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INTERNAL REPORT

PREDICTION OF DIELECTRIC VIRIAL COEFFICIENTS

FOR GAS MIXTURES FROM MOLECULAR THEORY

BY

K. R. Van Doren

J. L. Gordon

BRANCH   BRANCH OF FUNDAMENTAL RESEARCH

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K. R. Van Doren[1] and J. L. Gordon[2]

ABSTRACT

Statistical mechanical expressions for the first two dielectric virial coefficients are derived, and these expressions are reduced to computational forms for several well-known molecular models.

INTRODUCTION

The Helium Research Center is currently engaged in research concerning dielectric properties of gas mixtures; part of this research deals with the prediction of these dielectric properties from molecular theory. A virial expansion for the Clausius-Mosotti function has been proposed to account for the density dependence of this function, and statistical mechanical expressions have been derived for the first two virial coefficients (1, 2).[3] The derivations of these expressions are herein expanded in considerable detail, and reductions of these expressions to computational forms are performed for several well-known molecular models.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

PRELIMINARY CONCEPTS

Whenever a gas mixture is subjected to a uniform electric field, the dipole moments of the molecules of the mixture tend to align themselves in the direction of the field. These dipole moments are generally the sum of a permanent dipole moment and an induced dipole moment. The permanent dipole moment arises from a displacement of the centers of positive charge and of negative charge in the normal structure of the molecule (i.e., the structure of the molecule when no external forces are acting upon it); the induced dipole moment arises from a temporary displacement of these centers of charge from their normal positions. The temporary displacement of these centers of charge is determined by the force exerted by the electric field upon the charges within the molecule and by the ability of the molecule to deform from its normal structure; this ability is called the <u>polarizability</u> of the molecule. A quantitative definition of the dipole moment of a molecule is given in Appendix A, p 30, and a quantitative definition of the polarizability of a molecule is given in Appendix B, p. 38.

The macroscopic electric field, $\vec{E}$, within the gas mixture is, in general, different from the external electric field, $\vec{D}$, to which the gas mixture is subjected, since the dipole moments of the molecules give rise to electric fields. The relationship between these two fields is

$$\vec{D} = \epsilon\vec{E},$$

where ϵ denotes the dielectric constant of the gas mixture. It is shown in (<u>6</u>) that

$$\vec{D} = \vec{E} + 4\pi\vec{P},$$

where $\vec{P}$ denotes the polarization of the gas mixture, which is equal to the average dipole moment per unit volume of the mixture.

The polarization of the gas mixture is related to the local electric field, $\vec{F}$, at a molecule by the equation,

$$\vec{P} = n\chi^{(e)}\vec{F},$$

where n denotes the number of molecules per unit volume and $\chi^{(e)}$ denotes the electric susceptibility per molecule of the gas mixture. Combination of this equation with the above two equations yields

$$(\epsilon-1)\vec{E} = 4\pi n\chi^{(e)}\vec{F},$$

which implies that $\vec{F}$ has the direction of $\vec{E}$. The usual expression for $\vec{F}$ is

$$\vec{F} = \frac{1}{3}(\epsilon+2)\vec{E},$$

as shown in (3) and (6). Thus,

$$\left(\frac{\epsilon-1}{\epsilon+2}\right)V_m = \frac{4\pi N}{3}\chi^{(e)}, \tag{1}$$

where N = Avogadro's number. However, Kirkwood (5) has shown that the above expression for $\vec{F}$ is valid only for very low densities, so that equation 1, which is known as the Clausius-Mosotti equation, is valid only for very low densities. A more general equation,

$$\left(\frac{\epsilon-1}{\epsilon+2}\right)V_m = A(T) + B(T)\cdot\left(\frac{1}{V_m}\right) + C(T)\cdot\left(\frac{1}{V_m}\right)^2 + \cdots, \tag{2}$$

has been proposed (1, 2) to account for the variation of the Clausius-

Mosotti function, $\left(\dfrac{\varepsilon-1}{\varepsilon+2}\right)V_m$, with temperature, T, and molar density, $\dfrac{1}{V_m}$.

The coefficients A(T), B(T), C(T), etc., are the dielectric virial coefficients. Expressions for A(T) and B(T) can be derived by using equation 1 to evaluate the following limits:

$$A = \lim_{V_m \to \infty} \left(\frac{\varepsilon-1}{\varepsilon+2}\right)V_m,$$

and

$$B = \lim_{V_m \to \infty} \left[\left(\frac{\varepsilon-1}{\varepsilon+2}\right)V_m - A\right]V_m.$$

Although equation 1 is valid for very low densities, its use in evaluating the second limit could lead to an erroneous expression for B; for if the difference,

$$\left(\frac{\varepsilon-1}{\varepsilon+2}\right)V_m - \frac{4\pi N}{3}\chi^{(e)},$$

is of the order of $\dfrac{1}{V_m}$, then

$$\lim_{V_m \to \infty} \left[\frac{4\pi N}{3}\chi^{(e)} - A\right]V_m$$

is not the same as the second limit above. Because this difference is not known, equation 1 is used to evaluate the limit and thereby obtain a first approximation to B. Further investigation is needed either to confirm or to refine the expression thus obtained for B.

GENERAL EXPRESSIONS FOR A AND B

Consider an assembly of N molecules in a macroscopic spherical volume, V_m, which is maintained at a constant temperature, T, throughout. The molecules in this assembly possess potential energy due to inter-

molecular forces. If they are subjected to a uniform external electric field, $\vec{D}$, they will also possess potential energy due to the interaction of their dipole moments (induced or permanent) with the electric field. Letting $\vec{\mu}_{ij}$ denote the dipole moment of the jth molecule of species i, the potential energy of this molecule due to the interaction of its dipole moment with the external electric field is given by $-(\vec{\mu}_{ij} \cdot \vec{D})$.[4/] Thus the

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[4/] A discussion of this expression is given in Appendix A, p. 30.

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potential energy of the molecules depends upon their positions and the orientations of their dipole moments. Their positions and orientations can be specified by a single configuration vector, $\vec{\tau}$, which has 5N components (3 for the position of each molecule, and 2 more for its orientation). The total potential energy of the molecules is given by[5/]

[5/] A discussion of this expression is given in Appendix B, p. 38.

$$V(\vec{\tau}) - \sum_i \sum_j (\vec{\mu}_{ij} \cdot \vec{D}).$$

It follows from statistical mechanics ($\underline{4}$) that the probability that the configuration at a given instant will lie in the range $\vec{\tau}$ to $\vec{\tau}+\Delta\vec{\tau}$ is given by

$$\frac{\Delta\vec{\tau} \; \exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{1}{kT}\sum_i\sum_j(\vec{\mu}_{ij}\cdot\vec{D})\right]}{\int \exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{1}{kT}\sum_i\sum_j(\vec{\mu}_{ij}\cdot\vec{D})\right]d\vec{\tau}},$$

where the integration in the denominator is over the entire range of $\vec{\tau}$.

Hence, the average value of $\vec{\mu}_{pq}$ is

$$\overline{(\vec{\mu}_{pq})} = \frac{\int \vec{\mu}_{pq} \exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{1}{kT}\sum_i \sum_j (\vec{\mu}_{ij}\cdot\vec{D})\right]d\vec{\tau}}{\int \exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{1}{kT}\sum_i \sum_j (\vec{\mu}_{ij}\cdot\vec{D})\right]d\vec{\tau}}.$$

Assuming that $\overline{(\vec{\mu}_{pq})}$ has the same direction as $\vec{D}$, then $\overline{(\vec{\mu}_{pq})} = \overline{(\vec{\mu}_{pq}\cdot\hat{e})}\hat{e}$, where $\hat{e}$ denotes a unit vector in the direction of $\vec{D}$. Thus,

$$\overline{(\vec{\mu}_{pq})} = \hat{e}\overline{(\vec{\mu}_{pq}\cdot\hat{e})} = \frac{\hat{e}\int(\vec{\mu}_{pq}\cdot\hat{e})\exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{D}{kT}\sum_i \sum_j(\vec{\mu}_{ij}\cdot\hat{e})\right]d\vec{\tau}}{\int \exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{D}{kT}\sum_i \sum_j(\vec{\mu}_{ij}\cdot\hat{e})\right]d\vec{\tau}}. \quad (3)$$

Since all the molecules of species p are identical, then $\overline{(\vec{\mu}_{pq})} = \overline{(\vec{\mu}_{p1})}$ for $q=1,2,3,\cdots,x_p\cdot N$, where x_p denotes the mole fraction of species p. It now follows from the definitions of $\vec{P}$ and $\chi^{(e)}$ that

$$\vec{P} = \sum_p x_p n \overline{(\vec{\mu}_{p1})},$$

and

$$\chi^{(e)} = \frac{1}{F}\sum_p x_p \overline{(\vec{\mu}_{p1}\cdot\hat{e})}$$

where $\vec{F} = \vec{D}+\vec{E}'$ and $\vec{E}'$ is the component of the average polarizing field due to the electric moments of the molecules. Therefore,

$$\lim_{\substack{D\to 0 \\ V_m\to\infty}} \chi^{(e)} = \lim_{\substack{D\to 0 \\ V_m\to\infty}} \sum_p x_p \frac{\overline{(\vec{\mu}_{p1}\cdot\hat{e})}}{D}\cdot\frac{D}{F}$$

$$= \lim_{V_m\to\infty} \sum_p x_p \frac{\partial}{\partial D}\overline{(\vec{\mu}_{p1}\cdot\hat{e})}\Big|_{D=0},$$

since $\overline{(\vec{\mu}_{p1} \cdot \hat{e})} = 0$ for D=0 and $\lim\limits_{\substack{D \to 0 \\ V_m \to \infty}} \dfrac{D}{F} = 1$. The partial derivative in

this equation can be evaluated using equation 3 as follows.

