

Effective potential for ammonia vapour

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Abstract. The modified free-energy averaged potential for water vapour is extended to NH_3 vapour. The resulting temperature-dependent parameters are used to compute the second virial coefficient of NH_3 vapour which agrees with experimental results particularly at higher temperatures.

Keywords. Lennard-Jones potential; effective potential; second virial coefficient; ammonia vapour.

1. Introduction

While there have been many pair-potential energy models for spherical non-polar molecules, the angle-dependent 12-6-3 potential (Stockmayer 1941) is the only one that has been used extensively for the interaction of a pair of polar molecules. Rowlinson (1949) demonstrated the successful correlation of second virial coefficients of polar gases with the potential. Saxena and Joshi (1962) extended the model by using 18-6-3 and 28-7-3 powers on the reciprocal of the intermolecular separation. O'Connell and Prausnitz (1964) modified the Stockmayer potential by introducing the Kihara hard core model for the non-polar part of the interaction in place of the Lennard-Jones model. The 12-6-3 Stockmayer potential has been applied to the correlation of transport properties of dilute gases (Monchick and Mason 1961; Mason and Monchick 1962). Each of these models requires its own table of reduced integrals for calculating the physical properties.

Bae and Reed (1967) have taken a different approach. They assumed that during a single binary collision the relative orientation of the two molecules changes so rapidly that the collision could be described by an effective pair potential obtained by a particular method of averaging over all orientations. In the procedure of Monchick and Mason, at a given temperature there is a multiplicity of potential-energy curves, one for each orientation. In the procedure of Bae and Reed there is only one potential curve at each temperature, but as the temperature changes the averaging process leads to different curves.

Considerable success has been achieved in the calculation of transport properties of many dilute gases whose molecular interactions may be described by spherically symmetric potential functions. Similar calculations for systems which require angle-dependent potential functions have been more limited, probably because of the difficulty of evaluating properly the necessary collision integrals $\Omega^{(l,s)*}$. However,

this difficulty was removed with the introduction of an averaged potential which permits use of existing tables of the collision integrals $\Omega^{(l,s)*}$ for systems with isotropic potential by eliminating the need for a separate calculation of the contribution from the angle-dependent part of the potential.

The introduction of the averaged potential also permits the use of the familiar expression of the second virial coefficient $B(T)$ for systems with isotropic potential by eliminating the need for a separate derivation of the expression of $B(T)$ for the angle-dependent potentials.

2. Effective potential

Singh and Joshi (1980) have recently obtained the effective potential as the free-energy average of the Rowlinson (1951) potential, which is given by

$$\begin{aligned} \ll \phi(r, T) \gg = & 4\epsilon_0 \left[(\sigma_0/r)^{12} (1 + 14 \delta_{\max}^4 / 225T^{*3}) \right. \\ & \left. - (\sigma_0/r)^6 \left\{ 1 + \frac{\delta_{\max}^2}{3T^*} + \frac{\alpha_{\max}^2}{8T^*} \left(\frac{\sigma_0}{r} \right)^2 \right\} \right], \end{aligned} \quad (1)$$

$$\text{where } \delta_{\max} = \mu^2 / 2\epsilon_0 \sigma_0^3, \quad (2)$$

$$\alpha_{\max} = \mu Q / 2\epsilon_0 \sigma_0^4, \quad (3)$$

$$\text{and } T^* = kT / \epsilon_0. \quad (4)$$

In the above equations, r is the intermolecular separation, σ_0 is the value of r for which the Lennard-Jones (L-J) (12:6) potential $\phi(r) = 0$, ϵ_0 is the maximum energy of attraction (or depth of the potential well) which occurs at $r_0 = 2^{1/6} \sigma_0$, T is the temperature, k the Boltzmann constant, μ is the dipole moment and Q is the quadrupole moment. This is an effective potential which could now be used to calculate the equilibrium and non-equilibrium properties of complex polar fluids. However, it is not very convenient as it contains three inverse powers of r and has lost the simplicity of the L-J potential. This is not a very satisfactory feature. The wide applicability of the L-J potential results from the fact that several equilibrium and non-equilibrium properties of a gas can be easily expressed in terms of the two force parameters. Therefore, to achieve simplicity and elegance at the cost of rigour, we replace r^8 in the dipole-quadrupole term in (1) (containing α_{\max}^2) by $r^6 r_0^2$. Although the only justification of this replacement is the utility and convenience of the resulting expression, it is found that these far outweigh the error caused by the approximation. We have verified that the numerical error due to this approximation is negligibly small over a wide range of r (up to 10 Å) and over the temperature range of interest. Moreover the error decreases with increasing temperature.

This allows us to write (1) as a temperature-dependent effective potential in the L-J format

$$\phi_{\text{eff}}(r, T) = 4\epsilon_T [(\sigma_T/r)^{12} - (\sigma_T/r)^6], \quad (5)$$

where ϵ_T and σ_T are temperature-dependent parameters given by

$$\epsilon_T = \epsilon_0 \left(1 + \frac{14\delta_{\max}^4}{225T^{*3}} \right)^{-1} \left(1 + \frac{\delta_{\max}^2}{3T^*} + \frac{\alpha_{\max}^2}{10T^*} \right)^2, \quad (6)$$

$$\sigma_T = \sigma_0 (\epsilon_0/\epsilon_T)^{1/12} \left(1 + \frac{14\delta_{\max}^4}{225T^{*3}} \right)^{1/12}. \quad (7)$$

Singh and Joshi (1980) have successfully correlated the second virial coefficient of water vapour with this potential at higher temperatures.

