \mathbf{u}_2) &= 0, & r > \sigma(\hat{\mathbf{r}}, \mathbf{u}_1, \mathbf{u}_2), \\ \Phi(r, \mathbf{u}_1, \mathbf{u}_2) &= \infty, & r < \sigma(\hat{\mathbf{r}}, \mathbf{u}_1, \mathbf{u}_2). \end{aligned} \quad (2)$$

(b) The explicit calculation of the pair distribution function (PDF) for the HGO.

In order to solve the first problem, we compared several geometric properties of hard ellipsoids (HE) and of HGO cores. We found that for length to breadth ratios within the interval of [0.5, 2.0], the HGO cores and the HE are the almost identical. Hence, the excess free energy of the HGO can be estimated through integration, of the HE state equation given by Boublik.³¹ For the PDF, we studied several approximations. The best results were obtained with a procedure given by Steele and Sandler.³²

The calculation of TP's for the GOCE fluid can not proceed directly, since it is not possible in the present state of kinetic theory. Studies in simpler cases as those related to the HCB mentioned earlier¹⁰⁻¹⁸ can be an example. Efforts to deal with realistic potentials have been reported only for "simple fluids", i.e., the atomic fluids, and they have proven to be very difficult.³³⁻³⁷ Formally, kinetic theory has been developed only for the hard-sphere fluid,^{38,39} the square-well fluid,⁴⁰⁻⁴² and for systems interacting through a spherical hard-core plus an attractive tail.³³⁻³⁷ Even in these cases, there are several issues that remain to be solved.^{36,42}

Here, we will test a procedure that is an extension of the EDHST.³⁰ Probably, since the time of Enskog and latter, with the recognition that the dynamics of atomic liquids is mainly determined by the repulsive part of the interaction potential, there is a common belief that hard-sphere expressions can give good estimates of the TP's of actual fluids, if some state-dependent effective hard-sphere diameter is used. However, until the developing of the kinetic mean field equations, this issue could be included in the framework of kinetic theory. There are two lines of approach that give the appropriate theoretical support to the EDHST. The first one is based on the use the maximization of entropy principle subject to constraints developed

by Stell and his collaborators.^{33–36,41} The second was developed by Sung and Dahler using a Mori–Zwanzig formalism.³⁷ These two approaches derived originally by different means can be related.³⁶

In order to extend the EDHST to obtain the TP's for MF's in the dense regime, we will assume that the dynamics of the fluid is mainly determined by the repulsive part of the nonspherical interaction potential, that is, by the HGO potential. Hence, we assume that a reasonable good caricature of the TP's of the GOCE model fluid at high densities could be obtained through the HGO fluid. The parameters of the best HGO body that can represent the GOCE potential, at some specified thermodynamic state, can be given by the free energy calculation using the variational method. However, the TP's of the HGO model are not known either. Hence, we will follow a heuristic approach. In a further level of approximation, we could estimate these properties through hard-sphere expressions, if some method is implemented to obtain an effective hard-sphere fluid in terms of the parameters of the HGO fluid and of the thermodynamic state. Accurate estimates are expected, if the anisotropy of the original molecules to be modeled is not so large. In particular, to obtain this effective fluid we followed the Bellemans' method.⁴³

Quite recently we have used a similar scheme, but using the perturbation method with good results.⁴⁴ Following the same line of reasoning presented earlier, but using the blip function theory formalism,^{2,6,45} the properties of the system were given in terms of an appropriate HGO fluid, and in a similar way, the TP's properties of HGO were obtained through hard-sphere expressions following the procedure given in the blip function theory to deal with nonspherical potentials.⁶

The paper is organized as follows. In Sec. II the theory for the variational technique is developed in order to obtain the free energy for the GOCE fluid, and the procedure to obtain the TP's of the GOCE model through the hard-sphere kinetic theory. The specific details to obtain the state dependent effective diameter for the effective hard-sphere fluid in terms of the model potential will be presented here. In Sec. III we make some comments about the data used in order to compare our results. Finally, in Sec. IV, the numerical results are presented and discussed. Here, a comparison between several procedures to obtain TP's and experimental data is presented.

II. THEORY

A. Free energy

In this section we will describe our procedure devised to obtain the free energy for the GOCE fluid. Our starting point will be the inequality that gives an upper bound to the excess free energy for the GOCE system in terms of the excess free energy of a reference fluid, i.e., the HGO fluid. The excess free energy obtained in this way does not include the contribution due to translational and rotation.

In general, for a nonspherical model potential, $\Phi(r_{12}, \omega_1, \omega_2)$ describing the interaction in a MF, we can define a HB through the nonspherical potential expression:

$$\Phi^0(r_{12}, \omega_1, \omega_2) = 0, \quad r_{12} > d(\omega_1, \omega_2), \quad (3)$$

$$\Phi^0(r_{12}, \omega_1, \omega_2) = \infty, \quad r_{12} < d(\omega_1, \omega_2).$$

Here, r_{12} is the vector separating the centers of molecule 1 and 2, with molecular orientations ω_1 and ω_2 ($\omega_i = \phi_i, \vartheta_i, \chi_i$ for nonlinear, and ϑ_i, ϕ_i for linear molecules, respectively), and $d(\omega_1, \omega_2)$ is the closest distance between these two particles.

