

Analysis of the pressure virials and Clausius-Mossotti function for polyatomic gases*

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Statistical mechanical equations for the second pressure virial coefficient and the second and third dielectric virial coefficients for quadrupolar molecules are evaluated using the $m-6-8$ potential function. The results are compared with experimental data for nitrogen and fluorine. An approximate value for the quadrupole moment of fluorine is estimated. Agreement between theory and experiment is generally good.

I. INTRODUCTION

In previous publications,^{1,2} the $m-6-8$ potential function has been shown to be of practical value in correlating macroscopic properties of monatomic fluids. In this paper, we further extend³ the application of this potential function to simple non-polar polyatomic fluids. In particular, the dielectric constant and pressure virial coefficients of nitrogen and fluorine are considered. Nitrogen, as a common fluid with a relatively simple structure, is an obvious choice for this study, and fluorine, despite its toxic and extremely reactive nature, was also chosen because an extensive experimental investigation has been carried out at this laboratory yielding reliable, thermodynamically consistent fluorine property data.⁴⁻⁶ The results obtained from this investigation are instructive by themselves and encourage a more systematic and detailed study into the general relationship between statistical mechanical theory, the intermolecular potential function and experiment, for simple non-spherical molecules.

II. EQUATIONS

A. Intermolecular Potential

The calculations are based on the $m-6-8$ potential^{1,2} which has the form,

$$\varphi(r)(m-6-8) = \epsilon \left[\frac{6+2\gamma}{m-6} \left(\frac{\sigma}{r}\right)^m d^m - \frac{m-\gamma(m-8)}{m-6} \times \left(\frac{\sigma}{r}\right)^6 d^6 - \gamma \left(\frac{\sigma}{r}\right)^8 d^8 \right]. \quad (1)$$

σ is defined by the condition $\varphi(\sigma) = 0$, d is the ratio r_m/σ , where r_m is defined by $\varphi'(r_m) = 0$, and ϵ is given by $\varphi(r_m) = -\epsilon$. The parameters m and γ represent the strength of the repulsion and inverse eight attraction between the molecules, respectively. It has been shown⁷ that the $m-6-8$ is insufficiently flexible to be regarded as a theoretical representation of the intermolecular interaction, but it has been very successful when applied to the many different macroscopic properties (the viscosity coefficient, for example) of monatomic gases. We

thus regard the $m-6-8$ as a simple and convenient, but not exact, model to use as a basis for studies with polyatomic molecules.

For polyatomic molecules, there are extra terms in the intermolecular potential arising from the non-spherical interactions. Thus, for polarizable, quadrupolar molecules such as nitrogen and fluorine, we must consider the following general potential:

$$\varphi(r) = \varphi(\text{central}) + \varphi(\text{quadrupole}) + \varphi(\text{induced-dipole}) + \varphi(\text{shape}) + \varphi(\text{anisotropy}). \quad (2)$$

The first term is the spherical contribution—the $m-6-8$ in our case, the second term represents the electrostatic interactions of the permanent multipole moments (quadrupoles), and the third term represents the induced-dipole interactions caused by the induction effect of the quadrupole moments, and when applicable, by the presence of an external electric field. Finally, the last two terms depict the anisotropy in the repulsive and attractive forces, respectively. In our work, we have chosen to neglect these latter two contributions.³ Briefly, the reasoning behind this choice is as follows: (1) It is currently impossible to determine independently the parameters for the shape part of the potential and (2) we have previously shown³ for several quadrupolar gases (including nitrogen) that the spherical $m-6-8$ potential yields a very reasonable representation of experimental transport properties and pressure second virial coefficients and presumably, therefore, these contributions are at least partially accounted for in the selection of spherical potential parameters, m , γ , σ , and ϵ/k .