$$\frac{\partial}{\partial D}\overline{(\vec{\mu}_{p1} \cdot \hat{e})} =$$

$$\frac{\int \left[\frac{\partial}{\partial D}(\vec{\mu}_{p1} \cdot \hat{e}) + (\vec{\mu}_{p1} \cdot \hat{e})\frac{D}{kT}\sum_i\sum_j \frac{\partial}{\partial D}(\vec{\mu}_{ij} \cdot \hat{e}) + \frac{(\vec{\mu}_{p1} \cdot \hat{e})}{kT}\sum_i\sum_j(\vec{\mu}_{ij} \cdot \hat{e}) \right] \cdot \exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{D}{kT}\sum_i\sum_j(\vec{\mu}_{ij} \cdot \hat{e}) \right]d\vec{\tau}}{\int \exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{D}{kT}\sum_i\sum_j(\vec{\mu}_{ij} \cdot \hat{e}) \right]d\vec{\tau}}$$

$$-\frac{\overline{(\vec{\mu}_{p1} \cdot \hat{e})} \cdot \int \left[\frac{D}{kT}\sum_i\sum_j \frac{\partial}{\partial D}(\vec{\mu}_{ij} \cdot \hat{e}) + \frac{1}{kT}\sum_i\sum_j(\vec{\mu}_{ij} \cdot \hat{e}) \right] \cdot \exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{D}{kT}\sum_i\sum_j(\vec{\mu}_{ij} \cdot \hat{e}) \right]d\vec{\tau}}{\int \exp\left[-\frac{V(\vec{\tau})}{kT} + \frac{D}{kT}\sum_i\sum_j(\vec{\mu}_{ij} \cdot \hat{e}) \right]d\vec{\tau}}.$$

Hence,

$$\lim_{\substack{D \to 0 \\ V_m \to \infty}} \chi^{(e)} = \sum_p x_p \lim_{V_m \to \infty} \left[\langle \frac{\partial}{\partial D}(\vec{\mu}_{p1} \cdot \hat{e}) \rangle + \frac{1}{kT}\sum_i\sum_j \langle (\vec{\mu}_{p1} \cdot \hat{e})(\vec{\mu}_{ij} \cdot \hat{e}) \rangle \right], \qquad (4)$$

where

$$\langle f(\vec{\tau}) \rangle = \frac{\int f(\vec{\tau})\exp\left[-\frac{V(\vec{\tau})}{kT} \right]d\vec{\tau}}{\int \exp\left[-\frac{V(\vec{\tau})}{kT} \right]d\vec{\tau}}.$$

The second term on the right side of equation 4 can be simplified by considering the relationship between $(\vec{\mu}_{p1} \cdot \vec{\mu}_{ij})$ and $(\vec{\mu}_{p1} \cdot \hat{e})(\vec{\mu}_{ij} \cdot \hat{e})$ when D=0. Letting $\hat{e}_2$ and $\hat{e}_3$ denote unit vectors which are perpendicular to $\hat{e}$ and to each other, it follows that

$$\vec{\mu}_{ij} = (\vec{\mu}_{ij} \cdot \hat{e})\hat{e} + (\vec{\mu}_{ij} \cdot \hat{e}_2)\hat{e}_2 + (\vec{\mu}_{ij} \cdot \hat{e}_3)\hat{e}_3.$$

Therefore,

$$(\vec{\mu}_{p1} \cdot \vec{\mu}_{ij}) = (\vec{\mu}_{p1} \cdot \hat{e})(\vec{\mu}_{ij} \cdot \hat{e}) + (\vec{\mu}_{p1} \cdot \hat{e}_2)(\vec{\mu}_{ij} \cdot \hat{e}_2) + (\vec{\mu}_{p1} \cdot \hat{e}_3)(\vec{\mu}_{ij} \cdot \hat{e}_3).$$

Since the orientations of $\vec{\mu}_{p1}$ and $\vec{\mu}_{ij}$ are uncorrelated for D=0, unless

i=p and j=1, then

$$\langle (\vec{\mu}_{p1} \cdot \hat{e})(\vec{\mu}_{ij} \cdot \hat{e}) \rangle = \langle (\vec{\mu}_{p1} \cdot \hat{e}) \rangle \cdot \langle (\vec{\mu}_{ij} \cdot \hat{e}) \rangle,$$

unless i=p and j=1. But

$$\langle (\vec{\mu}_{ij} \cdot \hat{e}) \rangle = \langle (\vec{\mu}_{ij} \cdot \hat{e}_2) \rangle = \langle (\vec{\mu}_{ij} \cdot \hat{e}_3) \rangle = 0$$

and

$$\langle (\vec{\mu}_{ij} \cdot \hat{e})^2 \rangle = \langle (\vec{\mu}_{ij} \cdot e_2)^2 \rangle = \langle (\vec{\mu}_{ij} \cdot \hat{e}_3)^2 \rangle$$

because of the random orientation of $\vec{\mu}_{ij}$ for D=0. Hence,

$$\langle (\vec{\mu}_{p1} \cdot \hat{e})(\vec{\mu}_{ij} \cdot \hat{e}) \rangle = 0,$$

unless i=p and j=1, and

$$\langle (\vec{\mu}_{p1} \cdot \vec{\mu}_{p1}) \rangle = 3 \langle (\vec{\mu}_{p1} \cdot \hat{e})^2 \rangle.$$

Thus,

$$A = \frac{4\pi N}{3} \sum_p x_p \lim_{V_m \to \infty} \left[\langle \frac{\partial}{\partial D}(\vec{\mu}_{p1} \cdot \hat{e}) \rangle + \frac{1}{3kT} \langle (\vec{\mu}_{p1} \cdot \vec{\mu}_{p1}) \rangle \right] \qquad (5)$$

and

$$B = \lim_{V_m \to \infty} V_m \cdot \left\{ \frac{4\pi N}{3} \sum_p x_p \left[\langle \frac{\partial}{\partial D}(\vec{\mu}_{p1} \cdot \hat{e}) \rangle + \frac{1}{3kT} \langle (\vec{\mu}_{p1} \cdot \vec{\mu}_{p1}) \rangle \right] - A \right\}. \qquad (6)$$

Equations 5 and 6 provide means for deriving statistical mechanical

expressions for the first two dielectric virial coefficients.

THE FIRST DIELECTRIC VIRIAL COEFFICIENT

An expression for the first dielectric virial coefficient can be obtained by evaluating the limit on the right side of equation 5. For a dilute gas mixture, it is sufficient to consider only binary molecular encounters in deriving an expression for $(\vec{\mu}_{p1} \cdot \hat{e})$. It is shown in Appendix B that for two interacting molecules, neither of which has a permanent dipole moment, the expression for $(\vec{\mu}_{pq} \cdot \hat{e})$ averaged over all possible orientations is given approximately by

$$(\vec{\mu}_{pq} \cdot \hat{e})_{av.} \doteq \alpha_p D\left(1 + \frac{2\alpha_i \alpha_p}{r^6}\right),$$

where α_i denotes the molecular polarizability of species i and r denotes the distance between the two molecules. The term $\dfrac{2\alpha_i \alpha_p^2 D}{r^6}$ represents the component in the direction of $\vec{D}$ of the dipole moment induced in the molecule of species p by the dipole moment of the molecule of species i. Differentiation of the above expression with respect to D yields

$$\frac{\partial}{\partial D}(\vec{\mu}_{pq} \cdot \hat{e})_{av.} \doteq \alpha_p \left(1 + \frac{2\alpha_i \alpha_p}{r^6}\right).$$

Thus the contribution to $\langle \frac{\partial}{\partial D}(\vec{\mu}_{p1} \cdot \hat{e}) \rangle$ due to the induced dipole moments of species i is given by

$$\frac{2x_i N \alpha_i \alpha_p^2 \displaystyle\int_0^{R_m} \frac{\exp\left[-\dfrac{\phi_{pi}(r)}{kT}\right]}{r^6} \cdot 4\pi r^2 dr}{\displaystyle\int_0^{R_m} \exp\left[-\dfrac{\phi_{pi}(r)}{kT}\right] \cdot 4\pi r^2 dr},$$

where R_m denotes the radius of V_m and $\phi_{pi}(r)$ denotes the potential function for the intermolecular forces between molecules of species p and i. Therefore,

$$\langle\frac{\partial}{\partial\mathbf{D}}(\vec{\mu}_{p1}\cdot\hat{e})\rangle \doteq \alpha_p +2N\alpha_p^2 \sum_i \frac{x_i\alpha_i \int_0^{R_m} \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^4}dr}{\int_0^{R_m} \exp\left[-\frac{\phi_{pi}(r)}{kT}\right]r^2dr}. \tag{7}$$

Because $\phi_{pi}\to 0$ as $r\to\infty$, there exists a value, b, of r such that $\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]$ is essentially equal to 1 for $r>b$, so that

$$\int_0^{R_m} \exp\left[-\frac{\phi_{pi}(r)}{kT}\right]r^2dr \doteq \int_0^b \exp\left[-\frac{\phi_{pi}(r)}{kT}\right]r^2dr+\frac{1}{3}(R_m^3-b^3).$$

Hence,

$$\langle\frac{\partial}{\partial\mathbf{D}}(\vec{\mu}_{p1}\cdot\hat{e})\rangle \doteq \alpha_p +2N\alpha_p^2 \sum_i \frac{x_i\alpha_i \int_0^{R_m} \frac{1}{r^4}\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]dr}{\frac{1}{3}(R_m^3-b^3)+ \int_0^b \exp\left[-\frac{\phi_{pi}(r)}{kT}\right]r^2dr}. \tag{8}$$

Thus, if $\int_0^\infty \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^4}dr$ exists, then

$$\lim_{V_m\to\infty} \langle\frac{\partial}{\partial\mathbf{D}}(\vec{\mu}_{p1}\cdot\hat{e})\rangle = \alpha_p^{(0)},$$

where $\alpha_p^{(0)}$ denotes the polarizability of an isolated molecule of species p. Therefore, the contribution to $\langle\frac{\partial}{\partial\mathbf{D}}(\vec{\mu}_{p1}\cdot\hat{e})\rangle$ due to the induced dipole

moments of the other molecules does not affect the above limit. It is reasonable to assume that the limit is the same even if the molecules have permanent dipole moments. It follows from this assumption and equation 5 that

$$A = \frac{4\pi N}{3} \sum_p x_p \left[\alpha_p^{(0)} + \frac{(\mu_p^{(0)})^2}{3kT} \right],$$

(9)

where $\mu_p^{(0)}$ denotes the permanent dipole moment of a molecule of species p.

