

## Effective potential for water vapour

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**Abstract.** A suitable temperature dependence is introduced into the force parameters of the Lennard-Jones potential by taking the free-energy average of the Rowlinson potential. The resulting temperature-dependent parameters are used to calculate the effective potential, which is plotted for water vapour at a few different temperatures. The temperature-dependence of the second virial coefficient is shown for the cases of temperature-independent and temperature-dependent parameters of which the latter agrees very well with experimental results.

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

### 1. Introduction

A great deal of current effort is directed towards relating the equilibrium and non-equilibrium properties of gases, liquids and solids to behaviour at the atomic and molecular level. A knowledge of the effective intermolecular potential is necessary to understand these physical properties.

One of the oldest and most common potentials used in determining various properties of matter in the three phases is the Lennard-Jones (6 : 12) (L–J) potential (Lennard-Jones 1924)

$$\phi_{LJ}(r) = 4\epsilon_0[(\sigma_0/r)^{12} - (\sigma_0/r)^6], \quad (1)$$

where  $r$  is the intermolecular separation,  $\sigma_0$  is such that  $\phi_{LJ}(\sigma_0) = 0$  and  $\epsilon_0$  is the maximum energy of attraction (or depth of the potential well) which occurs at  $r_0 = 2^{1/6} \sigma_0$ . The L–J potential has been modified in different ways to explain various properties of gases (Kihara 1953; Boys and Shavitt 1956; Pollara and Funke 1959; Guggenheim and McGlashan 1960; Dymond *et al* 1965; Dymond and Alder 1969; Koo and Hsu 1970). These potential functions use additional parameters to control the depth and the width of the potential well, or to change the slope of the attractive tail, etc. However, none of these potentials has been found to be flexible enough to reproduce all the known low-density properties of even simple non-polar gases.

For polar molecules which have a complex charge distribution and have a tendency to form hydrogen bonds, the interaction potential (Rowlinson 1951; Hirschfelder *et al* 1964, p. 225) is given by

$$\phi(r, \omega) = \phi_{LJ}(r) - \frac{\mu^2}{r^3} g_{11}(\omega) + \frac{3\mu Q}{4r^4} g_{12}(\omega), \quad (2)$$

where  $\phi_{LJ}(r)$  is given by (1), and

$$g_{11}(\omega) = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi, \quad (3)$$

$$g_{12}(\omega) = \cos \theta_1 (3 \cos^2 \theta_2 - 1) - 2 \sin \theta_1 \sin \theta_2 \cos \theta_2 \cos \phi. \quad (4)$$

Further,  $\mu$  and  $Q$  are the electric dipole and quadrupole moments of the molecules,  $\theta_1$  and  $\theta_2$  the angles between the axes of the molecular dipoles and the line joining the molecular centres of the two molecules respectively,  $\phi$  the azimuthal angle in the plane perpendicular to this line, and  $\omega$  is a function of the angular coordinates. The functions  $g_{11}$  and  $g_{12}$  represent the angular dependence of the dipole-dipole and dipole-quadrupole interactions, respectively. If  $Q=0$ , (2) reduces to the familiar Stockmayer (1941) potential which describes well the interaction between polar molecules having simple charge distributions.

In this paper, we start with the Rowlinson potential given in (2), and use it to obtain an effective temperature-dependent potential. The effective potential is expressed in the L-J format with temperature-dependent parameters. This is used to calculate the temperature dependence of the second virial coefficient of water vapour which compares well with the experimental results.

## 2. Effective potential

Danon and Amdur (1969) 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

$$\langle \phi(r, T) \rangle = -kT \ln \left[ \int_{\omega} \exp(-\phi(r, \omega)/kT) d\omega / \int_{\omega} d\omega \right], \quad (5)$$

where  $T$  is the temperature and  $k$  the Boltzmann constant. To obtain the free energy average of the Rowlinson potential, (2), (3) and (4) are introduced into (5) and the exponential term is expanded in inverse powers of  $T$ . If only the first few non-vanishing terms of the expansion are retained, the result, containing terms upto inverse power  $r^{-12}$ , is

$$\langle \phi(r, T) \rangle = \phi_{LJ}(r) - \frac{\mu^4}{3r^6 kT} - \frac{\mu^2 Q^2}{8r^8 kT} + \frac{7\mu^8}{450r^{12} k^3 T^3}. \quad (6)$$

The Rowlinson potential in (2) is a moderately realistic representation of the interaction between two complex polar molecules. It has the additional advantage of retaining, after averaging according to (5), reciprocal powers of  $r$  as in L-J potential. The parameters, however, are now functions of temperature. It is possible, therefore, to calculate the transport properties by using collision integrals which have been tabulated for L-J potential if the temperature-dependent parameters of the effective potential are properly related to the temperature independent parameters of the isotropic potential.