In order to evaluate the dielectric constant, we must consider the fluid to be in the presence of an external electric field D . Hence, our model for the intermolecular potential becomes

$$\varphi(r, \omega_1, \omega_2, D) = \varphi(r)[m-6-8] + \varphi_{qq}(r, \omega_1, \omega_2) + \varphi_{ii}(r, \omega_1, \omega_2, D), \quad (3)$$

where, following McQuarrie and Levine⁸

$$\begin{aligned} \varphi_{\alpha q}(\mathbf{r}, \omega_1, \omega_2) &= \mathbf{Q} : \mathbf{V} : \mathbf{Q} \quad , \\ \varphi_{ii}(\mathbf{r}, \omega_1, \omega_2, \mathbf{D}) &= -\frac{1}{2}(\mathbf{D} - \mathbf{U} : \mathbf{Q}) \\ &\cdot \alpha \cdot (\mathbf{1} - \alpha \cdot \mathbf{T})^{-1} \cdot (\mathbf{D} - \mathbf{U} : \mathbf{Q}) . \quad (4) \end{aligned}$$

In these equations, ω_1 and ω_2 denote the angles describing the orientations of the molecules and \mathbf{T} , \mathbf{U} , and \mathbf{V} are the two-dimensional supermatrices^{8,9} whose components are the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interaction tensors. The Cartesian components of these tensors are

$$\begin{aligned} T_{\alpha\beta}(\mathbf{r}) &= \nabla_\alpha \nabla_\beta (1/r) , \\ U_{\alpha\beta\gamma}(\mathbf{r}) &= \nabla_\alpha \nabla_\beta \nabla_\gamma (1/r) , \end{aligned}$$

and

$$V_{\alpha\beta\gamma\delta}(\mathbf{r}) = \nabla_\alpha \nabla_\beta \nabla_\gamma \nabla_\delta (1/r) . \quad (5)$$

α is a matrix whose components are the molecular polarizability tensors and \mathbf{Q} is a supervector whose elements are the molecular quadrupole moment tensors. The elements of these tensors for axial molecules are

$$\begin{aligned} \alpha_{\beta\gamma} &= \bar{\alpha} [(1-\kappa)\delta_{\beta\gamma} + 3\kappa\hat{q}_\beta \hat{q}_\gamma] , \\ Q_{\alpha\beta} &= \hat{q}_\alpha \hat{q}_\beta \Theta , \end{aligned}$$

where $\bar{\alpha}$ is the mean molecular polarizability, Θ is the scalar quadrupole moment, κ is the polarizability anisotropy, and \hat{q} is the unit vector along the molecular axis.

B. Virial Expansions

The quantities of interest to us are the second and third pressure and dielectric virial coefficients appearing in the expansions,

$$p/\rho N_0 kT = 1 + B_p(T)\rho + C_p(T)\rho^2 + \dots , \quad (6)$$

$$(\epsilon - 1)/(\epsilon + 2)\rho = A_D + B_D(T)\rho + C_D(T)\rho^2 + \dots . \quad (7)$$

Equation (6) is the conventional virial expansion for the pressure p , and Eq. (7) is the Clausius-Mossotti function for the dielectric constant ϵ . In these expansions, ρ is the molar density, and n/V , $B_p(T)$, and $C_p(T)$ are the second and third pressure virial coefficients defined by

$$\begin{aligned} \frac{B_p(T)}{b_0} &= B_p^*(T^*) = B^*(T^*)[m-6-8] - \frac{21}{5} \frac{\Theta^{*4}}{T^{*2}} I_{10} \\ &+ \frac{216}{245} \frac{\Theta^{*6}}{T^{*3}} I_{15} - \frac{9\bar{\alpha}\Theta^{*2}}{T^*} I_8 \\ &+ \frac{108}{25} \frac{\bar{\alpha}^{*2}\kappa^2\Theta^{*2}}{T^*} I_{11} + \frac{216}{35} \frac{\bar{\alpha}^*\kappa\Theta^{*4}}{T^{*2}} I_{13} , \quad (8) \end{aligned}$$