THE SECOND DIELECTRIC VIRIAL COEFFICIENT FOR MIXTURES OF NON-POLAR GASES

An expression for the second dielectric virial coefficient for a mixture of non-polar gases can be obtained by evaluating the limit on the right side of equation 6. It follows from equations 6 and 9 that

$$B = \lim_{V_m \to \infty} V_m \left\{ \frac{4\pi N}{3} \sum_p x_p \left[\langle \frac{\partial}{\partial D}(\vec{\mu}_{p1} \cdot \hat{e}) \rangle - \alpha_p^{(0)} + \frac{1}{3kT} \langle \vec{\mu}_{p1} \cdot \vec{\mu}_{p1} \rangle \right] \right\},$$

since $\mu_p^{(0)} = 0$ for non-polar gases. Using equation 8 to evaluate $\langle \frac{\partial}{\partial D}(\vec{\mu}_{p1} \cdot \hat{e}) \rangle$ yields

$$B = \lim_{V_m \to \infty} V_m \left\{ \frac{8\pi N^2}{3} \sum_p x_p \alpha_p^2 \sum_i \frac{x_i \alpha_i \int_0^{R_m} \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^4} dr}{\frac{1}{3}(R_m^3 - b^3) + \int_0^b \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] r^2 dr} + \frac{4\pi N}{9kT} \sum_p x_p \langle \vec{\mu}_{p1} \cdot \vec{\mu}_{p1} \rangle \right\}$$

$$= \frac{32\pi^2 N^2}{3} \sum_p \sum_i x_p x_i \alpha_p^2 \alpha_i \int_0^\infty \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^4} dr + \lim_{V_m \to \infty} \frac{4\pi N}{9kT} V_m \sum_p x_p \langle \vec{\mu}_{p1} \cdot \vec{\mu}_{p1} \rangle,$$

(10)

since $V_m = \frac{4\pi}{3}R_m^3$. The limit on the right side of this equation may be different from zero for non-polar gases, even in the absence of an electrical field, because of the dipole moments induced in a molecule by the permanent quadrupole moments of other molecules. Assuming that all the molecules are cylindrically symmetric, then the dipole moment induced in a molecule of species p by the permanent quadrupole moment of a molecule of species i is given by (see Appendix A, p. 30)

$$\vec{\mu}_{pq} = \alpha_p \frac{3\Theta_i}{r^5}\left[\frac{r}{2}(5\cos^2\gamma - 1) - \hat{e}_1 r\cos\gamma\right],$$

where $\vec{r}$ denotes the vector from the molecule of species p to the molecule of species i, $\hat{e}_1$ denotes a unit vector in the direction of the axis of cylindrical symmetry of the molecule of species i, γ is the angle between the vectors $\vec{r}$ and $\hat{e}_1$, and Θ_i is the quadrupole moment of the molecules of species i as defined in Appendix A. Thus,

$$\vec{\mu}_{p1}\cdot\vec{\mu}_{p1} = \frac{9\alpha_p^2\Theta_i^2}{r^{10}}\left[\frac{r^2}{4}(5\cos^2\gamma - 1)^2 - (\vec{r}\cdot\hat{e})(5\cos^2\gamma - 1)r\cos\gamma + r^2\cos^2\gamma\right]$$

$$= \frac{9\alpha_p^2\Theta_i^2}{r^8}\left(\frac{5}{4}\cos^4\gamma - \frac{1}{2}\cos^2\gamma + \frac{1}{4}\right).$$

Therefore, the contribution to $\langle(\vec{\mu}_{p1}\cdot\vec{\mu}_{p1})\rangle$ due to the permanent quadrupole moments of molecules of species i is

$$x_iN\cdot\frac{9\alpha_p^2\Theta_i^2\displaystyle\int_0^{R_m}\int_0^{\pi}\frac{1}{r^8}\left(\frac{5}{4}\cos^4\gamma - \frac{1}{2}\cos^2\gamma + \frac{1}{4}\right)\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]r^2\sin\gamma\,d\gamma\,dr}{\displaystyle\int_0^{R_m}\int_0^{\pi}\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]r^2\sin\gamma\,d\gamma\,dr}.$$

Hence,

$$\langle (\vec{\mu}_{pl} \cdot \vec{\mu}_{pl}) \rangle = 3N\alpha_p^2 \sum_i x_i \Theta_i^2 \frac{\displaystyle\int_0^{R_m} \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^6} dr}{\displaystyle\int_0^{R_m} \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] r^2 dr}.$$

Because $\phi_{pi}(r) \to 0$ as $r \to \infty$, there exists a value, b, or r such that $\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]$ is essentially equal to 1 for $r > b$, so that

$$\int_0^{R_m} \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] r^2 dr \doteq \int_0^b \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] r^2 dr + \frac{1}{3}(R_m^3 - b^3)$$

and, consequently,

$$\langle (\vec{\mu}_{pl} \cdot \vec{\mu}_{pl}) \rangle = 3N\alpha_p^2 \sum_i x_i \Theta_i^2 \frac{\displaystyle\int_0^{R_m} \frac{1}{r^6} \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] dr}{\frac{1}{3}(r_m^3 - b^3) + \displaystyle\int_0^b \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] r^2 dr}.$$

Thus,

$$\lim_{V_m \to \infty} \frac{4\pi N}{9kT} V_m \sum_p x_p \langle (\vec{\mu}_{pl} \cdot \vec{\mu}_{pl}) \rangle = \frac{16\pi^2 N^2}{3kT} \sum_p x_p \left[\alpha_p^{(0)}\right]^2 \sum_i x_i \Theta_i^2 \int_0^\infty \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^6} dr,$$

since $V_m = \frac{4\pi}{3} R_m^3$. It follows from this equation and equation 10 that

$$B = \frac{32\pi^2 N^2}{3} \sum_p \sum_i x_p x_i \left[\alpha_p^{(0)}\right]^2 \alpha_i^{(0)} \int_0^\infty \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^4} dr$$

$$+ \frac{16\pi^2 N^2}{3kT} \sum_p \sum_i x_p x_i \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 \int_0^\infty \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^6} dr.$$

$$B = \frac{32\pi^2 N^2}{3} \sum_p x_p^2 \left[\alpha_p^{(0)}\right]^3 \int_0^\infty \frac{1}{r^4} \exp\left[-\frac{\phi_{pp}(r)}{kT}\right] dr$$

$$+ \frac{16\pi^2 N^2}{3kT} \sum_p x_p^2 \left[\alpha_P^{(0)}\right]^2 \Theta_p^2 \int_0^\infty \frac{1}{r^6} \exp\left[-\frac{\phi_{pp}(r)}{kT}\right] dr$$

$$+ \frac{32\pi^2 N^2}{3} \sum_{p<i} x_p x_i \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)}\right] \int_0^\infty \frac{1}{r^4} \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] dr$$

$$+ \frac{16\pi^2 N^2}{3kT} \sum_{p<i} x_p x_i \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2 \right\} \int_0^\infty \frac{1}{r^6} \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] dr.$$

$$B = \frac{16\pi^2 N^2}{3} \sum_p \sum_i x_p x_i \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)}\right] \int_0^\infty \frac{1}{r^4} \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] dr$$

$$+ \frac{8\pi^2 N^2}{3kT} \sum_p \sum_i x_p x_i \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2 \right\} \int_0^\infty \frac{1}{r^6} \exp\left[-\frac{\phi_{pi}(r)}{kT}\right] dr .$$

Therefore,

$$B = \sum_p \sum_i x_p x_i B_{pi}, \tag{11}$$

where

$$B_{pi} = \frac{16\pi^2 N^2}{3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)}\right] \int_0^\infty \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^4} dr$$

$$+ \frac{8\pi^2 N^2}{3kT} \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2 \right\} \int_0^\infty \frac{\exp\left[-\frac{\phi_{pi}(r)}{kT}\right]}{r^6} dr .$$

The integrals in the above expression cannot be evaluated until the functional form of $\phi_{pi}(r)$ is specified. Several forms have been proposed on the basis of various molecular models; the evaluation of the above expression is performed for some of them in the following sections. The models are considered in order of increasing complexity; generally speaking, the more complicated of these models are the more realistic ones.

