# Analysis of the viscosity and second virial coefficients of non-polar polyatomic gases using the m–6–8 potential

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One can use the m–6–8 potential (see equation (1 *b*) for a definition of the potential) to analyse the transport property coefficients of non-polar polyatomic gases to within experimental error over a wide temperature range, without having specifically to include nonspherical intermolecular interactions. As an example, we
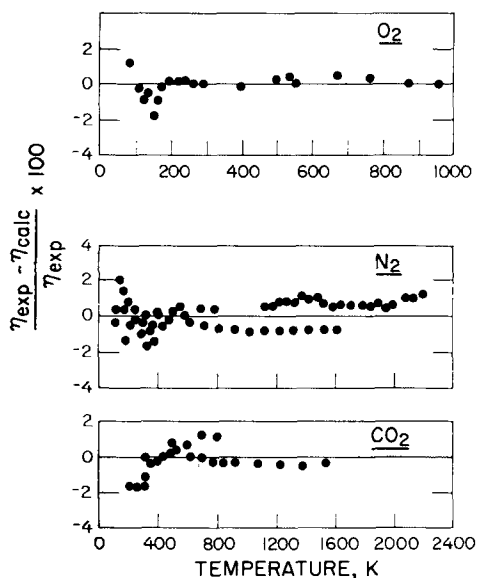


Figure 1. Viscosity coefficients for oxygen, nitrogen and carbon dioxide calculated via the spherical m–6–8 potential and compared with experiment.

show in figure 1 the deviations between theory and experiment for the viscosity coefficient $\eta$ of three quadrupolar gases : oxygen, nitrogen and carbon dioxide. The theoretical values were obtained from the kinetic theory expression [1] with the m–6–8 potential parameters, $m$, $\sigma$, $\gamma$, and $\epsilon/k$, in the table. The experimental values are discussed in detail in [2]. Figure 2 shows as dashed curves deviation plots for the spherical second virial coefficients $B$, which display systematic differences between theory and experiment. The experimental values were taken from [3].

| Gas | $m$ | $\gamma$ | $\epsilon/k$, K | $\sigma$, Å† | $10^{26}\Theta$, e.s.u. | $10^{24}\bar{\alpha}$, cm³ | $10^{24}(\alpha_\| - \alpha_\perp)$, cm³‡ |
|-----|-----|-----|-----|-----|-----|-----|-----|
| O₂ | 10 | 1·0 | 109·5 | 3·45 | $-0·4 \pm 0·1$ [12] | 1·568 [13] | 1·099 [15] |
| N₂ | 12 | 2·0 | 118·0 | 3·54 | $-1·4 \pm 0·1$ [12] | 1·730 [14] | 0·696 [15] |
| CO₂ | 14 | 1·0 | 282·0 | 3·68 | $-4·3 \pm 0·2$ [12] | 2·925 [14] | 2·100 [15] |

† $\text{Å} = 10^{-10}$ m.

‡ The polarizability anisotropy $\kappa$ is defined as $\kappa = (\alpha_\| - \alpha_\perp)/3\bar{\alpha}$.

The numbers in brackets refer to the literature references from which the experimental values were taken.



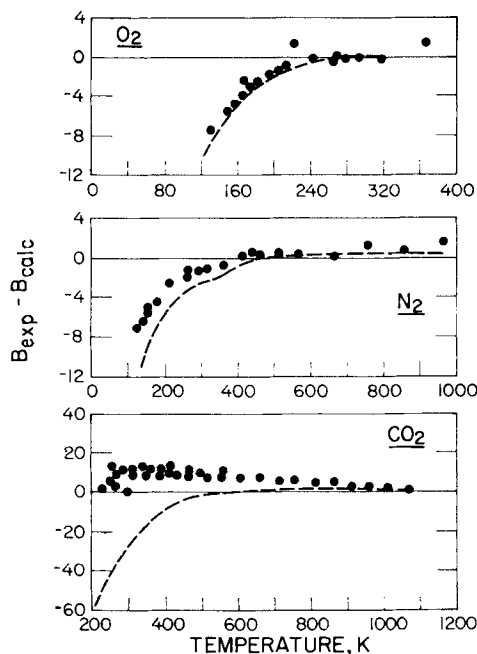Figure 2.  Comparison of experimental and calculated second virial coefficients (cm³/mole) for oxygen, nitrogen and carbon dioxide.  Dashed curves indicate deviations using the $m$-6-8 potentials as defined in equation (1 $b$) ; the points indicate the deviations using the $m$-6-8 potential with nonspherical modifications as defined in equation (1 $a$). Note the changes of scale and that the data for oxygen, both for the second virial and viscosity coefficients, are not as reliable as the corresponding data for the other two gases.

The results shown in figures 1 and 2 are consistent with the assumption made by previous authors [4-7] that the nonspherical interactions are more evident in the determination of the second virial coefficient than the viscosity coefficient.  Accordingly, we have recalculated the second virial coefficients for these three gases by modifying the $m$-6-8 potential.

A general potential for polarizable, quadrupolar molecules can be written in the form :

$$\phi = \phi(\text{spherical}) + \phi(\text{quadrupole–quadrupole}) + \phi(\text{quadrupole-induced dipole})$$
$$+ \phi(\text{shape}) + \phi(\text{anisotropy}).$$

The first term represents the spherical potential ($\phi_{m-6-8}$ in our case), the second and third terms represent the electrostatic interactions of the permanent and induced multipole moments, while the last two terms represent the anisotropy in the repulsive and dispersive forces, respectively. Here, however, we have chosen to neglect these latter two contributions. This is not an unreasonable choice for several reasons : (1) At the present time, it is impossible to determine independently the shape parameters ; (2) The anisotropy contributions have not been worked out in enough detail to be applied to the $m$–6–8 potential ; and (3) The spherical potential does reasonably well and hopefully, therefore, incorporates part of these corrections into the spherical parameters, especially that of the shape. Hence we can calculate the second virial coefficient using independently measured values of the quadrupole moment $\Theta$, mean molecular polarizability $\bar{\alpha}$, and polarizability anisotropy $\kappa$, without resorting to additional parameterization (i.e. a shape factor).