$$\frac{C_p(T)}{b_0^2} = C_p^*(T^*) = C^*(T^*)[m-6-8]$$

$$- \frac{252}{5} \frac{\Theta^{*4}}{T^{*2}} J_3 - \frac{108\bar{\alpha}^*\Theta^{*2}}{T^*} J_2 , \quad (9)$$

where

$$b_0 = 2\pi N_0 \sigma^3 / 3, \quad T^* = kT/\epsilon , \quad (10)$$

$$B^*(T^*)[m-6-8] = -3 \int_0^\infty dx x^2 f(x) ,$$

and

$$\begin{aligned} C^*(T^*)[m-6-8] &= -12 \int_0^\infty dz \int_0^z dy \\ &\times \int_{z-y}^{z+y} dx xf(x)yf(y)zf(z) . \quad (11) \end{aligned}$$

The reduced integration variables x, y , and z and the Mayer function, $f(x)$, are defined in the Appendix. A_D, B_D , and C_D are the first, second, and third dielectric virials given by

$$A_D/b_0 = A_D^* = 2\bar{\alpha}^* , \quad (12)$$

$$\begin{aligned} B_D(T)/b_0^2 &= B_D^*(T^*) = 24\bar{\alpha}^{*3}(1+2\kappa^2)I_6 \\ &+ 12(\bar{\alpha}^{*2}\Theta^{*2}/T^*)(1+\frac{4}{3}\kappa^2)I_8 , \quad (13) \end{aligned}$$

and

$$\begin{aligned} C_D(T)/b_0^3 &= C_D^*(T^*) = 144\bar{\alpha}^{*3}(1+2\kappa^2)J_4 \\ &+ (72\bar{\alpha}^{*2}\Theta^{*2}/T^*)(1+\frac{4}{3}\kappa^2)J_2 \\ &+ 72\bar{\alpha}^{*3}J_5 + (36\bar{\alpha}^{*2}\Theta^{*2}/T^*)J_6 . \quad (14) \end{aligned}$$

The reduced molecular quadrupole moment and polarizability are defined by $\Theta^{*2} = \Theta^2/(\epsilon\sigma^5)$ and $\bar{\alpha}^* = \bar{\alpha}/\sigma^3$. The I_n and J_n are dimensionless integrals which arise from expanding the nonspherical portion of the Boltzmann factor^{8,10-12} in the statistical expressions for the virials. A list and brief discussion of the calculation of these integrals is presented in the Appendix.

III. PARAMETER ESTIMATION AND DATA

A proper comparison between theory and experiment would require that the potential parameters and the electrostatic quantities, α, κ , and Θ , be taken from theory or independent experiment before insertion into Eqs. (8)–(14). In this program involving polyatomic molecules, we will generally assume that reliable independent values of the electrostatic quantities are available, otherwise the use of the potential requires excessive parametrization. However, our work with monatomic gases suggests that the spherical $m-6-8$ parameters are best determined from a fit of a macroscopic property such as the viscosity coefficient. We stress, however, that very definite criteria that the selection procedure must satisfy have been stated.¹³ (For example, we require that parameters obtained from one macroscopic property can be used to correlate another property without adjustment).

In order to obtain values of m, γ, σ , and ϵ/k for

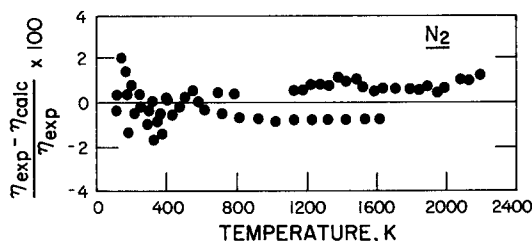


FIG. 1. Viscosity of nitrogen, comparison of calculations from Eq. (15) with data listed in Ref. 1. The m -6-8 spherical function was used with the parameters of Table I.