The free energy of the model potential and of the HB can be related, using the Gibbs–Bogoliubov inequality:⁴⁶

$$\int d\mathbf{r}^N d\omega^N F(\mathbf{r}^N, \omega^N) \log F(\mathbf{r}^N, \omega^N) > \int d\mathbf{r}^N d\omega^N F(\mathbf{r}^N, \omega^N) \log G(\mathbf{r}^N, \omega^N), \quad (4)$$

where F and G are two integrable, positive, arbitrary configuration space functions, defined in such a way that

$$\int d\mathbf{r}^N d\omega^N F(\mathbf{r}^N, \omega^N) = \int d\mathbf{r}^N d\omega^N G(\mathbf{r}^N, \omega^N), \quad (5)$$

one can obtain a bound for the free energy of a MF, selecting F and G as

$$F(\mathbf{r}^N, \omega^N) = \exp\{\beta[\Delta A^0 - \Psi^0(\mathbf{r}^N, \omega^N)]\}$$

and

$$G(\mathbf{r}^N, \omega^N) = \exp\{\beta[\Delta A - \Psi(\mathbf{r}^N, \omega^N)]\}, \quad (6)$$

where ΔA^0 refers to the excess free energy of the reference fluid, ΔA to the model fluid, and $\beta = 1/kT$. Limiting our derivation for systems where the total potential is given as a sum of pair terms,

$$\Psi(\mathbf{r}^N, \omega^N) = \sum_{i \neq j} \Phi(r_{ij}, \omega_i, \omega_j), \quad (7)$$

we can obtain from Eq. (4) the following expression:

$$\beta \Delta A / N \leq \beta \Delta A^0 / N + 2\pi\beta\rho \int W(r, \omega_1, \omega_2) \times g^0(r, \omega_1, \omega_2) r^2 dr d\omega_1 d\omega_2. \quad (8)$$

The zero superscript refers to properties related with $\Phi^0(r, \omega_1, \omega_2)$, N is the number of particles, ρ is the number density, and g^0 is the PDF. The function $W(r, \omega_1, \omega_2)$ is defined as

$$W(r, \omega_1, \omega_2) = \Phi(r, \omega_1, \omega_2) - \Phi^0(r, \omega_1, \omega_2). \quad (9)$$

Now, restricting our derivation for the case of interest here, i.e., the GOCE and the HGO potentials, $W(r, \omega_1, \omega_2)$ can be written as

$$W(r, \omega_1, \omega_2) = -\infty, \quad r > c\sigma(\hat{\mathbf{f}}, \mathbf{u}_1, \mathbf{u}_2), \quad (10)$$

$$W(r, \omega_1, \omega_2) = 4\epsilon_0 \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad r > c\sigma(\hat{\mathbf{f}}, \mathbf{u}_1, \mathbf{u}_2).$$

Here, following the same line of reasoning given in the work of Rasaiah and Stell,⁴ a factor c is introduced in Eq. (10). This factor will define the size of the HGO potential for the reference fluid, as $d(\omega_1, \omega_2) = c\sigma(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{f}})$, and it

will be chosen in such way that the right side of Eq. (8) will be a minimum. The procedure will be described later.

The inequality (8) can be written as

$$\beta\Delta A/N < \psi(c, \rho^*, T^*), \quad (11)$$

using the dimensionless variables $\rho^* = \rho\sigma_0^3$, $d^* = c^3\rho^*$, $T^* = kT/\epsilon_0$, and $y = r/c\sigma_0$, where

$$\psi(c, \rho^*, T^*) = \beta\Delta A^0/N + 2\pi T^{*-1} \rho^* c^{-3} [I_A(d^*) + (c^{-6} - 1)I_B(d^*)] \quad (12)$$

with $I_A(d^*)$ and $I_B(d^*)$ given by

$$I_A(d^*) = \int_0^\infty 4 \left[\left(\frac{f}{y} \right)^{12} - \left(\frac{f}{y} \right)^6 \right] g^0(y, \omega_1 \omega_2; d^*) \times y^2 dy d\omega_1 d\omega_2, \quad (13)$$

$$I_B(d^*) = \int_0^\infty 4 \left(\frac{f}{y} \right)^{12} g^0(y, \omega_1 \omega_2; d^*) y^2 dy d\omega_1 d\omega_2, \quad (14)$$

where f is (σ/σ_0) .

These equations are an extension of the Rasaiah and Stell work⁴ given for the atomic fluids. Although, they used a Padé approximant for estimating the free energy of the RP fluid (hard-sphere in their case), that formula is equivalent to that obtained by integrating of the Carnahan–Starling (CS) equation of state.⁴⁷ Since, the latter is simpler, we used an equation of state for hard nonspherical particles that can be reduced to the CS equation for the spherical case. One of the most confident state equations for this kind of system is that suggested by Boublik.³¹ This gives good results when compared with computer simulations, and can be written as

$$\beta P/\rho = 1/(1-\eta) + 3\alpha\eta/(1-\eta)^2 + [3\alpha^2\eta^2(1-2\eta) + 5\alpha\eta^3]/(1-\eta)^3. \quad (15)$$

From here, the expression for the excess free energy of the RP fluid needed in Eq. (12) can be obtained straightforwardly:

$$\beta\Delta A^0/N = [4\alpha(3\alpha-1) + 3\alpha(3-5\alpha)\eta]\eta/[2(1-\eta)^2] + (6\alpha^2-5\alpha-1)\ln(1-\eta). \quad (16)$$

In these equations, $\eta = \rho V$, V is the volume of the HB, $\alpha = RS/3V$, R is $(1/4\pi)$ times the mean curvature integral, and S is the surface area of the the HB.¹⁹

The excess free energy of the reference HGO fluid can be evaluated, if the geometrical parameters (volume, surface, and R) of the particles composing the fluid are provided. However, this information cannot be easily obtained from the interaction potential (2), because this only gives information about the separation between the centers of two particles when they come into contact for a given orientation. Hence, instead of being engaged in complex geometrical problem to obtain the mentioned geometrical parameters, we followed a different method. We assumed that the HGO fluid geometric parameters can be obtained

through the geometric parameters of a HE fluid. This can be justified, with the following considerations.

