

Sound velocity in water vapour

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Abstract. The effective potential is used to calculate the sound velocity of water vapour. The agreement between theoretical and experimental values confirms the validity of the effective potential.

Keywords. Lennard-Jones potential; effective potential; sound velocity; water vapour.

1. Introduction

In this paper using the Rowlinson potential we obtain an effective potential which is expressed in the Lennard-Jones (L-J) format with temperature-dependent parameters. This is applied to calculate the sound velocity in water vapour. The agreement between theoretical and experimental values confirms the validity of the effective potential.

2. Effective potential

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

$$\ll \varphi(r, T) \gg = \varphi_{L-J}(r) \cdot \frac{\mu^4}{3r^6 kT} - \frac{\mu^2 Q^2}{8r^8 kT} + \frac{7\mu^8}{450r^{12} k^3 T^3}, \quad (1)$$

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 curve. The averaging process gives a different potential energy curve at each temperature. Moreover, the functional form of $\ll \varphi \gg$ evolves into that of the Lennard-Jones potential with temperature-dependent parameters.

Defining a reduced dipole moment δ_{\max} , a reduced dipole-quadrupole moment a_{\max} and a reduced temperatures T^* by the following equations:

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

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

$$T^* = KT/\epsilon_0. \quad (2c)$$

Equation (1) can be written as

$$\begin{aligned} \ll \varphi(r, T) \gg = 4 \epsilon_0 \left[(\sigma_0/r)^{12} \left(1 + \frac{14 \delta_{\max}^4}{225 T^{*3}} \right) \right. \\ \left. - (\sigma_0/r)^6 \left\{ 1 + \frac{\delta_{\max}^2}{3 T^*} + \frac{a_{\max}^2}{10 T^*} \right\} \right]. \end{aligned} \quad (3)$$

This allows us to express (3) as a temperature-dependent effective potential in the L-J format

$$\varphi_{\text{eff}} = 4 \epsilon_T \left[\left(\frac{\sigma_T}{r} \right)^{12} - \left(\frac{\sigma_T}{r} \right)^6 \right], \quad (4)$$

where ϵ_T and σ_T are temperature-dependent parameters given by

$$\epsilon_T = \epsilon_0 \left(1 + \frac{14 \delta_{\max}^4}{225 T^{*3}} \right)^{-1} \left\{ 1 + \frac{\delta_{\max}^2}{3 T^*} + \frac{a_{\max}^2}{10 T^*} \right\}^2, \quad (5)$$

$$\sigma_T = \sigma_0 (\epsilon_0/\epsilon_T)^{1/12} \left(1 + \frac{14 \delta_{\max}^4}{225 T^{*3}} \right)^{1/12}. \quad (6)$$

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

$$(\epsilon_0/K)_{\text{H}_2\text{O}} = 356^\circ\text{K}; (\sigma_0)_{\text{H}_2\text{O}} = 2.725 \text{ \AA}, \mu_{\text{H}_2\text{O}} = 1.85 \times 10^{-18} \text{ esu},$$

$$Q_{\text{H}_2\text{O}} = 0.45 \times 10^{-26} \text{ esu}.$$

3. Sound velocity in liquid water

It is well-known that the sound velocity (Schuyer 1959) of liquids is a function of the compressibility χ and the density ρ

$$V^2 = 1/\chi\rho. \quad (7)$$

The temperature coefficient of V therefore is given by

$$\frac{1}{V} \frac{dV}{dT} = -\frac{1}{2} \left[\frac{1}{\chi} \frac{d\chi}{dT} + \frac{1}{\rho} \frac{d\rho}{dT} \right]. \quad (8)$$

In calculating the temperature coefficient of the compressibility it is supposed that the liquid contains N molecules per cm^3 which, under equilibrium conditions, are at a

distance r_0 from each other; when applying an external pressure p , this value is reduced by an amount Δr . Assuming that the forces are harmonic in nature

$$p = N^{2/3} f_{r=r_0} \Delta r, \quad (9)$$

where $f_{r=r_0}$ = force constant. At this pressure the volume is reduced from $Nr_0^3 = 1 \text{ cm}^3$ to $V = N(r_0 - \Delta r)^3$ so that χ is given by

$$\begin{aligned} \chi &= -d \ln V / dp, \\ &= -\frac{d}{dp} [3 \ln N + 3 \ln (r_0 - \Delta r)], \\ \chi &= \frac{3}{(r_0 - \Delta r)} \frac{d\Delta r}{dp}. \end{aligned}$$