a particular polyatomic fluid, an assumption used previously by us and by other authors¹⁴⁻¹⁷ is invoked: The dilute gas viscosity coefficient, η , can be represented by the kinetic theory expression derived for a spherically symmetric interaction potential. Thus, it is assumed that the equation,¹⁸

$$\eta = \frac{5}{16} [(mmkT)^{1/2} / \pi \sigma^2 \Omega^{(2,2)}(T)^*] \quad (15)$$

with the viscosity collision integral $\Omega^{(2,2)}(T)^*$ evaluated with the spherical m -6-8 potential, applies to nitrogen and fluorine. Tables of these collision integrals have been published for several m - γ sets.¹⁹ A fit of Eq. (15) to experimental data over a wide temperature range, specifically a range such that $T^* < 2$ and $T^* > 5$, determines the m -6-8 parameters. Alternatively, we have verified that a satisfactory m and γ can be found by simultaneously fitting viscosity and pressure second virial data for $T^* < 2$, assuming the form of Eq. (10) for B_p^* . The remaining parameters, σ and ϵ/k , are found from viscosity data alone. (In other words, the selection of m and γ appears to be weakly dependent on the presence of nonspherical interactions.)

Experimental viscosity and pressure second virial coefficients for nitrogen have been carefully selected for our previous work. Data sources are given in Refs. 1, 2, and 20 along with detailed discussions of the evaluation procedure. Viscosity coefficients for fluorine at low temperatures have been measured by Haynes.²¹ These results are considered to be the only reliable fluorine viscosities.²² The fluorine second pressure virials were extracted from pVT data obtained by one of us and are listed in Ref. 4.

Second virial coefficients of Eq. (8) will be compared with the corresponding data, but the third pressure virial, C_p , will not be discussed further. The reason for this is that previous evidence for monatomic gases,²³ indicates that nonadditivity in the potential makes a significant contribution to the third virial. Hence a comparison of third virials for polyatomic gases with Eq. (9) is unlikely

to be complete.

Fluorine dielectric constant measurements have been reported by us in Ref. 5. Given the densities as a function of temperature and pressure,⁶ the Clausius-Mossotti function was constructed over a wide temperature and density range. Here, we compare the function for given isotherms using Eq. (7). The theoretical and experimental dielectric second virial B_D will also be examined separately, but we point out that this quantity is not easily extracted from the experimental Clausius-Mossotti function. Unfortunately, nitrogen dielectric data are rather limited with respect to both the density and temperature range. We do, however, briefly compare our calculations with the results of Cole *et al.*²⁴ and Oudemans.²⁶

IV. RESULTS AND DISCUSSION

We first fitted the viscosity data to Eq. (15) with the spherical m -6-8 collision integrals. The results are presented as deviation curves in Figs. 1 and 2. The parameters obtained from this fitting procedure are listed in Table I. One can see that the data are correlated to within experimental error indicating, as previously reported,^{1,3} that the m -6-8 parameters so chosen are satisfactory. It is important to note, however, that this fit neither proves nor disproves the assumption that the viscosity of a quadrupolar gas can be represented by Eq. (15) calculated with a spherically symmetric potential. It signifies only that the m -6-8 potential is sufficiently flexible to be applicable to a gas such as nitrogen.

A. Nitrogen

Having determined effective values of m , γ , σ , and ϵ/k and given the values of α , κ , and Θ (listed in Table I), it is straightforward to determine B_p^* , B_D^* , and C_D^* and hence the unreduced virials B_p , B_D , and C_D . The solid points of Fig. 3 illustrate the deviation pattern for B_p (a similar curve was given in Ref. 3, but a slightly different value

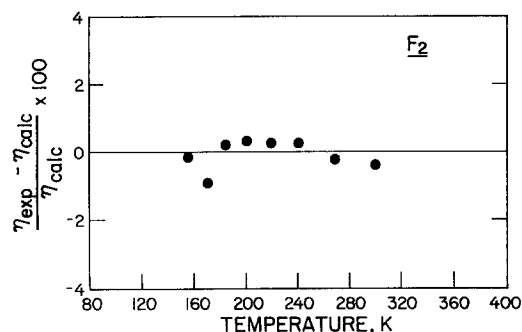


FIG. 2. Viscosity of fluorine, comparison of Eq. (15) calculated values with the measurements of Haynes.²⁰

TABLE I. Potential parameters.