Defining a reduced dipole moment  $\delta_{\max}$ , a reduced dipole-quadrupole moment  $\alpha_{\max}$  and a reduced temperature  $T^*$  by the equations

$$\delta_{\max} = \mu^2/2\epsilon_0\sigma_0^3, \tag{7a}$$

$$\alpha_{\max} = \mu Q/2\epsilon_0\sigma_0^4, \tag{7b}$$

$$T^* = kT/\epsilon_0, \tag{7c}$$

(6) can be written as

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

This is an effective pair-potential which is temperature-dependent; the binding energy and the hard-core diameter for the above potential would clearly depend on temperature.

This effective potential could now be used to calculate various properties of a polar gas. 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, in order to achieve simplicity and elegance at the cost of rigour, we replace  $r^6$  in the dipole-quadrupole term in (8) (containing  $\alpha_{\max}^2$ ) 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  $< 0.1\%$  over a wide range of  $r$  (upto  $10\text{\AA}$ ) and over the temperature range of interest.

This allows us to express (8) as a temperature-dependent effective potential in the L-J format

$$\phi_{\text{eff}}(r, T) = 4\epsilon_T [(\sigma_T/r)^{12} - (\sigma_T/r)^6], \tag{9}$$

where  $\epsilon_T$  and  $\sigma_T$  are temperature-dependent parameters given by

$$\epsilon_T = \epsilon_0 B^2/A, \quad \sigma_T = \sigma_0 (\epsilon_0 A/\epsilon_T)^{1/12}, \tag{10}$$

with  $A = 1 + 14 \delta_{\max}^4/225 T^{*3},$  (11a)

$$B = 1 + (10 \delta_{\max}^2 + 3 \alpha_{\max}^2)/30 T^*. \tag{11b}$$

Such a formal introduction of temperature in the potential is logical and should be consistent with the experimental data of gaseous properties, at least to the extent the Stockmayer potential is. This form of potential envisages that  $\epsilon_T$  and  $\sigma_T$  are temperature-dependent.

The values of  $\epsilon_T$  and  $\sigma_T$  calculated from (10) for water vapour are shown in figure 1 for the temperature range 400 K to 1000 K. The numerical values used are  $\epsilon_0/k = 356$  K,  $\sigma_0 = 2.725 \text{ \AA}$ ,  $\mu = 1.85 \times 10^{-18}$  esu,  $Q = 4.5 \times 10^{-27}$  esu. It is clear that the binding energy decreases with increasing temperature. It can be seen from figure 1 that the effective hard core diameter  $\sigma_T$  decreases upto 550 K and then again increases. It should be kept in mind that (6) is essentially a high temperature approximation.

It can be seen that with  $\alpha_{\max} = 0$ , these relations agree with those obtained by Danon and Amdur (1969) from the Stockmayer potential.

### 3. The second virial coefficient

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

$$B(T) = -\frac{\pi\sqrt{2}\sigma^3}{6} \sum_{n=0}^{\infty} \frac{2^n}{n!} \Gamma\left(\frac{2n-1}{4}\right) \left(\frac{\epsilon}{kT}\right)^{(2n+1)/4}, \quad (12)$$

where  $\epsilon$  and  $\sigma$  are the parameters of the L-J potential. In the derivation of this expression, it is nowhere assumed that  $\epsilon$  and  $\sigma$  are independent of temperature, although, of course, they are independent of  $r$ . Therefore let us define  $B_0(T)$  to be