If a comparison is made between the contact functions $d(\omega_1, \omega_2)$ for HGO and HE bodies, i.e., the closest distance of approach of two molecular centers for a fixed orientation, both at the same κ and σ_0 , we found differences of the order of 0.5% in the worst case, when $0.5 < \kappa < 2.0$. The contact functions for the HE's were obtained with the Peram and Wertheim algorithm.⁴⁸

The factor $\langle (\sigma(\hat{r}, \mathbf{u}_1, \mathbf{u}_2)/\sigma_0)^3 \rangle_{\omega_1, \omega_2}$ plays a significant role in molecular fluid models, like GOCE, HGO, and HE. Here, the angular brackets denote angular integration. In these models, some formulas of thermodynamic properties can be written as an expression involving a function depending on r only, equal for the three models, times that factor. The factor $\langle (\sigma(\hat{r}, \mathbf{u}_1, \mathbf{u}_2)/\sigma_0)^3 \rangle_{\omega_1, \omega_2}$ is almost the same for the HGO, and for the HE. We have calculated and compared this factor for both systems and they are very close; the difference is less than 0.1%. This can be expected from the way in which the GO model²⁰ definition relies on the ellipsoidal geometry. Reduced virial coefficients of systems made up of HE and of HGO can be an example, that illustrates this property. They have been compared by Bhethanabotla and Steele.²⁵ They found that these coefficients are almost identical for both systems if they have the same value of κ .

The aforementioned comments clearly suggest that the HGO and the HE are almost the same bodies. Therefore, the HGO fluid geometric parameters can be estimated through the hard ellipsoid fluid geometric parameters. Some authors have followed the same approach of using the same parameter α for HGO and HE bodies, provided that they have the same κ and σ_0 . The work of Boublik and Diaz-Peña⁴⁹ devoted to find a state equation for the HGO system can be an example.

Now, the volume needed in expression (16) can be calculated with the formula $V = \pi\sigma_0\kappa/6$. In the same way, α can be evaluated by the expressions given by Ishihara.⁵⁰

The PDF required in Eqs. (13) and (14) was calculated following the approximate procedure given by Steele and Sandler.³² Since, in the dense regime, the repulsive forces determine the fluid structure, the approximated equation for the PDF of the reference fluid can be written as³²

$$g^0(r, \omega_1 \omega_2) = \hat{y}_s(r) \exp[-\beta\Phi^0(r, \omega_1 \omega_2)], \quad (17)$$

where \hat{y}_s is expressed in terms of a convenient spherical reference potential (SRP), $u_s(r)$. In order to find this SRP, Steele and Sandler³² used the WCA method. For our case, the equation defining $u_s(r)$ is given by

$$\int \{ \exp[-\beta\Phi^0(r, \omega_1 \omega_2)] - \exp[-\beta u_s(r)] \} y_s(r) dr d\omega_1 d\omega_2 = 0. \quad (18)$$

Besides, in order to avoid density and temperature dependence of the SRP, the following condition must hold:³²

$$\exp[-\beta u_s(r)] = \langle \exp[-\beta\Phi^0(r, \omega_1 \omega_2)] \rangle_{\omega_1, \omega_2}. \quad (19)$$

TABLE I. Parameters of the integrals I_A and I_B .

κ	0.5	1.3	1.55
α	1.1795	1.0247	1.0697
A	-0.5222	-1.1869	-1.4740
B	-0.1516	-0.7157	-1.1695
C	-0.0179	-0.1660	-0.3773
D	0.0503	0.8910	2.9622
E	0.2580	0.5863	0.7281
F	0.1969	0.7505	1.5188
G	0.0286	0.1681	0.6027
H	0.0599	0.5140	3.5301

The calculation of the function $\hat{y}_s(r)$ was done with the Percus–Yevick theory, and the Ornstein–Zernike integral equation was solved using the algorithm of Labík, Malijevský, and Vořka.⁵¹

Now, the integrals I_A and I_B given by Eqs. (13) and (14) can be performed once the PDF is provided. These integrals are functions of the density only. Thus, a polynomial was fitted to each integral, for several values of κ , in the form

$$\begin{aligned} I_A &= A + Bd^* + Cd^{*2} + Dd^{*3}, \\ I_B &= E + Fd^* + Gd^{*2} + Hd^{*3}. \end{aligned} \quad (20)$$

The values for these constants are given in the Table I.

Finally, with the set of expressions given, the factor c defining the size of the HGO model for the reference fluid can be found, in such a way, that the right side of Eq. (11) can be minimized by an iterative calculation.

B. Transport properties

As mentioned in Sec. I, for the case of the atomic fluids there are two well connected starting points to obtain a procedure for estimating TP's, based on kinetic mean field theories.^{33,45} However, this is not the case for the interaction potential of interest here. Thus, an adaptation of the Enskog theory for fluids interacting through the GOCE model is implemented here, with the procedure of Sung and Dahler⁴⁵ given for the Lennard-Jones (LJ) interaction as a guide.