Gas	<i>m</i>	γ	$\sigma(\text{\AA})^a$	$\epsilon/k(^{\circ}\text{K})$	$10^{21}\alpha(\text{cm}^3)$	κ^b	$10^{26}\Theta(\text{esu})$
F ₂	12	2.0	3.32	138.0	1.243 ^c	0.200 ^d	0.75
N ₂	12	2.0	3.54	118.0	1.737 ^e	0.134 ^f	1.400 ^g

^a1 Å = 10⁻¹⁰ m.

^bThe polarizability anisotropy κ is defined by $\kappa = (\alpha_L - \alpha_T)/3\alpha$, where α_L and α_T are the longitudinal and transverse components of the polarizability, respectively. $\bar{\alpha}$ is the mean molecular polarizability $\alpha = (\alpha_L + 2\alpha_T)/3$.

^cReference 5.

^dThis value was estimated from the values of the polarizability for other similar fluids. It can be shown numerically that a variation of 50% in κ 's magnitude does not make a significant change in the virials.

^eReference 26.

^fN. J. Bridge and A. D. Buckingham, Proc. Roy. Soc. A295, 334 (1966).

^gA. D. Buckingham, R. L. Disch, and D. A. Dunmur, J. Am. Chem. Soc. 90, 3104 (1968).

of α was used). We regard this plot as satisfactory considering that the potential (3) only has four adjustable parameters, as for the monatomic gases. Figure 4 shows the calculated Clausius-Mossotti function compared to the data of Oudemans.²⁶ Agreement is good, but obviously the density range of the experimental data is limited.

Figure 5(a) compares the experimental dielectric virials for nitrogen with those calculated using several different values of Θ in Eq. (13). Included in this figure are some preliminary experimental values, but as was remarked above, reliable experimental second dielectric virials are difficult to obtain at this time. From this graph, it is clear that a meaningful comparison of theory and experiment can only be made for T^* less than 1.2. This is especially true if one wishes to assess the effect of the quadrupole moment on the second dielectric virial. An important consequence of this ob-

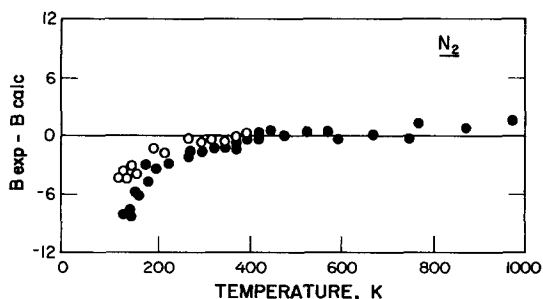


FIG. 3. Comparison between experimental and calculated pressure second virial coefficients (cubic centimeters/mole) for nitrogen. Data sources are given in Ref. 1. Solid points are differences obtained with the $m-6-8$ potential using given values of the quantities α , k , and Θ (Table I). Unfilled points are differences treating Θ as an adjustable parameter.