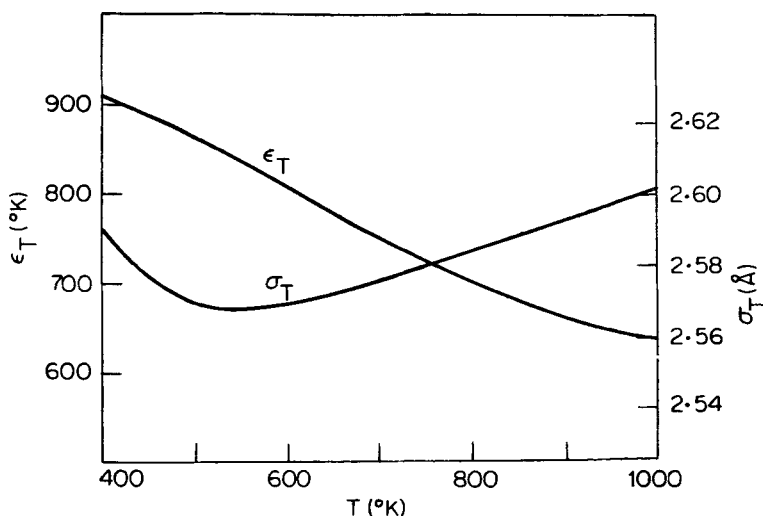


Figure 1. Temperature variation of the characteristic parameters of the effective potential for water vapour.

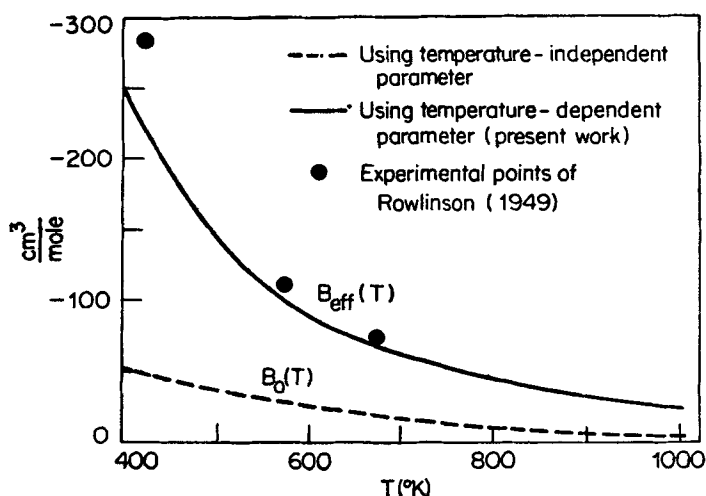


Figure 2. Temperature dependence of the second virial coefficient for water vapour.

given by (12) with  $\epsilon$  and  $\sigma$  replaced by  $\epsilon_0$  and  $\sigma_0$  respectively, and  $B_{\text{eff}}(T)$  to be given by (12) with  $\epsilon$  and  $\sigma$  replaced by  $\epsilon_T$  and  $\sigma_T$  respectively.  $B_0(T)$  and  $B_{\text{eff}}(T)$  would be the second virial coefficients of gases governed by the ordinary L-J and the effective potentials of (1) and (9), respectively.

We have calculated  $B_0(T)$  and  $B_{\text{eff}}(T)$  using the temperature-independent parameters given earlier and the temperature-dependent parameters shown in figure 1. The variation of  $B_0(T)$  and  $B_{\text{eff}}(T)$  with temperature is shown in figure 2. Rowlinson's experimental values (Rowlinson 1949) are also shown in this figure. It is evident that while  $B_0(T)$  lies much lower,  $B_{\text{eff}}(T)$  shows qualitative agreement with the experimental values. In fact, experimental values are on the higher side of  $B_{\text{eff}}(T)$ , and this suggests that the effective potential may contain a few more contributions. These could include, among others, the effect of hydrogen bonding which has not been taken into account so far.

#### 4. Conclusion

In searching for an effective pair potential which is both simple and workable, we thus see in the above that a temperature-dependent potential of the form of (9) is promising.

There have been numerous attempts already in print which are variations of the L-J potential in some form or the other of an *ad hoc* nature while the suggested potential (9) involves a regular variation of the characteristic parameters of the L-J potential.

To decide whether this is an accurate pair potential, it would be most desirable to test this model against other equilibrium and non-equilibrium properties.

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