THE RIGID ELASTIC SPHERE MODEL

The rigid elastic sphere model considers the molecules as rigid elastic spheres which neither attract nor repel each other. The inter-molecular potential function for this model is

$$\phi_{pi}(r) = \begin{cases} 0, & \text{for } r > \sigma_{pi}, \\ \infty, & \text{for } r < \sigma_{pi}, \end{cases}$$

where $\sigma_{pi} = \frac{1}{2}(\sigma_p + \sigma_i)$, and σ_p and σ_i denote the diameters of the molecules of species p and i. For this model,

$$B_{pi} = \frac{16\pi^2 N^2}{3}\, \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)}\right] \int_{\sigma_{pi}}^{\infty} \frac{dr}{r^4} + \frac{8\pi^2 N^2}{3kT}\left\{\left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2\right\} \int_{\sigma_{pi}}^{\infty} \frac{dr}{r^6}.$$

Therefore,

$$B_{pi} = \frac{16\pi^2 N^2}{9\sigma_{pi}^3}\, \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)}\right] + \frac{8\pi^2 N^2}{15kT\sigma_{pi}^5}\left\{\left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2\right\}. \quad (12)$$

POINT CENTERS OF REPULSION

This model considers the molecules as points which repel each other with a force which is inversely proportional to the distance between them. The intermolecular potential function for this model is

$$\phi_{pi}(r) = \frac{d}{r^\delta}, \quad d > 0, \ \delta > 0.$$

As $\delta \to \infty$, ϕ_{pi} approaches the intermolecular potential function for the rigid elastic sphere model, so that δ is a measure of the "hardness" or "softness" of the molecules. For point centers of repulsion,

$$B_{pi} = \frac{16\pi^2 N^2}{3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)} \right] \int_0^\infty \frac{\exp\left[-\frac{1}{kT}\left(\frac{d}{r}\right)^\delta \right]}{r^4} dr$$

$$+ \frac{8\pi^2 N^2}{3kT} \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2 \right\} \int_0^\infty \frac{\exp\left[-\frac{1}{kT}\left(\frac{d}{r}\right)^\delta \right]}{r^6} dr.$$

Letting $y = \frac{1}{kT}\left(\frac{d}{r}\right)^\delta$, it follows that

$$B_{pi} = \frac{16\pi^2 N^2}{3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)} \right] \int_\infty^0 \frac{\exp(-y)}{\sigma_{pi}^4 \left(\frac{d}{kTy}\right)^{\frac{4}{\delta}}} \left[-\frac{1}{\delta}\left(\frac{d}{kTy}\right)^{\frac{1}{\delta}} \right] \frac{dy}{y}$$

$$+ \frac{8\pi^2 N^2}{3kT} \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2 \right\} \int_\infty^0 \frac{\exp(-y)}{\sigma_{pi}^6 \left(\frac{d}{kTy}\right)^{\frac{6}{\delta}}} \left[-\frac{1}{\delta}\left(\frac{d}{kTy}\right)^{\frac{1}{\delta}} \right] \frac{dy}{y}.$$

Therefore,

$$B_{pi} = \frac{16\pi^2 N^2}{3\delta} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)} \right] \left(\frac{kT}{d}\right)^{\frac{3}{\delta}} \int_0^\infty y^{\frac{3}{\delta}-1} \exp(-y) dy$$

$$+ \frac{8\pi^2 N^2}{3\delta} \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right] \Theta_p^2 \right\} \left(\frac{kT}{d}\right)^{\frac{5}{\delta}} \int_0^\infty y^{\frac{5}{\delta}-1} \exp(-y) dy.$$

Thus,

$$
B_{pi} = \frac{16\pi^2 N^2}{3^\delta} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)} \right] \left(\frac{kT}{d} \right)^{\frac{3}{\delta}} \cdot \Gamma\left(\frac{3}{\delta} \right)
$$

$$
+ \frac{8\pi^2 N^2}{3^\delta} \left\{ \left[\alpha_p^{(0)} \right]^2 \Theta_i^2 + \left[\alpha_i^{(0)} \right]^2 \Theta_p^2 \right\} \left(\frac{kT}{d} \right)^{\frac{5}{\delta}} \cdot \Gamma\left(\frac{5}{\delta} \right), \tag{13}
$$

where $\Gamma(x) = \int_0^\infty y^{x-1} \exp(-y) dy$ is the gamma function.

THE SUTHERLAND MODEL

The Sutherland model considers the molecules as rigid elastic

spheres which attract each other with a force which is inversely pro-

portional to the distance between them. The intermolecular potential

energy function for this model is

$$
\phi_{pi}(r) = \begin{cases} -\epsilon_{pi}\left(\frac{\sigma_{pi}}{r} \right)^\delta, & \text{for } r > \sigma_{pi}, \\ \infty, & \text{for } r < \sigma_{pi}, \end{cases}
$$

where $\epsilon_{pi} > 0$ and $\delta > 0$. As $\delta \to \infty$, this model approaches the rigid elastic

sphere model, but δ is a measure of the "strength" or "weakness" of

the attractive force, rather than the "softness" or "hardness" of the

molecules (c.f., point centers of repulsion). The quantity ϵ_{pi} repre-

sents the maximum energy of attraction and is sometimes called the

"depth of the potential well." For the Sutherland model,

$$B_{pi} = \frac{16\pi^2 N^2}{3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)}\right] \int_{\sigma_{pi}}^{\infty} \frac{\exp\left[\dfrac{\epsilon_{pi}}{kT}\left(\dfrac{\sigma_{pi}}{r}\right)^\delta\right]}{r^4} dr$$

$$+ \frac{8\pi^2 N^2}{3kT} \left\{\left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2\right\} \int_{\sigma_{pi}}^{\infty} \frac{\exp\left[\dfrac{\epsilon_{pi}}{kT}\left(\dfrac{\sigma_{pi}}{r}\right)^\delta\right]}{r^6} dr.$$

Letting $y = \dfrac{\epsilon_{pi}}{kT}\left(\dfrac{\sigma_{pi}}{r}\right)^\delta$, it follows that

$$B_{pi} = \frac{16\pi^2 N^2}{3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)}\right] \int_{\frac{\epsilon_{pi}}{kT}}^{0} y^{\frac{3}{\delta}} \exp(y)\, \sigma_{pi}^{-4} \left(\frac{\epsilon_{pi}}{kT}\right)^{-\frac{4}{\delta}} \left(\frac{-\sigma_{pi}}{\delta}\right) \left(\frac{\epsilon_{pi}}{kT}\right)^{\frac{1}{\delta}} \frac{dy}{d}$$

$$+ \frac{8\pi^2 N^2}{3kT} \left\{\left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2\right\} \int_{\frac{\epsilon_{pi}}{kT}}^{0} y^{\frac{5}{\delta}} \exp(y)\, \sigma_{pi}^{-6} \left(\frac{\epsilon_{pi}}{kT}\right)^{-\frac{6}{\delta}} \left(\frac{-\sigma_{pi}}{\delta}\right) \left(\frac{\epsilon_{pi}}{kT}\right)^{\frac{1}{\delta}} \frac{dy}{d}.$$

Therefore,

$$B_{pi} = \frac{16\pi^2 N^2}{36\sigma_{pi}^3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)}\right] \left(\frac{\epsilon_{pi}}{kT}\right)^{-\frac{3}{\delta}} \int_0^{\frac{\epsilon_{pi}}{kT}} y^{\frac{3}{\delta}-1} \exp(y) \, dy$$

$$+ \frac{8\pi^2 N^2 \left\{\left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2\right\}}{36\sigma_{pi}^5 kT} \left(\frac{\epsilon_{pi}}{kT}\right)^{-\frac{5}{\delta}} \int_0^{\frac{\epsilon_{pi}}{kT}} y^{\frac{5}{\delta}-1} \exp(y) \, dy .$$

The integrals in the above expression can be evaluated by expanding $\exp(y)$

in a power series, with the results that

$$\int_0^{\frac{\epsilon_{pi}}{kT}} y^{\frac{3}{\delta}-1} \exp(y) \, dy = \sum_{n=0}^{\infty} \int_0^{\frac{\epsilon_{pi}}{kT}} y^{\frac{3}{\delta}-1} \cdot \frac{y^n}{n!} \, dy = \sum_{n=0}^{\infty} \frac{\left(\frac{\epsilon_{pi}}{kT}\right)^{\frac{3}{\delta}+n}}{\left(\frac{3}{\delta}+n\right) n!} ,$$

and

$$\int_0^{\frac{\epsilon_{pi}}{kT}} y^{\frac{5}{\delta}-1} \exp(y) \, dy = \sum_{n=0}^{\infty} \int_0^{\frac{\epsilon_{pi}}{kT}} y^{\frac{5}{\delta}-1} \cdot \frac{y^n}{n!} \, dy = \sum_{n=0}^{\infty} \frac{\left(\frac{\epsilon_{pi}}{kT}\right)^{\frac{5}{\delta}+m}}{\left(\frac{5}{\delta}+n\right) n!} .$$

Thus,

$$B_{pi} = \frac{16\pi^2 N^2}{3\delta\sigma_{pi}^3} \alpha_p^{(0)}\alpha_i^{(0)}\left[\alpha_p^{(0)}+\alpha_i^{(0)}\right]\left(\frac{\epsilon_{pi}}{kT}\right)^{-\frac{3}{\delta}} \sum_{n=0}^{\infty} \frac{\left(\frac{\epsilon_{pi}}{kT}\right)^{\frac{3}{\delta}+n}}{\left(\frac{3}{\delta}+n\right)n!}$$

$$+ \frac{18\pi^2 N^2\left\{\left[\alpha_p^{(0)}\right]^2\Theta_i^2+\left[\alpha_i^{(0)}\right]^2\Theta_p^2\right\}}{3\delta\sigma_{pi}^5 kT}\left(\frac{\epsilon_{pi}}{kT}\right)^{-\frac{5}{\delta}} \sum_{n=0}^{\infty} \frac{\left(\frac{\epsilon_{pi}}{kT}\right)^{\frac{5}{\delta}+n}}{\left(\frac{5}{\delta}+n\right)n!} . \qquad (14)$$

THE LENNARD-JONES (12-6) MODEL

The Lennard-Jones model essentially combines the Sutherland model with point centers of repulsion. According to the Lennard-Jones model, the molecules attract each other when the distance between them is larger than their collision diameter, σ_{pi}, and they repel each other when this distance is less than σ_{pi}. The intermolecular potential function for this model is

$$\phi_{pi}(r) = 4\epsilon_{pi}\left[\left(\frac{\sigma_{pi}}{r}\right)^{12}-\left(\frac{\sigma_{pi}}{r}\right)^6\right], \quad \epsilon_{pi}>0. \underline{6/}$$

6/ Exponents other than 12 and 6 can be used with this model, but these are most common.