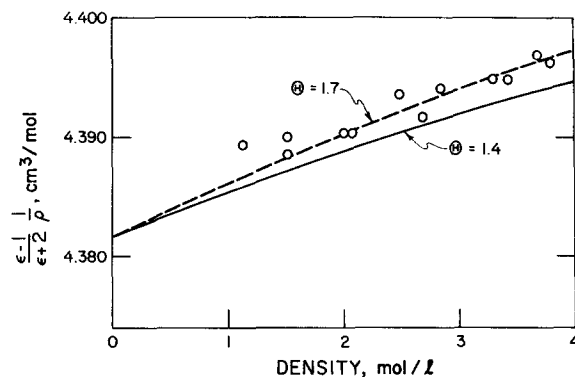


FIG. 4. Comparison of the Clausius-Mossotti function for nitrogen at temperatures of 306 and 313°K (essentially indistinguishable). Data from Ref. 26. The solid line is the calculated value from Eq. (7) using the independent quadrupole moment; $\Theta = 1.4 \times 10^{-26}$ esu, while the dashed curves are the corresponding value using an adjusted moment of 1.7×10^{-26} esu.

servation is that the validity of Eq. (13), which has been questioned for some of the lighter elements, e.g., He and Ne,^{25,27,28} cannot be adequately tested for N₂ until reliable data in this temperature range are available.

In the context of fitting virial coefficients, most

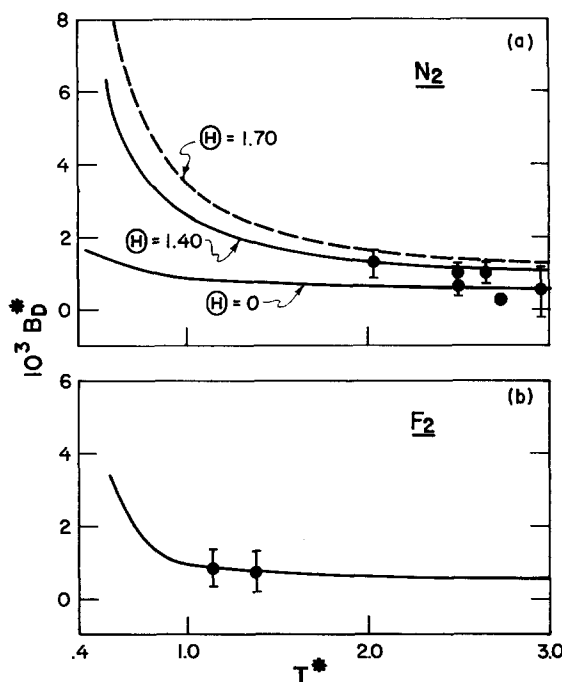


FIG. 5. (a) The reduced dielectric second virial coefficient calculated with Eq. (13) using three different quadrupole moments compared to the data of Refs. 24 and 26. (b) The reduced calculated dielectric virials for fluorine are compared with preliminary data from Ref. 5.

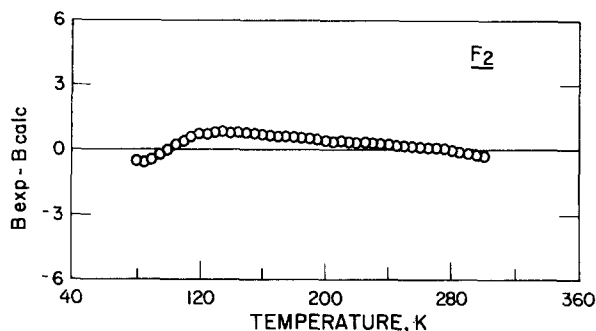


FIG. 6. Pressure second virial deviations (units of cubic centimeters/mole) for fluorine. Data from Ref. 4.