3. The second virial coefficient

As an extension of the effective potential (Singh and Joshi 1980), we calculate the second virial coefficient of ammonia vapour. A simple expression for the second virial coefficient has been given by Kihara (1978, equation (6.5)), which can be written as

$$B(T) = -\frac{\pi\sqrt{2}\sigma^3}{6} \sum_{n=0}^{\infty} \frac{2^n}{n!} \Gamma\left(\frac{2n-1}{4}\right) (\epsilon/kT)^{(2n+1)/4}, \quad (8)$$

where ϵ and σ are the parameters of the L-J potential and $\Gamma(x)$ is the gamma function. Let us define $B_0(T)$ to be given by (8) with ϵ and σ replaced by ϵ_0 and σ_0 respectively, and $B_{\text{eff}}(T)$ to be given by (8) with ϵ and σ replaced by ϵ_T and σ_T respectively.

Since the coefficient of viscosity is not particularly sensitive to long range forces (Danon and Amdur 1969) such as those associated with permanent dipole-dipole and dipole-quadrupole interactions, we might expect that the present values of σ_0 and ϵ_0 would not be very much different from those obtained by omitting the dipole-quadrupole term. Therefore we take the numerical values for ammonia vapour from Danon and Amdur (1969), which are $\epsilon_0/k = 340$ K, $\sigma_0 = 3.13$ Å, $\mu = 1.47 \times 10^{-18}$ esu, $Q = -2.32 \times 10^{-26}$ esu. Then the values of ϵ_T and σ_T calculated from (6) and (7) are shown in figure 1 for the temperature range 200 K to 550 K. The variation of $B_0(T)$ and $B_{\text{eff}}(T)$ with temperature along with experimental values is shown in figure 2.

4. Results and discussion

It is evident from figure 2 that while $B_0(T)$ lies much lower, $B_{\text{eff}}(T)$ compares well with the experimental results. Also while there is a good agreement between experimental and calculated results at higher temperatures, there is a large discrepancy at lower temperatures suggesting that the interaction potential for molecules which

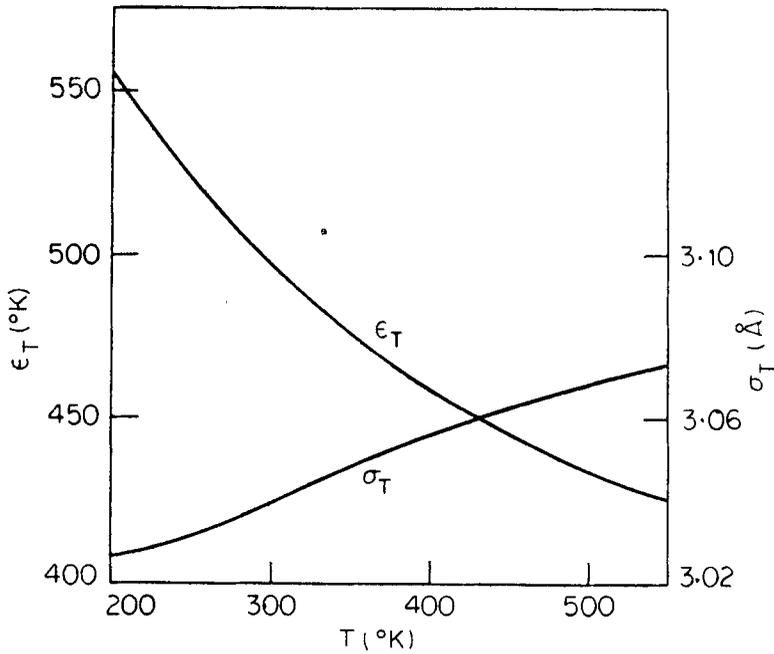


Figure 1. Temperature variation of the characteristic parameters of the effective potential for NH_3 vapour.

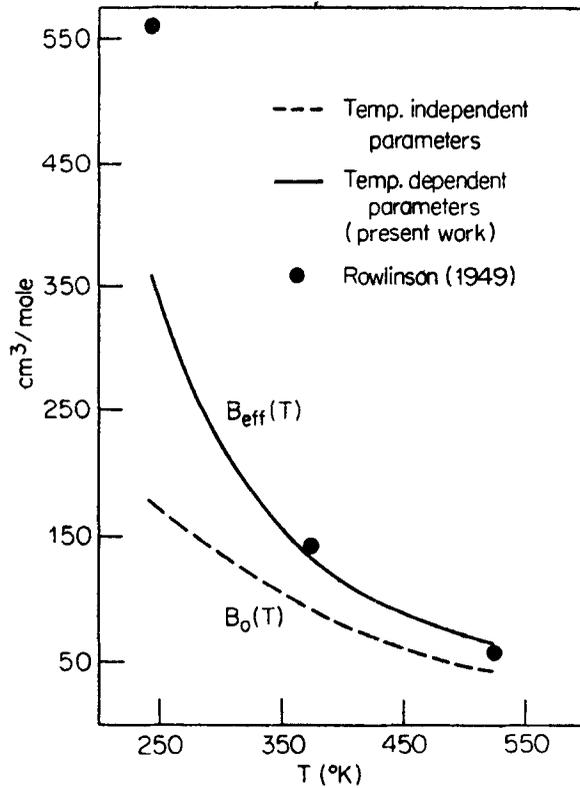


Figure 2. Temperature dependence of the second virial coefficient for NH_3 vapour.

have complex charge distribution and have a tendency to form hydrogen bonds must contain a few more contributions. These could include terms accounting for the interaction of higher multipoles (quadrupole-quadrupole), and the effect of hydrogen bonding. The inclusion of the hydrogen bonding term into the interaction potential will probably improve the results to a great extent at lower temperatures while it would not affect the results at higher temperatures because as the temperature increases the hydrogen bonds start breaking.

This potential is yet to be tested for other complex polar gases because experimental data on quadrupole moments are not available at present for these gases.

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