The basic idea to obtain TP's in our approach is quite simple, and it is responsible of much of the progress done in the equilibrium theory of dense molecular liquids. In a dense fluid, the repulsive forces which are nearly convex hard-core interactions dominate the liquid structure. Hence, we expect that attractive forces, dipole–dipole interactions, and any other slowly varying forces play a minor role in the fluid behavior. Thus, if a dense liquid is composed of nearly spherical molecules, its structure should be very similar to that of a HCB fluid. Now, in a further level of approximation, this HCB fluid can be described in terms of a fluid made up of hard spheres of an appropriate effective diameter, a fluid that can be handled with the hard-sphere kinetic theory in order to predict the thermal conductivity (λ) and the shear viscosity (η) of our original fluid, i.e., the GOCE model fluid. Of course, since the HCB characteristics depend on the thermody-

amic state in order to reflect the somewhat soft repulsive r dependence of the model potential, and on the anisotropy parameters of the GOCE model, the effective diameter of the hard-sphere fluid must do the same. The reference fluid that dominates the structure of the molecular fluid have been characterized in the free energy calculation given earlier. Thus, following our basic assumptions the TP's of our model system in the dense regime can be calculated through the evaluation of the TP's of a hard sphere fluid with an effective diameter d_0 . To obtain this effective diameter we used the Bellemans' method,⁴³ which should apply provided the anisotropy of the HCB is not too great. Here, the contact distance $d(\omega_1, \omega_2)$ can be expanded as

$$d(\omega_1, \omega_2, \alpha) = d_0 + \alpha \gamma(\omega_1, \omega_2) d_0, \quad (21)$$

where $\gamma(\omega_1, \omega_2)$ is defined so that $d(\omega_1, \omega_2, \alpha=1) = d(\omega_1, \omega_2)$, and d_0 is the effective hard sphere diameter given by

$$d_0 = \langle d(\omega_1, \omega_2) \rangle_{\omega_1, \omega_2}. \quad (22)$$

Once the effective diameter is calculated at some thermodynamic state, the TP's for the GOCE fluid can be obtained using the Enskog kinetic theory.

Hence, following our basic assumptions, the TP's of our model system in the dense regime can be estimated through the evaluation of the TP's of the hard-sphere fluid with the effective diameter d_0 . We hope that this procedure will improve the estimation of TP's of actual fluids, since there is a large body of evidence^{52–55} that support the idea that the predictions of the Enskog theory can be made to agree with the experiment quite well, when an effective diameter is introduced. The actual potential in these fluids is probably better modeled with a three parameter potential, like the GOCE model, than with a two parameter potential, as is commonly used.^{52–55}

The hard-sphere kinetic theory that will be used here, is the so called revised Enskog theory (RET) first derived by van Beijeren and Ernst.³⁸ Here, the hard-sphere radial distribution function is the same functional of the number density as the radial distribution function of a system in nonuniform equilibrium. The RET equation can be solved by the use of the Chapman–Enskog solution method. The molecular fluxes and the transport coefficients for dense hard-sphere fluid, up to the Navier–Stokes level, can be directly obtained on the basis of the procedure used in Refs. 39 and 56. Here, we only present the final expressions to obtain the TP's for pure fluids:

$$\eta = \frac{1}{\chi^c} \left[1 + \frac{4}{3} \left(\frac{2}{3} \pi n \sigma^3 \chi^c \right) + 0.7615 \left(\frac{2}{3} \pi n \sigma^3 \chi^c \right)^2 \right] \eta_0, \quad (23)$$

$$\lambda' = \frac{1}{\chi^c} \left[1 + \frac{6}{5} \left(\frac{2}{3} \pi n \sigma^3 \chi^c \right) + 0.7575 \left(\frac{2}{3} \pi n \sigma^3 \chi^c \right)^2 \right] \lambda_0, \quad (24)$$

where

$$\eta_0 = \frac{5}{16\pi\sigma^2} (\pi m k T)^{1/2}, \quad (25)$$

$$\lambda_0 = \frac{75k}{64\pi\sigma^2} \left(\frac{\pi kT}{m} \right)^{1/2} \quad (26)$$

In these expressions, n is the number density, σ is the hard-sphere diameter, m is the mass of the particle, χ^c is the pair distribution at contact, T is the absolute temperature, and k is Boltzmann's constant.

The evaluation of Eqs. (23) and (24) requires the knowledge of χ^c . We used the approximate expression of Carnahan and Starling,⁴⁷ since it appears to be quite accurate when compared to molecular dynamics data.

MD calculations have proven that Enskog's expressions for transport coefficients are not exact, since these do not take into account velocity correlations in the dense regime. Correction multiplicative factors to the Enskog expressions have been given by Dymond⁵⁷ (Dymond's correction) for shear viscosity and thermal conductivity, although for the case of shear viscosity van der Gulik and Trappeniers⁵⁸ have modified these expressions on the basis of the computations given by Michels and Trappeniers.⁵⁹ The correction factors are

$$\begin{aligned} C_\eta &= 1.02 + 10.61(n^* - 0.495)^3 \\ &\quad + 247.49(n^* - 0.813)^3, \quad n^* > 0.813 \\ &= 1.02 + 10.61(n^* - 0.495)^3, \quad 0.593 < n^* < 0.813 \\ &= 1.02, \quad 0.593 > n^* \end{aligned} \quad (27a)$$

$$C_\lambda = 0.99 + 0.1597n^* - 0.7464n^{*2} + 1.2115n^{*3} - 0.5583n^{*4}. \quad (27b)$$

In all of the previous equations $n^* = n\sigma^3$.

III. THE SOURCES OF EXPERIMENTAL DATA

Accurate values from computer simulations are needed to make a stringent test of the procedures developed earlier, for calculating the free energy, and the TP's of the GOCE fluid. For the case of the free energy, there are enough published data to make this comparison. However, for the case of TP's, as far as we know, there are no published data for this model. Although some data have been published for molecular fluids,^{60,61} they are not useful in the discussion of our results. Hence, we used experimental data to make our comparisons, although, unfortunately, there are only three fluids characterized in the context of the GOCE potential.²¹ These are nitrogen, benzene, and carbon dioxide, and their parameters, i.e., ϵ_0 , σ_0 , and κ , were fitted in order to reproduce thermodynamic properties.