From equation (9)

$$\begin{aligned} d\Delta r / dp &= 1 / N^{2/3} f_{r=r_0}, \\ \chi &\cong \frac{3}{(r_0 - \Delta r)} \frac{1}{N^{2/3} f_{r=r_0}}, \\ \chi &= 3r_0 / f, \end{aligned} \quad (10)$$

$$\frac{1}{\chi} \frac{d\chi}{dT} = \frac{1}{r_0} \frac{dr_0}{dT} - \frac{1}{f} \frac{df}{dT}.$$

Therefore $\left(\frac{1}{r_0} \frac{dr_0}{dT} = -\frac{1}{3\rho} \frac{d\rho}{dT} \right)$. (11)

The temperature coefficient of compressibility would be

$$\frac{1}{\chi} \frac{d\chi}{dT} = -\frac{1}{3\rho} \frac{d\rho}{dT} - \frac{1}{f} \frac{df}{dT}. \quad (12)$$

Now the temperature coefficient of the force constant f can be calculated if the interaction energy between two molecules is known. We can write (4) in another form

$$\varphi_{\text{eff}} = \frac{a(T)}{r^n} - \frac{b(T)}{r^m}$$

where $b(T) = 4\epsilon_T \sigma_T^m$ and $a(T) = 4\epsilon_T \sigma_T^n$,

$$\left(\frac{d\varphi_{\text{eff}}}{dr} \right) = -na(T) r^{-(n-1)} + mb(T) r^{-(m-1)}. \quad (13)$$

Therefore $\left(\frac{d\varphi_{\text{eff}}}{dr}\right)_{r=r_0} = 0$,

$$\text{and } a(T) = \frac{m}{n} b(T) r_0^{(n-m)}, \quad (14)$$

$$\frac{d^2 \varphi_{\text{eff}}}{dr^2} = + n(n+1) a(T) r^{(n-2)} - m(m+1) b(T) r^{(-m-2)},$$

$$f_{r=r_0} = \left(\frac{d^2 \varphi}{dr^2}\right)_{r=r_0} = n(n+1) a(T) r_0^{(n-2)} - m(m+1) b(T) r_0^{(-m-2)}, \quad (15)$$

and substituting the value of $a(T)$ in (15), we get

$$f = m(n-m) b(T) r_0^{(-m-2)}. \quad (16)$$

Now differentiating (16) we get

$$\begin{aligned} \frac{df}{dT} &= m(n-m) \left[b(T) \left\{ -(m+2) r_0^{(-m-3)} \frac{dr_0}{dT} + r_0^{(-m-2)} \frac{db(T)}{dT} \right\} \right], \\ &= - m(n-m) (m+2) b(T) r_0^{(-m-3)} \frac{dr_0}{dT} + m(n-m) r_0^{(-m-2)} \frac{db(T)}{dT}, \\ &= m(n-m) r_0^{(-m-2)} \left[\frac{db(T)}{dT} - (m+2) b(T) \frac{1}{r_0} \frac{dr_0}{dT} \right]. \end{aligned}$$

$$\text{Therefore } \frac{1}{r_0} \frac{dr_0}{dT} = - \frac{1}{3\rho} \frac{d\rho}{dT},$$

$$\begin{aligned} \frac{df}{dT} &= m(n-m) r_0^{(-m-2)} \left[\frac{db(T)}{dT} + \frac{(m+2)}{3\rho} b(T) \frac{d\rho}{dT} \right], \\ \frac{1}{f} \frac{df}{dT} &= \left(\frac{m+2}{3\rho} \right) \frac{d\rho}{dT} + \frac{db(T)}{dT} / b(T). \end{aligned} \quad (17)$$

From (17), (8) and (12), we get

$$\frac{1}{V} \frac{dV}{dT} = \frac{m}{6\rho} \frac{d\rho}{dT} + \frac{db(T)}{dT} / 2b(T).$$