previous work¹⁴⁻¹⁷ has treated the quadrupole moment as an adjustable parameter. The values for Θ were obtained for a given gas by requiring a good fit of experimental pressure second virial coefficients. However, because the spherical part of the previously used potentials, e. g., the Lennard-Jones 12-6, was not flexible enough to represent the spherical part of the intermolecular interaction and because further parameters such as the shape factor [associated with the fourth term of Eq. (2)] were needed to obtain the necessary agreement between theory and experiment, the values of Θ obtained, had the same significance as say σ or ϵ/k . Here, however, we have a good effective model for the spherical part of the potential and we do not require parameters outside those given in Table I to obtain a reasonable agreement between theoretical and experimental second virials. Consequently, it is interesting to discover how much the quadrupole moment can change from the chosen fixed value in order to reduce the deviations observed in Fig. 3. For nitrogen, we found that $\Theta = 1.70 \times 10^{-26}$ esu gave an improved deviation pattern as indicated by the unfilled circles in Fig. 3. This value is approximately 20% higher than the independently measured value. The corresponding Clausius-Mossotti function and reduced second dielectric virials are shown as dashed curves in Figures 4 and 5(a).

B. Fluorine

Unfortunately, a reliable independent estimate of the quadrupole moment for fluorine does not exist. Consequently, we have no alternative but to treat Θ as an adjustable parameter. A fit of the pressure virials is given in Fig. 6, having found a best value of 0.75×10^{-26} esu for Θ . Based on the corresponding fit with nitrogen, this number is probably too high by about 20%-30%. We do, however, regard it as important that we can estimate Θ to this precision at all.

With this value of Θ and the fluorine parameters

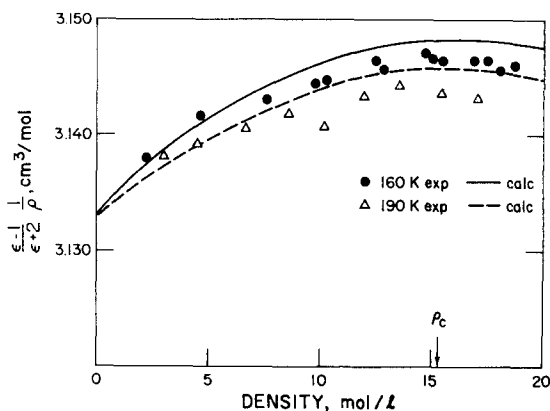


FIG. 7. Clausius-Mossotti function for fluorine. Data from Ref. 5. Calculations with the $m-6-8$ potential.

given in Table I, the dielectric virials B_D and C_D were calculated and the Clausius-Mossotti (CM) function was constructed for two temperatures; 160 and 190 °K. The comparison with experiment is displayed in Fig. 7. Although the specific agreement between the theoretical and experimental iso-terms is only modest, the figure illustrates two significant features: (1) The temperature dependence at constant density is correctly predicted to be negative and (2) a maximum in the function is predicted to occur at around the correct density. In comparison, Fig. 8 shows the corresponding curves calculated by one of us using the Lennard-Jones 12-6 potential. It is clear that replacing the 12-6 with the $m-6-8$ leads to a considerably im-

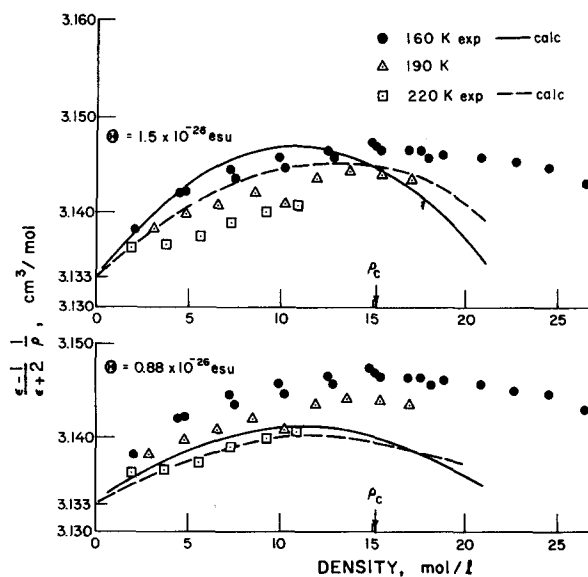


FIG. 8. Clausius-Mossotti function for fluorine calculated with the 12-6 potential. This figure has been taken from Ref. 5, compare to Fig. 7.

proved representation of the data, and this improvement has been achieved without requiring a quadrupole moment which is clearly too large. [$\Theta = 1.5$ for the 12-6 as compared to $\Theta = 0.75$ ($\text{all} \times 10^{-26}$ esu) for the $m-6-8$]. From a theoretical point of view, however, it is possible that this agreement is somewhat fortuitous owing to the fact that we have neglected nonadditivity effects in the intermolecular potential and we have neglected all dielectric virials higher than the third. As a matter of interest, the reduced second dielectric virials for fluorine have been plotted separately in Fig. 5(b).