It is clear that the comparison to be presented could not be a good test of our procedure to estimate TP's, not only by the fact that actual fluids do not interact through the GOCE model, but, in addition, there is not enough information to support the quality of the reported parameters in the estimation of TP's. TP's appear to be quite sensible to the potential parameters, at least, this is the case for atomic fluids. In particular, we have not used the parameters for the carbon dioxide, since they have shown some drawbacks to fit thermodynamic properties.²¹

TABLE II. Parameters for the GOCE model (from Ref. 21).

	Nitrogen GOCE	Benzene	
		GOCE1	GOCE2
σ_0 (Å)	3.37	6.3	6.474
ϵ_0 (k/\bar{K}^1)	94	300	265
κ	1.3	0.5	0.5

The molecular dynamic simulation results useful for the comparison of the free energy were obtained from the work of Sediawan *et al.*,²⁶ for different values of density, temperature, and κ . They reported simulations for $\kappa=0.5$ and 1.55, at reduced temperatures of 1.0 and 1.5, and for $\kappa=1.3$ at reduced temperatures of 1.0, 1.5, 2.0, and 3.0; in both cases, in a wide range of densities.

The parameters for the GOCE potentials used to model nitrogen and benzene, are shown in Table II. The accurate experimental data for nitrogen were obtained from Stephan *et al.*⁶² and Jacobsen *et al.*⁶³ and, for benzene, from Ramires *et al.*⁶⁴ and Assael *et al.*⁶⁵

IV. RESULTS AND DISCUSSION

A. Free energy

To evaluate the usefulness of our procedure, the free energy of the GOCE fluid was calculated, as described in Sec. II A, and compared with results coming from molecular dynamics simulations. In addition, our calculations were also compared with the excess free energy calculations obtained with perturbation theory. This is the blip function theory developed by Weeks, Chandler, and Andersen,² but generalized to molecular fluids. The perturbation theory calculations were obtained from the work of Boublik,²⁸ and of Singh *et al.*²⁹ The excess free energies calculated with our procedure, with the perturbation theory, and the molecular dynamics data, are presented in Figs. 1–3.

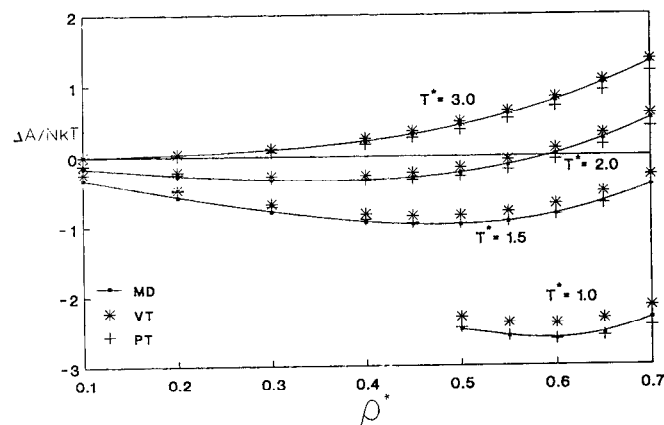


FIG. 1. Comparison between the excess free energy from molecular dynamics data (MD), variational theory (VT), and perturbation theory (PT) for GOCE fluid, with a length to breadth ratio of 1.3.

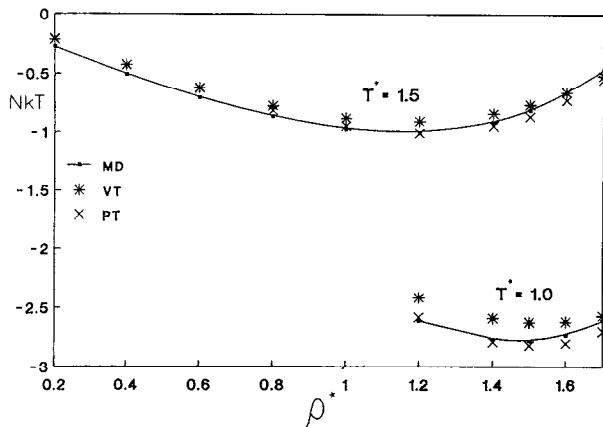


FIG. 2. Comparison between the excess free energy from molecular dynamics data (MD), variational theory (VT), and perturbation theory (PT) for GOCE model, with a length to breadth ratio of 0.5.

In Fig. 1, the values for the excess free energy of the GOCE fluid are presented, for a particular length to breadth ratio ($\kappa=1.3$), at several reduced densities and reduced temperatures. We can see there that our procedure gives the correct qualitative behavior as compared with molecular simulations. Our results are little bit above the molecular simulation data, as expected from a variational procedure, since it gives an upper bound for the free energy of the GOCE fluid. Thus, as a rule variational theory will overestimate. From a quantitative point of view, our procedure, in spite of the underlying approximations, is quite good. The percent deviation from simulations is on the average of the order of 4.7% upwards, for the temperatures and the densities presented in Fig. 1. However, in some regions it is very close to molecular simulation data ($T^* > 2$, and $\rho^* > 0.6$). When the precision of our calculations are compared with that of the perturbation theory, we found that perturbation theory is, in general, closer to simulation results. The percent deviation of perturbation theory calculations from molecular dynamics data is

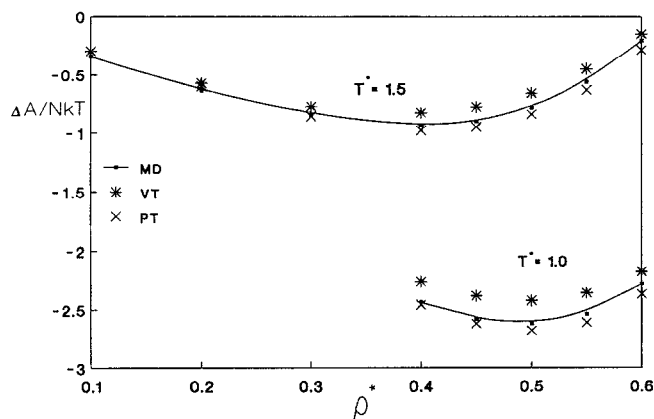


FIG. 3. Comparison between the excess free energy from molecular dynamics data (MD), variational theory (VT), and perturbation theory (PT) for GOCE model, with a length to breadth ratio of 1.55.