It was proved by quantum theory (London 1930) that at large distances the interaction energy is proportional to r^{-6} . It is therefore natural to use the value of $m = 6$

$$\frac{1}{V} \frac{dV}{dT} = \frac{1}{\rho} \frac{d\rho}{dT} + \frac{db(T)}{2b(T) dT},$$

$$\text{or } \frac{dV}{V} = \frac{d\rho}{\rho} + \frac{db(T)}{2b(T)}.$$

Integrating

$$\log V = \log \rho + \frac{1}{2} \log b(T) + \lambda_r,$$

or
$$V = \rho b^{1/2}(T) \left(\frac{V_r}{\rho_r b_r^{1/2}(T)} \right), \tag{18}$$

where ρ_r , V_r and $b_r(T)$ are the values of ρ , V and $b(T)$ at any reference temperature.

Now we use this relation to calculate the sound velocity in water vapour. We see that this equation represents the experimental data (Weast 1978) as shown in figure 2.

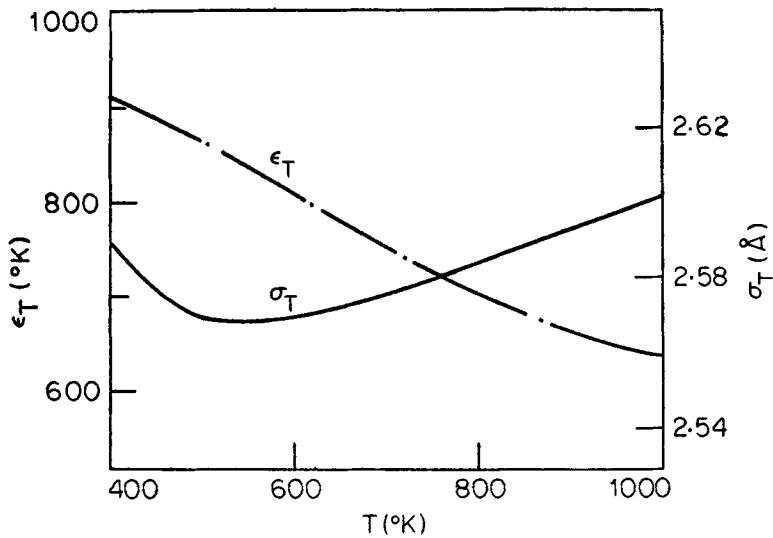


Figure 1. Temperature variation of the characteristic parameters of the effective potential for water vapour.

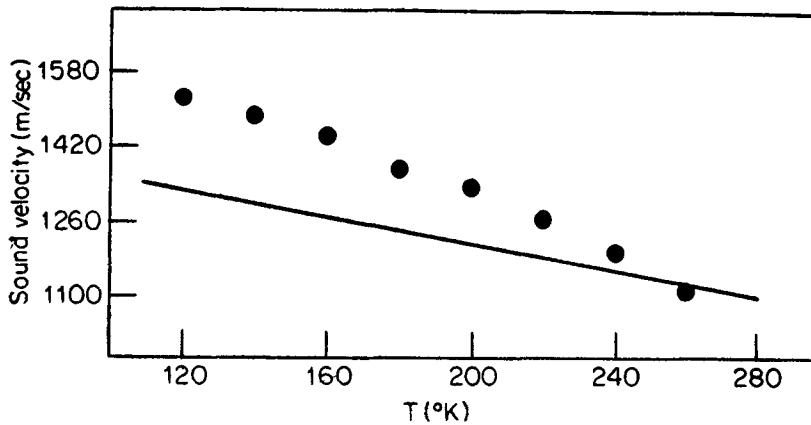


Figure 2. Temperature variation of sound velocity in water vapour.

4. Conclusion

The effective potential obtained by taking the free-energy average of the Rowlinson potential is a reliable one for correlating sound velocity in water vapour using temperature-dependent parameters. As $a_{\max} = 0$, these relations reduce to those obtained by Danon and Amdur (1969) from the Stockmayer (1941) potential.

Summarizing there are two main conclusions of this paper: First, equation (1) is essentially a high temperature approximation. Second, while there is a good agreement between experimental and calculated values at room temperatures, a large discrepancy exists at lower temperatures which suggests that the interaction potential for molecules which have complex charge distribution must contain a few more contributions. These could include terms accounting for the interaction of higher multipoles, 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 results at higher temperatures because as the temperature increases the hydrogen bonds start breaking and in turn do not contribute anything.

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