As in the Sutherland model, ϵ_{pi} represents the maximum energy of attraction; the maximum attraction occurs when $r = \sigma_{pi}\sqrt[6]{2}$. For the Lennard-Jones (12-6) model,

$$B_{pi} = \frac{16\pi^2 N^2}{3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + {}_i^{(0)} \right] \int_0^\infty \frac{\exp\left\{ \frac{-4\epsilon_{pi}}{kT} \left[\left(\frac{\sigma_{pi}}{r}\right)^{12} - \left(\frac{\sigma_{pi}}{r}\right)^6 \right] \right\}}{r^4} dr$$

$$+ \frac{8\pi^2 N^2}{3kT} \left\{ \left[\alpha_p^{(0)} \right]^2 \Theta_i^2 + \left[\alpha_i^{(0)} \right]^2 \Theta_p^2 \right\} \int_0^\infty \frac{\exp\left\{ \frac{-4\epsilon_{pi}}{kT} \left[\left(\frac{\sigma_{pi}}{r}\right)^{12} - \left(\frac{\sigma_{pi}}{r}\right)^6 \right] \right\}}{r^6} dr.$$

Letting $x = \frac{4\epsilon_{pi}}{kT} \left(\frac{\sigma_{pi}}{r}\right)^{12}$, it follows that

$$B_{pi} = \frac{16\pi^2 N^2}{3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)} \right] \int_\infty^0 \frac{\exp\left[-x + 2\left(\frac{\epsilon_{pi}}{kT}\right)^{\frac{1}{2}} x^{\frac{1}{2}} \right]}{\sigma_{pi}^4 \left(\frac{4\epsilon_{pi}}{xkT}\right)^{\frac{1}{12}}} \left(\frac{-\sigma_{pi}}{12}\right) \left(\frac{4\epsilon_{pi}}{xkT}\right)^{\frac{1}{12}} \frac{dx}{x}$$

$$+ \frac{8\pi^2 N^2}{3kT} \left\{ \left[\alpha_p^{(0)} \right]^2 \Theta_i^2 + \left[\alpha_i^{(0)} \right]^2 \Theta_p^2 \right\} \int_\infty^0 \frac{\exp\left[-x + 2\left(\frac{\epsilon_{pi}}{kT}\right)^{\frac{1}{2}} x^{\frac{1}{2}} \right]}{\sigma_{pi}^6 \left(\frac{4\epsilon_{pi}}{xkT}\right)^{\frac{6}{12}}} \left(\frac{-\sigma_{pi}}{12}\right) \left(\frac{4\epsilon_{pi}}{xkT}\right)^{\frac{i}{12}} \frac{dx}{x}.$$

Therefore,

$$B_{pi} = \frac{4\pi^2 N^2}{9\sigma_{pi}^3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)} \right] \left(\frac{4\epsilon_{pi}}{kT} \right)^{-\frac{1}{4}} \int_0^\infty x^{-\frac{3}{4}} \exp\left[-x + 2\left(\frac{\epsilon_{pi}}{kT} \right)^{\frac{1}{2}} x^{\frac{1}{2}} \right] dx$$

$$+ \frac{2\pi^2 N^2}{9kT\sigma_{pi}^5} \left\{ \left[\alpha_p^{(0)} \right]^2 \Theta_i^2 + \left[\alpha_i^{(0)} \right]^2 \Theta_p^2 \right\} \left(\frac{4\epsilon_{pi}}{kT} \right)^{-\frac{1}{12}} \int_0^\infty x^{-\frac{7}{12}} \exp\left[-x + 2\left(\frac{\epsilon_{pi}}{kT} \right)^{\frac{1}{2}} x^{\frac{1}{2}} \right] dx.$$

Letting $y = 2\left(\frac{\epsilon_{pi}}{kT} \right)^{\frac{1}{2}}$, it follows that

$$B_{pi} = \frac{4\pi^2 N^2}{9\sigma_{pi}^3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)} \right] \cdot y^{-\frac{1}{2}} \int_0^\infty x^{-\frac{3}{4}} \exp(-x) \cdot \exp\left(x^{\frac{1}{2}} y \right) dx$$

$$+ \frac{2\pi^2 N^2}{9kT\sigma_{pi}^5} \left\{ \left[\alpha_p^{(0)} \right]^2 \Theta_i^2 + \left[\alpha_i^{(0)} \right]^2 \Theta_p^2 \right\} y^{-\frac{5}{6}} \int_0^\infty x^{-\frac{7}{12}} \exp(-x) \cdot \exp\left(x^{\frac{1}{2}} y \right) dx.$$

The integrals in the above expression can be evaluated by expanding $\exp\left(x^{\frac{1}{2}} y \right)$ in a power series, with the results that

$$\int_0^\infty x^{-\frac{3}{4}} \exp(-x) \cdot \exp\left(x^{\frac{1}{2}}y\right) = \sum_{n=0}^\infty \int_0^\infty x^{-\frac{3}{4}} \frac{\left(x^{\frac{1}{2}}y\right)^n}{n!} \exp(-x) dx$$

$$= \sum_{n=0}^\infty \frac{y^n}{n!} \int_0^\infty x^{\left(\frac{2n-3}{4}\right)} \exp(-x) dx$$

and

$$\int_0^\infty x^{-\frac{7}{12}} \exp(-x) \cdot \exp\left(x^{\frac{1}{2}}y\right) = \sum_{n=0}^\infty x^{-\frac{7}{12}} \frac{\left(x^{\frac{1}{2}}y\right)^n}{n!} \exp(-x) dx$$

$$= \sum_{n=0}^\infty \frac{y^n}{n!} \int_0^\infty x^{\left(\frac{6n-7}{12}\right)} \exp(-x) dx.$$

Hence,

$$B_{pi} = \frac{4\pi^2 N^2}{9\sigma_{pi}^3} \alpha_p^{(0)} \alpha_i^{(0)} \left[\alpha_p^{(0)} + \alpha_i^{(0)}\right] y^{-\frac{1}{2}} \sum_{n=0}^\infty \frac{y^n}{n!} \Gamma\left(\frac{2n+1}{4}\right)$$

$$+ \frac{2\pi^2 N^2}{9kT\sigma_{pi}^5} \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2 \right\} y^{-\frac{5}{6}} \sum_{n=0}^\infty \frac{y^n}{n!} \Gamma\left(\frac{6n+5}{12}\right),$$

where Γ is the gamma function, as before. Since $y = 2\left(\dfrac{\epsilon_{pi}}{kT}\right)^{\frac{1}{2}}$, the second term in this expression can be written as

$$\frac{2\pi^2 N^2 \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2 \right\}}{9\left(\dfrac{4\epsilon_{pi}}{y^2}\right)\sigma_{pi}^5} \; y^{-\frac{5}{6}} \sum_{n=0}^{\infty} \frac{y^n}{n!} \, \Gamma\!\left(\frac{6n+5}{12}\right) =$$

$$\frac{\pi^2 N^2 \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2 \right\}}{18\epsilon_{pi}\sigma_{pi}^5} \; y^{\frac{7}{6}} \sum_{n=0}^{\infty} \frac{y^n}{n!} \, \Gamma\!\left(\frac{6n+5}{12}\right).$$

Thus,

$$B_{pi} = \frac{4\pi^2 N^2}{9\sigma_{pi}^3} \alpha_p^{(0)}\alpha_i^{(0)}\left[\alpha_p^{(0)}+\alpha_i^{(0)}\right] \; y^{-\frac{1}{2}} \sum_{n=0}^{\infty} \frac{y^n}{n!} \, \Gamma\!\left(\frac{2n+1}{4}\right)$$

$$\frac{\pi^2 N^2 \left\{ \left[\alpha_p^{(0)}\right]^2 \Theta_i^2 + \left[\alpha_i^{(0)}\right]^2 \Theta_p^2 \right\}}{18\epsilon_{pi}\sigma_{pi}^5} \; y^{\frac{7}{6}} \sum_{n=0}^{\infty} \frac{y^n}{n!} \, \Gamma\!\left(\frac{6n+5}{12}\right). \qquad (15)$$

SUMMARY

The prediction of the first and second dielectric virial coefficients for gas mixtures from molecular theory requires a knowledge of the following molecular properties: (1) the polarizability, $\alpha_p^{(0)}$, and the permanent dipole and quadrupole moments, $\mu_p^{(0)}$ and Θ_p, of an isolated molecule of

species p of the mixture, and (2) the intermolecular parameters for the

particular model used. The intermolecular parameters and permanent

dipole and quadrupole moments can be determined from experimental PVT

data or transport property data (3,7). Experimental dielectric data

can be used to determine $\alpha_p^{(0)}$ and $\mu_p^{(0)}$ by means of a curve fit of the

form given in equation 9 to a plot of A vs T. Then B can be predicted

by using these values for $\alpha_p^{(0)}$ and the values for Θ_p and the inter-

molecular parameters determined as mentioned above by means of equations

12, 13, 14, or 15. It is also possible to determine the values for Θ_p

and the intermolecular parameters from experimental dielectric data by

means of a curve fit of the form given in equations 12, 13, 14, or 15.

to a plot of B vs T. A Mathatron[7/] program for the prediction of B

[7/] Specific trade names used are given for information only and do

not imply endorsement by the Bureau of Mines.