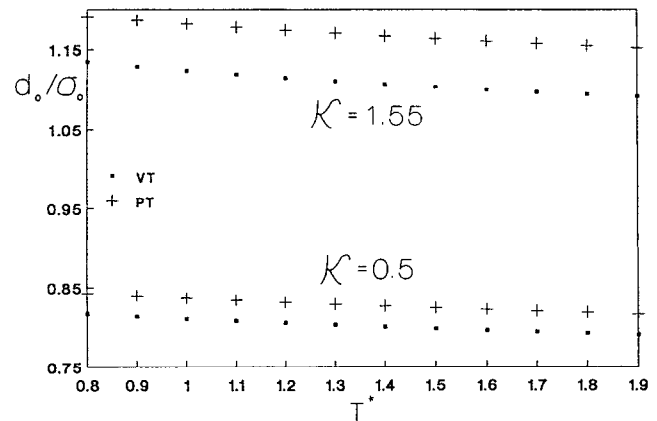


FIG. 4. Effective diameters as a function of reduced temperature, $T^*=kT/\epsilon_0$, for the GOCE model obtained from variational (VT) and perturbation (PT) theories, at two length to breadth ratios ($\rho\sigma_0^3=0.6$).

around 3.1%, for the cases presented in Fig. 1. However, at high densities and high temperatures the variational theory calculations are closer to simulation data.

In Figs. 2 and 3, we present the same kind of results as earlier, but for other two values of the length to breadth ratio ($\kappa=0.5$ and $\kappa=1.55$). Since the lack of simulation data, we present our comparisons for two temperatures only. These figures show almost the same features as described for Fig. 1. At a temperature $T^*=1$, perturbation theory gives better results. However, at $T^*=1.5$ for $\kappa=0.5$ and $\kappa=1.55$, both theories present almost the same deviation from simulation data. The overall percent deviation when $\kappa=0.5$, is of the order of 2.8% for perturbation theory and of 3.1% for variational theory. For $\kappa=1.55$, the percent deviation is of the order of 3.3% and of 4.6%, for perturbation and variational theories, respectively.

From Fig. 2, we can see that there is a point, at $T^*=1.5$ and $\rho^*=1.7$, where the value of the excess free energy obtained by the variational technique is less than the value of molecular dynamics. It is not clear if the origin of this strange result comes from our procedure or from the precision of the simulation.

B. Transport properties

Shear viscosity and thermal conductivity for the GOCE fluid were calculated using the effective diameter hard sphere theory in the way described in Sec. II B. Hence, our first point to study was the behavior of the effective diameters, d_0 , at different thermodynamic states. Figures 4 and 5 present the behavior of the effective diameters obtained through Eq. (22) with respect to temperature and density. In addition, we included in these figures the effective diameters obtained with the perturbation theory for the GOCE fluid.⁴⁴

Figure 4 shows that the effective diameter, as expected, decreases as the temperature increases. As also expected, in Fig. 5 we show that at high densities the effective diameter decreases as density increases. The effective diameters calculated with the variational theory are always below the

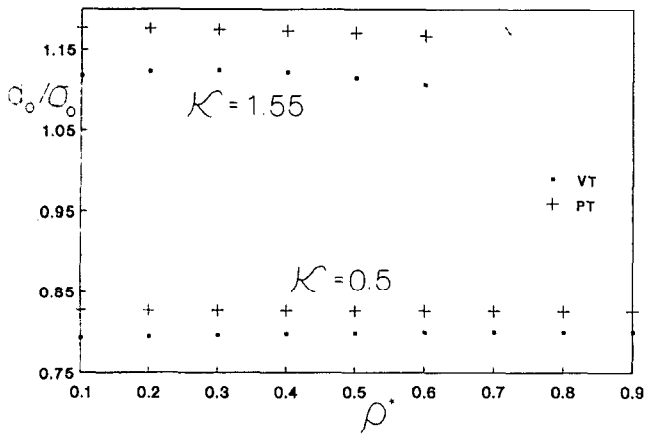


FIG. 5. Effective diameters as a function of reduced density, $\rho^* = \rho\sigma_0^3$, for the GOCE model obtained from variational (VT) and perturbation (PT) theories, at two length to breadth ratios ($kT/\epsilon_0=1.4$).

effective diameters calculated with the perturbation theory, in the same way as in the case of potentials with spherical symmetry.³³ This only reflects the difference between both approaches. This difference increases at high densities.