We have then for the modified $m$–6–8 potential :

$$\phi(r_{12}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) = \phi_{m-6-8}(r_{12}) + \phi_{q-i}(r_{12}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) + \phi_{q-q}(r_{12}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2), \qquad (1\,a)$$

where

$$\phi_{m-6-8}(r_{12}) = \epsilon \left[ \frac{6+2\gamma}{m-6} \left(\frac{r_m}{r_{12}}\right)^m - \frac{m-\gamma(m-8)}{m-6} \left(\frac{r_m}{r_{12}}\right)^6 - \gamma\left(\frac{r_m}{r_{12}}\right)^8 \right] \qquad (1\,b)$$

and

$$\phi_{q-q}(r_{12}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) = \mathbf{Q} : \mathbf{V} : \mathbf{Q}, \qquad (2\,a)$$

$$\phi_{q-i}(r_{12}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2) = -\tfrac{1}{2}\mathbf{U} : \mathbf{Q} \cdot (1 - \boldsymbol{\alpha} \cdot \mathbf{T})^{-1} \cdot \boldsymbol{\alpha} \cdot \mathbf{U} : \mathbf{Q}. \qquad (2\,b)$$

In these equations, $\phi_{m-6-8}(r_m) = -\epsilon$, $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$ denote the angles describing the orientations of the molecules and $\mathbf{T}$, $\mathbf{U}$, $\mathbf{V}$ are the two-dimensional matrices [11, 16] describing the dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interaction tensors whose cartesian components are

$$T_{\alpha\beta}(r_{12}) = \nabla_\alpha \nabla_\beta (1/r_{12}),$$

$$U_{\alpha\beta\gamma}(r_{12}) = \nabla_\alpha \nabla_\beta \nabla_\gamma (1/r_{12})$$

and

$$V_{\alpha\beta\gamma\delta}(r_{12}) = \nabla_\alpha \nabla_\beta \nabla_\gamma \nabla_\delta (1/r_{12}).$$

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

$$\alpha_{\beta\gamma} = \bar{\alpha}[(1-\kappa)\delta_{\beta\gamma} + 3\kappa\hat{q}_\beta\hat{q}_\gamma]$$

$$Q_{\alpha\beta} = \hat{q}_\alpha\hat{q}_\beta\Theta,$$

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

The expressions for the various contributions to the reduced virial coefficient, $B^*(T^*) = B(kT/\epsilon)/(2\pi\sigma^3 N/3)$, where $N$ is Avogadro's number and $\phi_{m-6-8}(\sigma) = 0$,

were found by using the standard technique [8–11] of expanding the nonspherical portion of the Boltzmann factor and performing the angular integrations analytically. Including terms up to third order in the expansion parameters $\Theta^{*2} = \Theta^2/(\epsilon\sigma^5)$ and $\bar{\alpha}^* = \bar{\alpha}/\sigma^3$, we find

$$B^*(T^*) = B^*_{m-6-8}(T^*) - \frac{21}{5}\frac{\Theta^{*4}}{T^{*2}} I_{10} + \frac{216}{245}\frac{\Theta^{*6}}{T^{*3}} I_{15} - \frac{9\bar{\alpha}^*\Theta^{*2}}{T^*} I_8$$

$$+ \frac{108}{25}\frac{\alpha^{*2}\Theta^{*2}}{T^*} \kappa^2 I_{11} + \frac{216}{35}\frac{\bar{\alpha}\kappa\Theta^{*4}}{T^{*2}} I_{13},$$

where $I_n$ are dimensionless integrals defined by

$$I_n = \int_0^\infty x^{-n+2} \exp\left[-\phi^*_{m-6-8}(x)/T^*\right] dx,$$

where $x = r_{12}/\sigma$ and $\phi^*_{m-6-8}(x) = \phi_{m-6-8}/\epsilon$. These integrals were calculated as a function of the reduced temperature $T^* = kT/\epsilon$ by means of a Gauss–Legendre integration scheme. The deviation curves thus obtained are shown as the solid points in figure 2.

In summary, the spherically symmetric $m$–6–8 potential function has been used to analyse the dilute gas viscosity and second virial coefficient data for $O_2$, $N_2$ and $CO_2$. Agreement between theory and experiment was found to be satisfactory for the viscosity, but as anticipated, modifications are required for the second virial coefficient. Therefore we recalculated the second virials by including terms for the quadrupole–quadrupole and quadrupole–induced dipole interactions in the intermolecular potential. The agreement with experiment was improved, the improvement for oxygen being less obvious than for nitrogen or carbon dioxide. The oxygen viscosity data are not as accurate as that for $N_2$ and $CO_2$, so the spherical part of the potential may not be as satisfactory for $O_2$. We note that, unlike most previous work, $\Theta$ was not treated as an adjustable parameter nor were extra parameters, such as a shape factor, introduced. We are re-evaluating the effect of the electrostatic interactions on the collision integrals which enter into the kinetic theory expression for the viscosity coefficient. It is possible that a recalculation of the $m$–6–8 parameters will further diminish the systematic differences between theory and experiment which are still observed in figure 2.

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