V. CONCLUSION

Statistical mechanical expressions for the dilute gas viscosity coefficient, equilibrium pressure second virial coefficient, and the second and third dielectric virial coefficients are given for the $m-6-8$ potential and compared with the corresponding data for nitrogen and fluorine. Since the comparisons are generally successful, we have demonstrated that different moderately dense gas properties (transport, equilibrium, and dielectric) for these quadrupolar molecules can be represented in a consistent manner by statistical mechanics. For fluorine, the comparisons have led to a value of the quadrupole moment, $\Theta = 0.75 \times 10^{-26}$ esu. Although approximate (probably 20% too high), this estimate is probably the best available at this time. The investigation also clarifies some areas for further work. For example, calculations are in progress to calculate the collision integrals for an angularly dependent $m-6-8$ potential—hopefully, agreement between theoretical and experimental pressure and dielectric virials will then be improved. We have also suggested that further experimental measurements of the dielectric constant should cover densities such that a possible maximum in the Clausius-Mossotti function could be observed, and that they should also cover a temperature range such that the second dielectric virial, B_D , can be better compared with theory.

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APPENDIX

Given below are the reduced forms for the I and J integrals^{8,29} appearing in Eqs. (8)–(9) and (12)–

(14). The reduction scheme is defined as follows: $(x, y, z) = (r_{12}, r_{13}, r_{23})/\sigma$; $\varphi^*(x) = \varphi_{m-6-8}(x)/\epsilon$; and $f(x) = \exp[-\varphi^*(x)/T^*] - 1$. r_{ij} represents the magnitude of the vectorial distance between molecules i and j , viz., $r_{12} = |r_{12}|$,

$$I_n = \int_0^\infty dx x^{-n+2} \exp[-\varphi^*(x)/T^*],$$

$$J_2 = \int_0^\infty dz \int_0^z dy \int_{z-y}^{z+y} dx z f(z) y f(y) x^{-7} \exp[-\varphi^*(x)/T^*],$$

$$J_3 = \int_0^\infty dz \int_0^z dy \int_{z-y}^{z+y} dx z f(z) y f(y) x^{-9} \exp[-\varphi^*(x)/T^*],$$

$$J_4 = \int_0^\infty dz \int_0^z dy \int_{z-y}^{z+y} dx z f(z) y f(y) x^{-5} \exp[-\varphi^*(x)/T^*],$$

$$J_5 = \int_0^\infty dz \int_0^z dy \int_{z-y}^{z+y} dx (3W^2 - 1) z^{-2} y^{-2} \\ \times \exp\{-[\varphi^*(y) + \varphi^*(z)]/T^*\} x f(x),$$

$$J_6 = \int_0^\infty dz \int_0^z dy \int_{z-x}^{z+y} dx (5W^3 - 3W) z^{-3} y^{-3} \\ \times \exp\{-[\varphi^*(y) + \varphi^*(z)]/T^*\} x f(x),$$

$$W = (z^2 + y^2 - x^2)/2zy.$$

These integrals were numerically evaluated as a function of T^* by means of one- and three-dimensional Clenshaw-Curtis quadratures,³⁰ respectively. This method of integration was chosen because of its speed, accuracy, and more importantly, the availability of a reliable error estimate.³¹ All of the calculations are believed to be accurate to within ± 1 in the fourth decimal place.

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