Figure 6 shows an example of the behavior of the reduced shear viscosity ($\eta^* = \eta\sigma_0^2/\sqrt{m\epsilon_0}$), and of the reduced thermal conductivity ($\lambda^* = \lambda\sigma_0/k\sqrt{m/\epsilon_0}$) for the GOCE fluid with a length-to-breadth ratio equal to 0.5, both as a function of the reduced density. In Fig. 6 we also included the calculations using the EDHST with the effective diameter calculated with perturbation theory. As we can see, when variational theory is used to obtain the effective diameters, the TP's are smaller than when the diameters are calculated with the perturbation theory. Of course, this result only reflects the difference between the effective diameters obtained by those theories, at the same thermodynamic state. A similar behavior has been re-

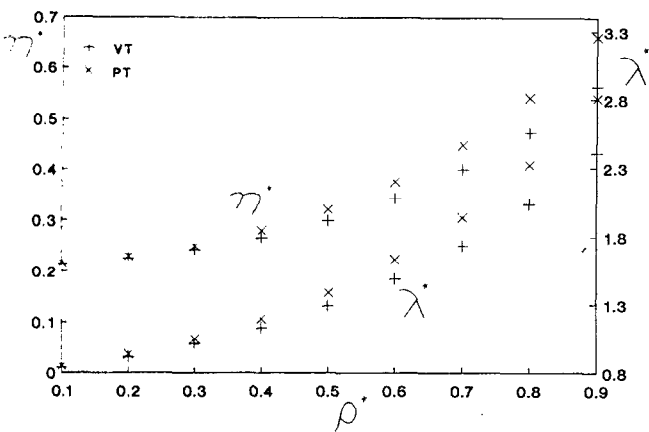


FIG. 6. Reduced transport properties ($\eta^* = \eta\sigma_0^2/\sqrt{m\epsilon_0}$; $\lambda^* = \lambda\sigma_0^2/k\sqrt{m/\epsilon_0}$) given by EDHST as a function of reduced density, $\rho^* = \rho\sigma_0^3$, evaluated for systems interacting with GOCE potential, with $\kappa=0.5$ and $kT/\epsilon_0=1.4$.

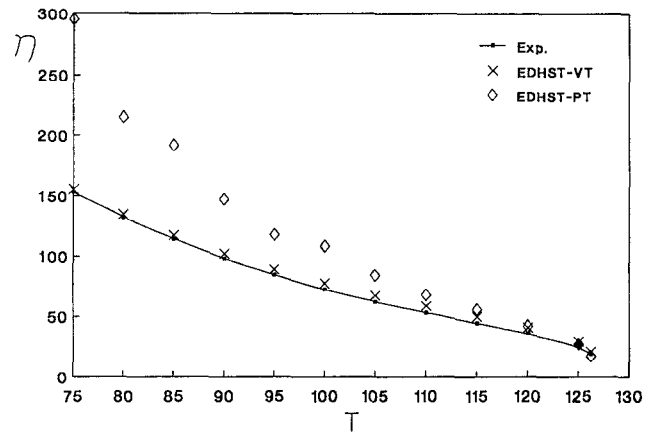


FIG. 7. Comparison between shear viscosity calculations for nitrogen along the liquid coexistence curve and experimental data. Calculations were performed with EDHST for nitrogen modeled with the GOCE potential, and the effective diameters were obtained with variational theory (EDHST-VT), and with perturbation theory (EDHST-PT). The units of shear viscosity are Pa s and the temperature is given in K.

ported when EDHST is used to study the TP's of the LJ fluid.³⁰

In Fig. 7, our predictions for the shear viscosities of liquid N_2 , modeled with the GOCE model potential along the coexistence curve and the experimental data, are presented. Here, the shear viscosities are calculated with the EDHST, but in two versions. In the first one the effective diameters are calculated with variational theory, i.e., Eq. (22). In the second one, the effective diameters are calculated with the perturbation theory; for details see Ref. 44. As we can see in Fig. 7, the results when the variational theory is used are remarkably good. These results are quite better than those obtained using EDHST, but with the actual fluid modeled with the LJ potential.⁶⁶

In order to compare thermal conductivities with experimental data some corrections must be introduced related to the internal degrees of freedom. Until now, we have considered that the process of energy transfer is only due to translation of the molecules. For thermal conductivity, a contribution of rotational and other internal degrees of freedom is expected, although in the range of few percent.⁵² Hence, if we want to compare our calculations using EDHST and experimental data, we need to take into account the contribution to transport from the internal degrees of freedom. In order to consider this, we followed the same approach as in previous works,⁶⁷⁻⁶⁹ and suggested by the work of Mason and Monchick⁷⁰ for polyatomic gases in the dilute regime, on the basis of Wang-Chang-de Boer theory.⁷¹ Mason and Monchick showed that the thermal conductivity can be separated into two contributions: one dealing with the transfer of thermal energy due to the translational motion of the molecules, and one dealing with the transfer of energy due to changes in the internal energy of the molecules. Here, we will assume that the thermal conductivity of a dense fluid can be split into a part due to the transfer of energy by molecular motion and by collision transfer (λ'), given by EDHST, and a part due to the

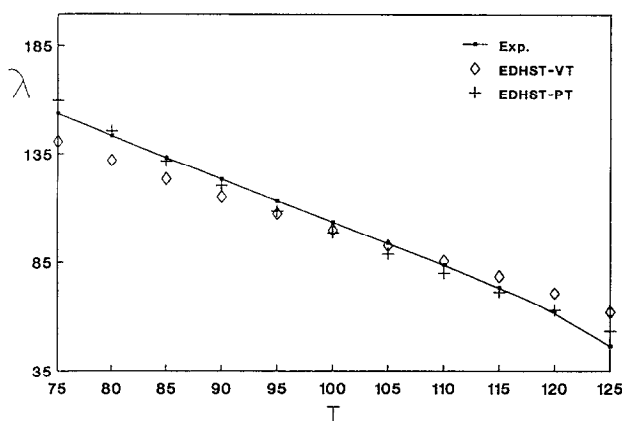


FIG. 8. Comparison between thermal conductivity calculations for nitrogen along the liquid coexistence curve and experimental data. Calculations were performed with EDHST for nitrogen modeled with the GOCE potential, and the effective diameters were obtained with variational theory (EDHST-VT), and with perturbation theory (EDHST-PT). The units of thermal conductivity are $\text{mW m}^{-1} \text{K}^{-1}$, and the temperature is given in K.

