Effective potential and the viscosity of complex polar fluids

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Abstract. The effective potential is used to calculate the viscosity of complex polar vapours like water and ammonia. The agreement between theory and experiment confirms the validity of the effective potential.

Keywords. Lennard-Jones potential; effective potential; viscosity; collision integral; water vapour.

1. Introduction

Considerable success has been attained in calculating the transport properties of many dilute gases whose molecular interactions may be described by spherically symmetric potential function. Similar calculations for systems which require angular-dependent potential have been more limited, probably because of the difficulty in evaluating the necessary collision integrals $\Omega^{(l, s)*}$. However,t his difficulty was removed with the introduction of an effective potential which permits use of existing tabulations of the collision integrals (Hirschfelder *et al* 1964) for systems with isotropic potential by eliminating the need for a separate calculation of the contribution from the angular-dependent part of the potential.

The orientation-dependent potential used in this paper includes the dipole-quadrupole interaction term in addition to the dipole-dipole interaction.

$$\phi(r, \omega) = \phi_{\text{L-J}} - \frac{\mu^2}{r^3} g_{11}(\omega) + \frac{3\mu Q}{4r^4} g_{12}(\omega), \tag{1}$$

where $\phi_{\text{L-J}}(r)$ is the well-known Lennard-Jones potential (Lennard-Jones 1924), and

$$g_{11}(\omega) = 2 \cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi, \tag{2}$$

$$g_{12}(\omega) = \cos\theta_1 (3 \cos^2\theta_2 - 1) - 2 \sin\theta_1 \sin\theta_2 \cos\theta_2 \cos\phi. \tag{3}$$

Further, μ and Q are the electric dipole and quadrupole moments of the molecules, θ_1 and θ_2 the angles between the axes of the molecular dipoles and the line joining the molecular centres of the two molecules respectively, ϕ the azimuthal angle in the plane perpendicular to this line, and ω is a function of the angular coordinates.

In the present paper, we use the Rowlinson potential given in (1) to obtain an effective temperature-dependent potential. The effective potential is expressed in the L-J format with temperature-dependent parameters. This is applied to calculate the viscosity of the complex polar vapours, water and ammonia. The agreement between theoretical and experimental values confirms the validity of the effective potential.

2. Effective potential

Singh and Joshi (1980) and Pathak *et al* (1981) take the effective potential as the free-energy average, over the angular variables, of the anisotropic pair potential $\phi(r, \omega)$, which is given by

$$\ll \phi\,(r, T) \gg \;=\phi_{\text{L-J}}\,(r) - \frac{\mu^4}{3r^6kT} - \frac{\mu^2Q^2}{8r^8kT} + \frac{7\mu^8}{450\ r^{12}k^3T^3}, \tag{4}$$

where T is the temperature and k the Boltzmann constant. This hypothesis obviates the consideration at a given temperature of a multiplicity of potential energy curves by replacing the multiplicity with the one free-energy average curve. The averaging process gives a different potential energy curve at each temperature. Moreover, the functional form of $\ll \phi \gg$ evolves into that of the Lennard-Jones potential with temperature-dependent parameters.

We define a reduced dipole moment δ_{max}, a reduced dipole-quadrupole moment α_{max} and a reduced temperature T^* by the following equations:

$$\delta_{\text{max}} = \mu^2/2\epsilon_0\sigma_0^3, \tag{5a}$$

$$\alpha_{\text{max}} = \mu Q/2\epsilon_0\sigma_0^4, \tag{5b}$$

$$T^* = kT/\epsilon_0. \tag{5c}$$

As has been done by Singh and Joshi (1980) and Pathak *et al* (1981) (4) can be written as

$$\ll \phi\,(r, T) \gg \;= 4\epsilon_0 \left[(\sigma_0/r)^{12}\,(1 + 14\,\delta^4_{\text{max}}/225\ T^{*3}) \right.$$

$$\left. - (\sigma_0/r)^6\,\left\{ 1 + \frac{\delta^2_{\text{max}}}{3T^*} + \frac{\alpha^2_{\text{max}}}{10T^*} \right\} \right]. \tag{6}$$

This allows us to express (6) as a temperature-dependent effective potential in the L-J format

$$\phi_{\text{eff}} = 4\epsilon_T\,[(\sigma_T/r)^{12} - (\sigma_T/r)^6], \tag{7}$$

where ϵ_T and σ_T are temperature-dependent parameters given by

$$\epsilon_T = \epsilon_0 \left(1 + \frac{14\delta_{max}^4}{225T^{*3}}\right)^{-1} \left(1 + \frac{\delta_{max}^2}{3T^*} + \frac{\alpha^2 max}{10T^*}\right), \tag{8}$$

$$\sigma_T = \sigma_0 \, (\epsilon_0/\epsilon_T)^{1/12} \left(1 + \frac{14\delta_{max}^4}{225T^{*3}}\right)^{1/12}. \tag{9}$$