---

using equation 15 is available at the Helium Research Center, and an

IBM 1620 program for the determination of the values for Θ_p and the

intermolecular parameters by means of a curve fit of the form given in

equation 15 to a plot of B vs T is available at the Helium Activity

Branch of Automatic Data Processing.

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APPENDIX A

A molecule can be considered as an assembly of 2m point charges, m of which have an elementary positive charge, e, and m of which have an elementary negative charge, -e. The positions of the positive charges can be specified by m vectors: $\vec{r}_1$, $\vec{r}_2$, $\vec{r}_3$, $\cdots$, $\vec{r}_m$, and the positions of the negative charges can be specified by m vectors: $\vec{r}_{m+1}$, $\vec{r}_{m+2}$, $\vec{r}_{m+3}$, $\cdots$, $\vec{r}_{2m}$. The center of positive charge is specified by the vector:

$$\vec{r}_+ = \frac{1}{m} \sum_{i=1}^{m} \vec{r}_i,$$

and the center of the negative charge is specified by the vector:

$$\vec{r}_- = \frac{1}{m} \sum_{i=m+1}^{2m} \vec{r}_i.$$

Letting $\vec{\ell} = \vec{r}_+ - \vec{r}_-$, it follows that

$$m e \vec{\ell} = e \left(\sum_{i=1}^{m} \vec{r}_i - \sum_{i=m+1}^{2m} \vec{r}_i \right)$$

$$= \sum_{i=1}^{m} e\vec{r}_i + \sum_{i=m+1}^{2m} (-e)\vec{r}_i$$

$$= \sum_{i=1}^{2m} q_i \cdot \vec{r}_i,$$

where

$$q_i = \begin{cases} e, & \text{if } 1 \leq i \leq m \\ -e, & \text{if } m+1 \leq i \leq 2m. \end{cases}$$

The vector $\vec{\mu} = \sum\limits_{i=1}^{2m} q_i \vec{r}_i$ is called the <u>dipole</u> <u>moment</u> of the molecule;

as shown above, it is equal to the product of the total positive charge

and the vector $\vec{\ell}$, which represents the displacement of the center of

positive charge from the center of negative charge.

The concept of a simple dipole is useful in visualizing the electri-

cal properties of the molecule which arise from the fact that it has a

dipole moment. A simple dipole consists of a positive point charge, q,

and a negative point charge, -q, which are separated by a distance, d,

which is of the order of molecular dimensions. If $q = me$, $d = |\vec{\ell}| = \ell$,

and the charges q and -q are located at the centers of positive charge

and negative charge, then the dipole moment of the simple dipole is

$$q\vec{r}_+ + (-q)\vec{r}_- = me(\vec{r}_+ - \vec{r}_-)$$
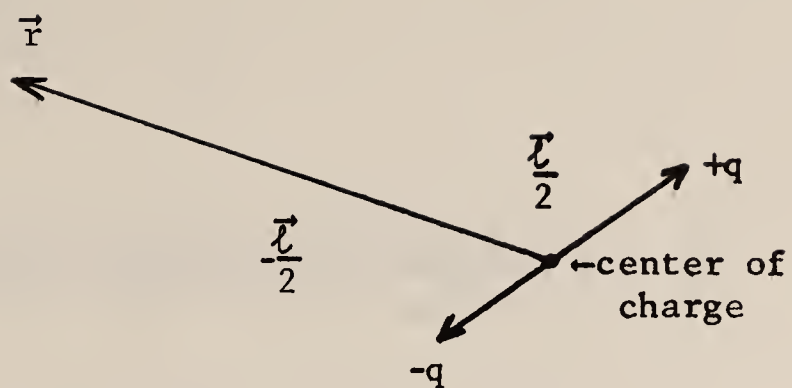
$$= me\vec{\ell}$$

$$= \vec{\mu},$$

so that the dipole moment of the simple dipole is identical to the

dipole moment of the molecule.

The electric field due to a simple dipole can be derived as follows.

$U(\vec{r})$ = electrostatic potential

at $\vec{r}$ due to dipole

$$= \frac{q}{|\vec{r}-\frac{\vec{\ell}}{2}|} - \frac{q}{|\vec{r}+\frac{\vec{\ell}}{2}|}$$

Because

$$\left|\vec{r}-\frac{\vec{\ell}}{2}\right| = \sqrt{\left(\vec{r}-\frac{\vec{\ell}}{2}\right)\cdot\left(\vec{r}-\frac{\vec{\ell}}{2}\right)}$$

$$= \sqrt{r^2+\frac{\ell^2}{4}-(\vec{r}\cdot\vec{\ell})}$$

$$= r\sqrt{1+\frac{\ell^2-4(\vec{r}\cdot\vec{\ell})}{4r^2}}$$

and, similarly,

$$\left|\vec{r}+\frac{\vec{\ell}}{2}\right| = r\sqrt{1+\frac{\ell^2+4(\vec{r}\cdot\vec{\ell})}{4r^2}},$$

then

$$U(\vec{r}) = \frac{q}{r}\left\{\left[1+\frac{\ell^2-4(\vec{r}\cdot\vec{\ell})}{4r^2}\right]^{-\frac{1}{2}}-\left[1+\frac{\ell^2+4(\vec{r}\cdot\vec{\ell})}{4r^2}\right]^{-\frac{1}{2}}\right\}.$$

Expanding the right side of this equation by using the binomial series

yields

$$U(\vec{r}) = \frac{q}{r}\left\{1-\frac{1}{2}\left[\frac{\ell^2-4(\vec{r}\cdot\vec{\ell})}{4r^2}\right]+\frac{3}{8}\left[\frac{\ell^2-4(\vec{r}\cdot\vec{\ell})}{4r^2}\right]^2-\cdots\right.$$

$$\left.-1+\frac{1}{2}\left[\frac{\ell^2+4(\vec{r}\cdot\vec{\ell})}{4r^2}\right]-\frac{3}{8}\left[\frac{\ell^2+4(\vec{r}\cdot\vec{\ell})}{4r^2}\right]^2+\cdots\right\},$$

provided $-1<\dfrac{\ell^2-4(\vec{r}\cdot\vec{\ell})}{4r^2}<1$. Hence, $U(\vec{r}) \doteq \dfrac{(\vec{r}\cdot\vec{\mu})}{r^3}$ for $r \gg \ell$.

The electric field due to the simple dipole is given by the expression,

$$-\text{grad } U(\vec{r}) = -\left(\hat{i}\frac{\partial U}{\partial x}+\hat{j}\frac{\partial U}{\partial y}+\hat{k}\frac{\partial U}{\partial z}\right),$$

where $\hat{i}$ denotes the unit vector from the center of charge in the direction of $\vec{\ell}$, $\hat{j}$ and $\hat{k}$ denote unit vectors which are perpendicular to each other and to $\hat{i}$ at the center of charge, and x, y, and z denote the components of $\vec{r}$ in the directions of $\hat{i}$, $\hat{j}$, and $\hat{k}$. Thus,
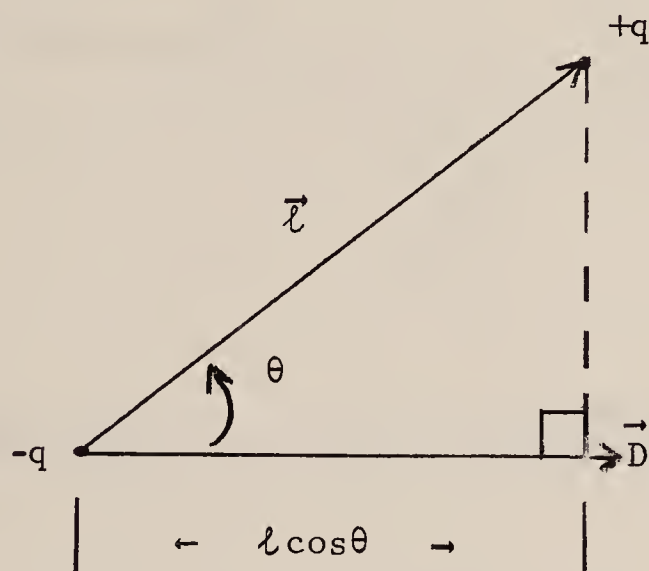
$$-\text{grad } U(\vec{r}) = -\hat{i}\left[\frac{1}{r^3}\frac{\partial(\vec{r}\cdot\vec{\mu})}{\partial x}-\frac{3(\vec{r}\cdot\vec{\mu})}{r^4}\frac{\partial r}{\partial x}\right]-\hat{j}\left[\frac{1}{r^3}\frac{\partial(\vec{r}\cdot\vec{\mu})}{\partial y}-\frac{3(\vec{r}\cdot\vec{\mu})}{r^4}\frac{\partial r}{\partial y}\right]$$

$$-\hat{k}\left[\frac{1}{r^3}\frac{\partial(\vec{r}\cdot\vec{\mu})}{\partial z}-\frac{3(\vec{r}\cdot\vec{\mu})}{r^4}\frac{\partial r}{\partial z}\right]$$

$$= \frac{3(\vec{r}\cdot\vec{\mu})}{r^5}\left(\hat{i}x+\hat{j}y+\hat{k}z\right)-\frac{1}{r^3}\left(\hat{i}\mu_x+\hat{j}\mu_y+\hat{k}\mu_z\right),$$

where μ_x, μ_y, and μ_z denote the components of $\vec{\mu}$ in the directions of $\hat{i}$, $\hat{j}$, and $\hat{k}$. Therefore,

$$-\text{grad } U(\vec{r}) = \frac{3(\vec{r}\cdot\vec{\mu})\vec{r}}{r^5} - \frac{\vec{\mu}}{r^3}.$$

If a simple dipole is subjected to a uniform electric field, $\vec{D}$, then its potential energy becomes a function of its orientation with respect to the field. This can be seen from the following considerations.

$$\text{potential energy} = -\sum \left(\overrightarrow{\text{force}}\right)\cdot\left(\overrightarrow{\text{displacement}}\right)$$

$$= -\left(qD\right)\left(\ell\cos\theta\right)$$

$$= -q\left(\vec{D}\cdot\vec{\ell}\right)$$

$$= -\left(\vec{\mu}\cdot\vec{D}\right).$$

This expression is also valid for the potential energy of the molecule when it is subjected to a uniform electric field.[1]

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[1] Debeye, Polar Molecules, p. 27. Dover Publications, Inc., New York, N. Y., 1929.