energy transfer associated with the internal degrees of freedom of the molecules through diffusion (λ''). Terms involving the interchange of translational and internal energy through inelastic collisions have not been considered. This correction will improve the EDHST results mainly at moderate densities. Thus

$$\lambda = \lambda' + \lambda'' \quad (28)$$

In addition, we assume that λ'' can be represented by the first order approximation formula given by Mason and Monchick for quasielastic collisions:

$$\lambda'' = \rho D C_v'' / M = \lambda_0'' / \chi^c, \quad (29)$$

where D is the self-diffusion coefficient and λ_0'' is the internal contribution to λ in the dilute hard sphere gas, C_v'' is the molar heat capacity at constant volume for the internal degrees of freedom, and M is the molecular weight.

To obtain a general formula for the evaluation of λ_0'' , for real fluids, the modified Eucken correlation for polyatomic gases was used^{69,72}

$$\lambda_0'' = f_{\text{int}}(C_p^0 - 5R/2)\eta_0/M, \quad (30)$$

where η_0 is the dilute gas viscosity, C_p^0 is the ideal gas molar heat capacity at constant pressure, R is the gas constant, M is the molecular weight, and f_{int} has a constant value of 1.32

The values of C_p^0 were obtained by an expansion in terms of the temperature up to sixth order. The coefficients used were those reported in the TRAPP computer program.⁶⁹

In Fig. 8, the values for thermal conductivity of N_2 modeled with the GOCE model potential along the coexistence curve and the experimental data are presented. Here, as earlier, the thermal conductivities are calculated with the EDHST, in two versions. In the first one the effective diameters are calculated with variational theory,

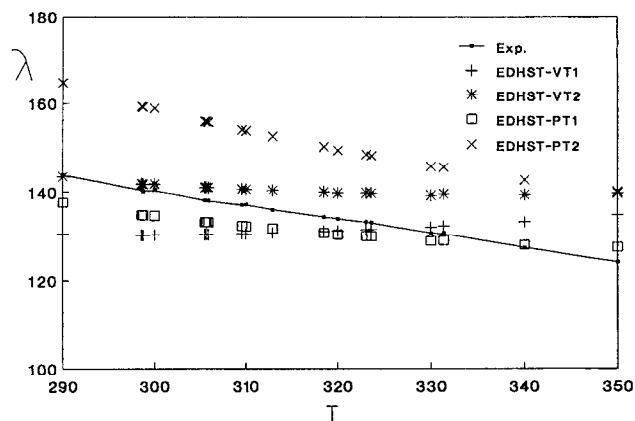


FIG. 9. Comparison between thermal conductivity calculations for benzene along the liquid coexistence curve and experimental data. Calculations were performed with EDHST for benzene modeled with the GOCE potential, and the effective diameters were obtained with variational theory (EDHST-VT), and with perturbation theory (EDHST-PT). The units of thermal conductivity are $\text{mW m}^{-1} \text{K}^{-1}$ and the temperature is given in K.

i.e., Eq. (22). In the second one, the effective diameters are calculated with the perturbation theory.⁴⁴ As we can see in Fig. 8, at low temperature the variational diameters underestimate λ , and at high temperatures there is an overestimation, although the percent deviation is of the order of 5% overall. For this case, EDHST with effective diameters coming from perturbation theory gives slightly better results.

In Fig. 9, we present the experimental data and the EDHST calculations for the thermal conductivities of benzene, modeled with GOCE. As before, we used effective diameters coming from variational and from perturbation theories. For this particular case, we can use two sets of parameters for the GOCE model potential, (see Table II). The results are not that good, as expected. The predicted values along the coexistence line are almost constant when the variational theory is used to obtain the effective diameters. When the perturbation theory is used to obtain the effective diameters, with parameters labeled as GOCE2, the thermal conductivities have a correct trend, but quite above the experimental results, and when the parameters labeled as GOCE1 are used, we obtain results closer to the experimental data, but with a bad trend. One can see here that our procedure is very sensitive to the selection of GOCE parameters. This is due to the high sensitivity of the hard-sphere TP's expressions to variations in the hard-sphere diameter.

A clear explanation of the deviation between calculated and experimental thermal conductivities, mainly for the case of benzene, is not so easy. There are several possibilities: (a) benzene is not well modeled with the GOCE potential, (b) the parameters for the GOCE potential are not of enough quality to be used in the evaluation of TP's, and (c) the contribution of the internal degrees of freedom is not so simple as assumed here. Viscosities are quite well predicted, whereas it is not the case for thermal

conductivities. A more fundamental explanation may be obtained in the work of Theodosopulu and Dahler.¹³ They showed that, for nonspherical particles, the shear viscosity is not affected by the rotational motion, however, on the other hand, for the case of the thermal conductivity, the situation is quite different. There is a contribution of the molecular rotation, although it is not practicable in the present state of the theory. Thus, we could expect that the shear viscosity can be predicted more precisely than the thermal conductivity.

In summary, the procedure presented in this paper constitutes the first attempt to predict numbers for excess free energies and for TP's of molecular fluids using the variational theory. The results for the free energies are encouraging since they are very close to simulation data. The results for the case of TP's are, in general, better than those presented quite recently⁴⁴ in a similar study, where EDHST with effective diameter obtained with perturbation theory was used. We hope this type of study will motivate simulation work in molecular fluids, in particular, on TP's.

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