Such a formal introduction of temperature in the potential is quite logical because it involves a regular variation of the characteristic parameters of the L-J potential. The numerical values used, to get ϵ_T and σ_T are as given below:

For water vapour:

$$(\epsilon_0/k)_{H_2O} = 356 \text{ K}, \quad (\sigma_0)_{H_2O} = 2 \cdot 725 \text{ Å},$$

$$\mu_{H_2O} = 1 \cdot 85 \times 10^{-18} \text{ esu}, \quad Q_{H_2O} = 0 \cdot 45 \times 10^{-26} \text{ esu}$$

For ammonia vapour:

$$(\epsilon_0/k)_{NH_3} = 340 \text{ K}, \quad (\sigma_0)_{NH_3} = 3 \cdot 13 \text{ Å},$$

$$\mu_{NH_3} = 1 \cdot 47 \times 10^{-18} \text{ esu and } Q_{NH_3} = -2 \cdot 32 \times 10^{-26} \text{ esu}.$$

3. Viscosity

The Chapman-Enskog solution of the Boltzmann equation provides one with a formally complete solution of the problem of describing the transport properties of dilute gases. In particular, one obtains expressions which relate the transport coefficients appearing in the experimental phenomenological flow equations to the intermolecular potential function. The expression for viscosity in g/cm/sec for complex polar fluids according to Chapman-Enskog (1952), is given by

$$\eta \times 10^7 = 266 \cdot 93 \, (MT)^{1/2} / \sigma_T^2 \, \Omega^{(2,2)*} \, (T_d^*), \tag{10}$$

where M is the molecular mass in atomic mass units and T is the absolute temperature σ_T, the collision diameter of a molecule of the gas, is also the temperature-dependent parameter of the effective pair potential given by (7), and $\Omega^{(2,2)*}$ is the appropriate collision integral which is a function of the reduced temperature T_d^* which is defined as $T_d^* = kT/\epsilon_T$. The temperature-dependent parameters, calculated from (8) and (9) have been used to calculate the viscosity of ammonia and water vapours. The calculated values of viscosity are found to be in very good agreement with the experimental values as shown in figure 1.

4. Conclusion

The effective potential obtained by taking the free-energy average of the Rowlinson potential is a reliable one for correlating the viscosity of complex polar gases using
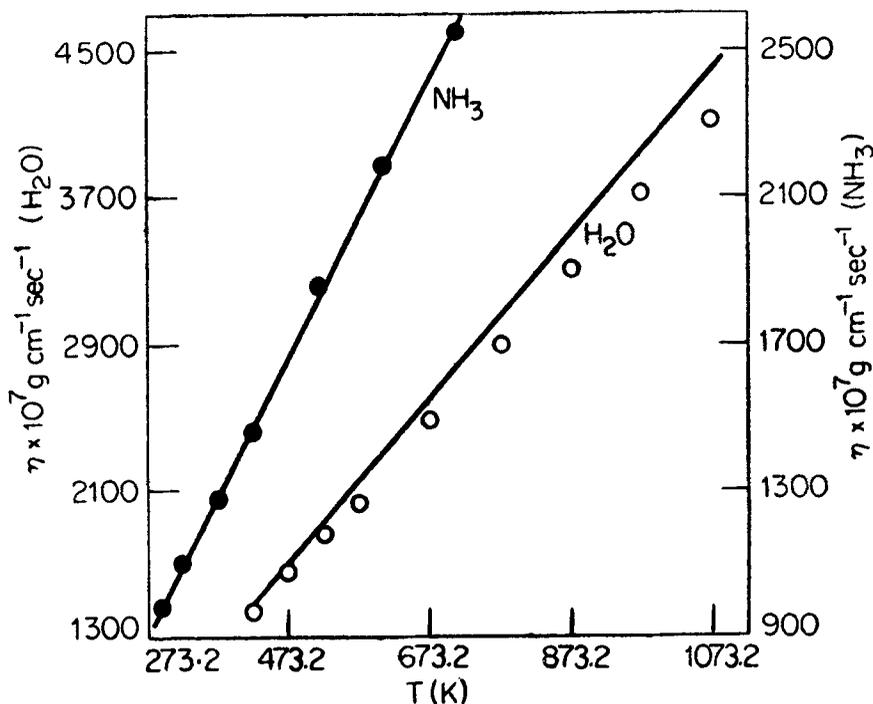
Figure 1. Temperature dependence of coefficient of viscosity of ammonia and water vapour. ● and ○ are experimental points for NH_3 and H_2O respectively; ———— calculated.

temperature-dependent parameters and the tables of reduced collision integrals for the 12-6 Lennard-Jones potential.

It should be borne in mind that (4) is essentially a high temperature approximation. It is also seen that with $a_{max} = 0$, these relations agree with those obtained by Danon and Amdur (1969) from the Stockmayer (1941) potential.

Acknowledgement

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