The electric field due to the charge distribution of the molecule can be expanded into a series, the first two non-zero terms of which are the contributions to the electric field due to the dipole and quadrupole
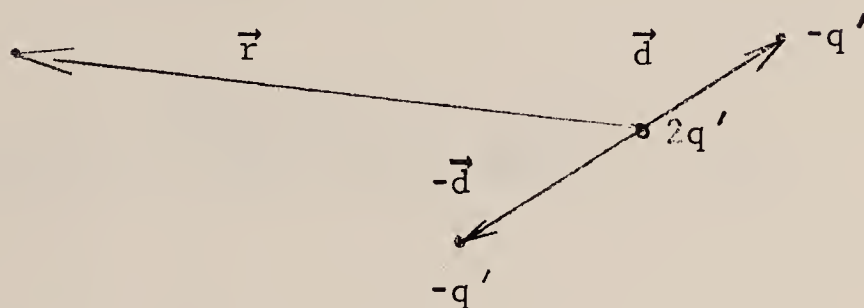
moments of the molecule.[2/] The quadrupole moment of a cylindrically

[2/] Reitz, J. R., and F. J. Milford, Foundations of Electromagnetic

Theory, pp. 39-41. Addison-Wesley Publishing Co., Reading, Mass.,

2nd ed., 1967.

symmetric molecule can be shown to be identical to the quadrupole moment

of a simple quadrupole, which consists of a positive point charge, $2q'$,

and two negative point charges, $-q'$, which lie on a line containing the

positive point charge and are located at equal distances from it, as

shown below

$U(\vec{r})$ = electrostatic potential

at $\vec{r}$ due to quadrupole

$$= \frac{2q'}{|\vec{r}|} - \frac{q'}{|\vec{r} + \vec{d}|} - \frac{q'}{|\vec{r} - \vec{d}|}.$$

Because $|\vec{r}| = \sqrt{\vec{r} \cdot \vec{r}} = r$, $|\vec{r}+\vec{d}| = \sqrt{(\vec{r}+\vec{d}) \cdot (\vec{r}+\vec{d})}$, and $|\vec{r}-\vec{d}| = \sqrt{(\vec{r}-\vec{d}) \cdot (\vec{r}-\vec{d})}$,

then

$$U(r) = \frac{2q'}{r} - \frac{q'}{\sqrt{(\vec{r} \cdot \vec{r}) + 2(\vec{r} \cdot \vec{d}) + (\vec{d} \cdot \vec{d})}} - \frac{q'}{\sqrt{(\vec{r} \cdot \vec{r}) - 2(\vec{r} \cdot \vec{d}) + (\vec{d} \cdot \vec{d})}}$$

$$= \frac{2q'}{r} - \frac{q'}{\sqrt{r^2 + 2xd + d^2}} - \frac{q'}{\sqrt{r^2 - 2xd + d^2}},$$

where $d = /\vec{d}/ = \sqrt{\vec{d}\,\vec{d}}$, and x denotes the component of $\vec{r}$ in the direction

of $\vec{d}$. The second and third terms on the right can be expanded into series

as follows.

$$\frac{q'}{\sqrt{r^2 + 2xd + d^2}} = \frac{q'}{r}\left[1 + \left(\frac{2xd + d^2}{r^2}\right)\right]^{-\frac{1}{2}}$$

$$= \frac{q'}{r}\left[1 - \frac{1}{2}\left(\frac{2xd + d^2}{r^2}\right) + \frac{\left(-\frac{1}{2}\right)\left(-\frac{3}{2}\right)}{2}\left(\frac{2xd + d^2}{r^2}\right)^2 + \cdots\right],$$

provided $-1 < \left(\frac{2xd + d^2}{r^2}\right) < 1.$ Similarly,

$$\frac{q'}{\sqrt{r^2 - 2xd + d^2}} = \frac{q'}{r}\left[1 - \frac{1}{2}\left(\frac{d^2 - 2xd}{r^2}\right) + \frac{\left(-\frac{1}{2}\right)\left(-\frac{3}{2}\right)}{2}\left(\frac{d^2 - 2xd}{r^2}\right)^2 + \cdots\right],$$

provided $-1 < \left(\frac{d^2 - 2xd}{r^2}\right) < 1.$ Hence,

$$U(\vec{r}) = \frac{q'}{r}\left[\frac{d^2}{r^2} - \frac{3}{4}\left(\frac{d^4}{r^4} + \frac{4x^2d^2}{r^4}\right) + \cdots\right]$$

$$= \frac{q'd^2}{r^5}\left(r^2 - 3x^2\right) - \frac{3q'd^4}{4r^5} + \cdots.$$

Thus,

$$U(\vec{r}) \doteq \frac{q'd^2}{r^5}\left(r^2 - 3x^2\right),$$

whenever r >> d. The quadrupole moments of simple quadrupoles and cylindrically symmetric molecules are usually represented by a scalar quantity, Θ, even though the quadrupole moment is itself a second-order tensor. For the simple quadrupole, $\Theta = -2q'd^2$. Therefore,

$$U(\vec{r}) = \frac{-\Theta}{2r^5}\left(3x^2 - r^2\right).$$

The electric field due to the simple quadrupole is given by the expression,

$$-\text{grad } U(\vec{r}) = -\left(\hat{i}\,\frac{\partial U}{\partial x} + \hat{j}\,\frac{\partial U}{\partial y} + \hat{k}\,\frac{\partial U}{\partial z}\right)$$

where $\hat{i}$ denotes the unit vector from the center of charge in the direction of $\vec{d}$, $\hat{j}$ and $\hat{k}$ denote unit vectors which are perpendicular to each other and $\hat{i}$ at the center of the charge, and y and z denote the components of $\vec{r}$ in the directions of $\hat{j}$ and $\hat{k}$. Using the above expression for $U(\vec{r})$,

$$-\text{grad } U(r) = -\frac{\Theta}{2r^5}\left[\hat{i}\left(6x - 2r \cdot \frac{x}{r}\right) - \hat{j}\,2r \cdot \frac{y}{r} - \hat{k} \cdot 2r \cdot \frac{z}{r}\right]$$

$$+ \frac{5\Theta}{2r^6}\left(3x^2 - r^2\right)\left(\hat{i} \cdot \frac{x}{r} + \hat{j} \cdot \frac{y}{r} + \hat{k} \cdot \frac{z}{r}\right)$$

$$= \frac{\Theta}{r^5}\left(\vec{r} - 3\hat{i}x\right) + \frac{5\Theta}{2r^6}\left(3x^2 - r^2\right)\left(\frac{\vec{r}}{r}\right)$$

$$= \frac{\Theta}{r^5}\left[\vec{r}\left(1 + \frac{15x^2}{2r^2} - \frac{5}{2}\right) - 3\hat{i}x\right]$$

$$= \frac{3\Theta}{r^5}\left[\frac{\vec{r}}{2}\left(\frac{5x^2}{r^2} - 1\right) - \hat{i}x\right].$$

For the consideration of contributions to the electric field due to an arbitrary charge distribution in ascending orders of multiple moments, refer to Jackson, J. D., Classical Electrodynamics, Chapter 4, John Wiley & Sons, Inc., New York, 1963.

APPENDIX B

The polarizability, $\alpha_p^{(0)}$, of an isolated molecule of species p is defined by the equation,

$$\vec{\mu}_p' = \alpha^{(0)}\vec{D},$$

where $\vec{\mu}_p'$ denotes the dipole moment induced in the molecule by a uniform weak electric field, $\vec{D}$. The polarizability, α_p, of a molecule of species p in the presence of other molecules is defined by the equation,

$$\vec{\mu}_p' = \alpha_p\vec{F},$$

where $\vec{\mu}_p'$ here denotes the dipole moment induced in the molecule by a weak local electric field, $\vec{F}$, at the molecule. If all the molecules are subjected to a uniform weak electric field, $\vec{D}$, then

$$\vec{F} = \vec{D} + \vec{E}',$$

where $\vec{E}'$ denotes the electric field at the molecule of species p due to the dipole moments of the other molecules. Because $\vec{\mu}_p'$ is a function of the other molecules, which are in turn functions of the total dipole moment, $\vec{\mu}_p$, a complex interaction situation arises.

Consider the interaction of the induced dipoles of two non-polar molecules in the presence of a uniform weak electric field, $\vec{D}$. If the distance between the molecules is large compared to molecular dimensions, then the equations describing the interaction are

$$\vec{\mu}_{pq} = \alpha_p [\vec{D} + \vec{E}'_{ij}]$$

and

$$\vec{\mu}_{ij} = \alpha_i [\vec{D} + \vec{E}'_{pq}],$$

where $\vec{E}'_{ij}$ and $\vec{E}'_{pq}$ denote the electric fields due to the dipole moments of the molecules of species i and p. Using the expression derived in Appendix A for the electric field due to a simple dipole,

$$\vec{\mu}_{pq} = \alpha_p \left[\vec{D} + \frac{3(\vec{r} \cdot \vec{\mu}_{ij})\vec{r}}{r^5} - \frac{\vec{\mu}_{ij}}{r^3} \right].$$

and

$$\vec{\mu}_{ij} = \alpha_i \left[\vec{D} + \frac{3(\vec{r} \cdot \vec{\mu}_{pq})\vec{r}}{r^5} - \frac{\vec{\mu}_{pq}}{r^3} \right],$$

where α_p and α_i denote the molecular polarizabilities for species p and i and $\vec{r}$ denotes the vector from the molecule of species p to the molecule of species i. These equations can be solved for $\vec{\mu}_{pq}$ and $\vec{\mu}_{ij}$ by first solving for $(\vec{r} \cdot \vec{\mu}_{pq})$ and $(\vec{r} \cdot \vec{\mu}_{ij})$ and then substituting these expressions into the equations. It follows from the first equation that

$$\vec{r} \cdot \vec{\mu}_{pq} = \alpha_p \left[(\vec{r} \cdot \vec{D}) + \frac{3(\vec{r} \cdot \vec{\mu}_{ij})(\vec{r} \cdot \vec{r})}{r^5} - \frac{(\vec{r} \cdot \vec{\mu}_{ij})}{r^3} \right]$$

$$= \alpha_p \left[(\vec{r} \cdot \vec{D}) + \frac{2(\vec{r} \cdot \vec{\mu}_{ij})}{r^3} \right].$$

Similarly,

$$(\vec{r} \cdot \vec{\mu}_{ij}) = \alpha_i \left[(\vec{r} \cdot \vec{D}) + \frac{2(\vec{r} \cdot \vec{\mu}_{pq})}{r^3} \right].$$

Solving these two equations for $(\vec{r} \cdot \vec{\mu}_{pq})$ and $(\vec{r} \cdot \vec{\mu}_{ij})$,

$$(\vec{r} \cdot \vec{\mu}_{pq}) = \frac{\alpha_p (\vec{r} \cdot \vec{D}) \left(1 + \dfrac{2\alpha_i}{r^3} \right)}{\left(1 - 4 \dfrac{\alpha_p \alpha_i}{r^6} \right)}$$

and

$$(\vec{r} \cdot \vec{\mu}_{ij}) = \frac{\alpha_i (\vec{r} \cdot \vec{D}) \left(1 + \dfrac{2\alpha_p}{r^3} \right)}{\left(1 - 4 \dfrac{\alpha_p \alpha_i}{r^6} \right)}.$$

Substituting these expressions into the original equations yields:

$$\vec{\mu}_{pq} + \frac{\alpha_p}{r^3} \vec{\mu}_{ij} = \alpha_p \vec{D} + \frac{3\alpha_p \alpha_i (\vec{r} \cdot \vec{D}) \left(1 + \dfrac{2\alpha_p}{r^3} \right) \vec{r}}{r^5 \left(1 - 4 \dfrac{\alpha_p \alpha_i}{r^6} \right)}$$

and

$$\vec{\mu}_{ij} + \frac{\alpha_i}{r^3} \vec{\mu}_{pq} = \alpha_i \vec{D} + \frac{3\alpha_p \alpha_i (\vec{r} \cdot \vec{D}) \left(1 + \dfrac{2\alpha_i}{r^3} \right) \vec{r}}{r^5 \left(1 - 4 \dfrac{\alpha_p \alpha_i}{r^6} \right)}.$$

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Solving these equations for $\vec{\mu}_{pq}$,

$$\vec{\mu}_{pq} = \frac{\alpha_p \vec{D}\left(1 - \frac{\alpha_i}{r^3}\right)}{\left(1 - \frac{\alpha_p \alpha_i}{r^6}\right)} + \frac{3\alpha_p \alpha_i (\vec{r}\cdot\vec{D})\left(1 + \frac{\alpha_p}{r^3} - 2\frac{\alpha_p \alpha_i}{r^6}\right)\vec{r}}{r^5\left(1 - \frac{\alpha_p \alpha_i}{r^6}\right)\left(1 - 4\frac{\alpha_p \alpha_i}{r^6}\right)}.$$

This expression for $\vec{\mu}_{pq}$ has singularities at $r^3 = \sqrt{\alpha_p \alpha_i}$ and at

$r^3 = 2\sqrt{\alpha_p \alpha_i}$. Because $\sqrt{\alpha_p \alpha_i}$ is of the order of the volume occupied

by a molecule,[1] these singularities occur when the distance between the

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[1] See section 5-2 of Reitz and Milford, loc cit.

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molecules is of the order of molecular dimensions; therefore, the singu-

larities can be attributed to the breakdown at these distances of the

expressions for the fields due to the dipole moments of the molecules.

Thus, the singularities are artifical; they can be removed by expanding

the expressions for $\vec{\mu}_{pq}$ into power series $\frac{1}{r}$ and truncating these series

appropriately. Since an average involving $(\vec{\mu}_{pq} \cdot \hat{e})$ is needed rather than

$\vec{\mu}_{pq}$ itself, a simpler procedure is to average $(\vec{\mu}_{pq} \cdot \hat{e})$ over all possible

orientations of the two molecules and then to expand the resulting

expressions into series. Using the above expression for $\vec{\mu}_{pq}$,

$$\left(\vec{\mu}_{pq} \cdot \hat{e}\right) = \frac{\alpha_p D \left(1 - \dfrac{\alpha_i}{r^3}\right)}{\left(1 - \dfrac{\alpha_p \alpha_i}{r^6}\right)} + \frac{3\alpha_p \alpha_i D \left(1 + \dfrac{\alpha_p}{r^3} - 2\dfrac{\alpha_p \alpha_i}{r^3}\right) \cos^2 \beta}{r^3 \left(1 - \dfrac{\alpha_p \alpha_i}{r^6}\right)\left(1 - 4\dfrac{\alpha_p \alpha_i}{r^6}\right)} ,$$

where β denotes the angle between the vectors $\vec{r}$ and $\vec{D}$. Averaging this expression over all possible orientations of r with respect to $\hat{e}$ yields:

$$\left(\vec{\mu}_{pq} \cdot \hat{e}\right)_{av.} = \frac{\alpha_p D \left(1 - \dfrac{\alpha_i}{r^3}\right)}{\left(1 - \dfrac{\alpha_p \alpha_i}{r^6}\right)} + \frac{\alpha_p \alpha_i D \left(1 + \dfrac{\alpha_p}{r^3} - 2\dfrac{\alpha_p \alpha_i}{r^6}\right)}{r^3 \left(1 - \dfrac{\alpha_p \alpha_i}{r^6}\right)\left(1 - 4\dfrac{\alpha_p \alpha_i}{r^6}\right)}$$

$$\left(\vec{\mu}_{pq} \cdot \hat{e}\right)_{av.} = \frac{\alpha_p D}{\left(1 - \dfrac{\alpha_p \alpha_i}{r^6}\right)} \left[1 + \frac{\alpha_p \alpha_i}{r^6} \left(\frac{1 + 2\dfrac{\alpha_i}{r^3}}{1 - 4\dfrac{\alpha_p \alpha_i}{r^6}}\right)\right] .$$

Expanding $\dfrac{1}{\left(1 - \dfrac{\alpha_p \alpha_i}{r^6}\right)}$ and $\left(\dfrac{1 + 2\dfrac{\alpha_i}{r^3}}{1 - 4\dfrac{\alpha_p \alpha_i}{r^3}}\right)$ into power series in $\dfrac{1}{r}$ and

performing the indicated multiplication yields

$$\left(\vec{\mu}_{pq} \cdot \hat{e}\right)_{av.} = \alpha_p D \left(1 + 2\frac{\alpha_p \alpha_i}{r^6} + 2\frac{\alpha_p \alpha_i^2}{r^9} + \cdots\right) .$$

Thus,

$$\left(\vec{\mu}_{pq} \cdot \hat{e}\right)_{av.} \doteq \alpha_p D \left(1 + 2\frac{\alpha_p \alpha_i}{r^6}\right).$$

The term $\dfrac{2\alpha_i\alpha_p^2 D}{r^6}$ represents the component in the direction of $\vec{D}$ of

the dipole moment induced in the molecule of species p by the dipole

moment of the molecule of species i, and it is therefore a dipole-dipole

interaction term. Even when D=0, a similar term can arise.[2] The effect

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[2] See Section 1.3 of Hirschfelder, J. O., C. F. Curtiss, and R. B.

Bird. Molecular Theory of Gases and Liquids. John Wiley & Sons,

Inc., New York, 1954, 1,249 pp.

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of the dipole-dipole interaction term on the potential energy of the two-

molecule configuration when D=0 is included in the intermolecular poten-

tial energy function, $\phi_{pi}(r)$, for the two molecules. The effects of

dipole-dipole interaction terms on the total potential energy of the N-

molecule configuration when D=0 are included in the intermolecular

potential energy function, $V(\vec{T})$, for the configuration $\vec{T}$. If the dipole-

dipole interaction term for D≠0 is neglected, the total potential energy

for the configuration is approximately $V(\vec{T}) - \sum_i \sum_j (\vec{\mu}_{ij} \cdot \vec{D})$, since the

potential energy of interaction of $\vec{\mu}_{ij}$ with $\vec{D}$ is equal to $-(\vec{\mu}_{ij} \cdot \vec{D})$, as

shown in Appendix A. However, if the dipole-dipole interaction term for

D≠0 is included, the expression for the total potential energy is much

more complicated. Perhaps a better approximation to the total potential

energy would be $V(\vec{T}) - \sum_i \sum_j (\vec{\mu}_{ij} \cdot \vec{E})$, since $\vec{E}$ includes the polarization

effects of $\vec{D}$. Although this approximation yields an expression for

$(\vec{\mu}_{pq})$ which is different from the one derived in the text, the resulting

expressions for A and B are the same for both approximations.