

## Vibrational Interaction Potentials\*

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An expression is derived for the interaction potential arising from the correlative vibrational motion of fluctuating dipolar diatomic molecules, using as model the Morse oscillator. The theory is applied to two interacting NaCl molecules. The vibrational dipole–dipole coefficient,  $C_6$ , is strongly temperature dependent with a value at room temperature of  $3.788 \times 10^{-62}$  erg cm<sup>6</sup>.

**Key words:** Van der Waals – Vibrational – Intermolecular – Interaction – Potential.

### 1. Introduction

The reaction-field approach to long-range intermolecular forces [1] treats the interaction as arising from the correlations of the charge-fluctuations in neighboring molecules. The fundamental quantities in terms of which the interaction potentials are expressed are the dynamic polarizability tensors  $\alpha(\omega) = \alpha'(\omega) - i\alpha''(\omega)$ , where  $\alpha'(\omega)$  and  $\alpha''(\omega)$  are respectively the real and imaginary parts of the complex polarizability  $\alpha(\omega)$  which, in general, depends on frequency and temperature. The pair potential for two interacting molecules,  $i$  and  $j$ , whose

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centers are a distance  $R$  apart, may be written [2]

$$\phi^{(2)} = -\frac{\hbar}{2\pi} \operatorname{Re} \int_0^\infty i d\omega \operatorname{tr} (\boldsymbol{\alpha}_1 \cdot \mathbf{T}_{12} \cdot \boldsymbol{\alpha}_{21} \cdot \mathbf{T}_{21}) \coth \frac{\hbar\omega}{2kT} \quad (1a)$$

where  $\hbar$  and  $k$  are Planck's and Boltzmann's constants respectively;  $T$  is the absolute temperature and  $\mathbf{T}_{12}$  is the dipole coupling tensor

$$\mathbf{T}_{12} = R^{-5} \left[ \mathbf{I} - \frac{3\mathbf{R}\mathbf{R}}{R^2} \right].$$

The pair potential can be written alternatively and more concisely as a function of the polarizabilities,  $\boldsymbol{\alpha}(-iy_l)$ , along the imaginary frequency axis where the polarizabilities are real and nonvanishing only at the discrete points  $-iy_l$  ( $l = 0, 1, 2, \dots$ ). In terms of these  $\boldsymbol{\alpha}$ 's,  $\phi^{(2)}$  takes the form [1, 2]

$$\phi^{(2)} = -kT \sum'_{l=0} \operatorname{tr} [\boldsymbol{\alpha}_1(-iy_l) \cdot \mathbf{T}_{12} \cdot \boldsymbol{\alpha}_2(-iy_l) \cdot \mathbf{T}_{21}] \quad (1b)$$

where the prime on the summation sign denotes that the leading ( $l = 0$ ) term is multiplied by  $\frac{1}{2}$ .

Expressions (1a) and (1b) have been applied to the forces arising from fluctuations of electronic coordinates, to forces produced by fluctuations of the rotational coordinates, and to the forces arising from combinations of electronic and rotational fluctuations [3]. These fluctuations give rise respectively to the dispersion, orientation and induction forces [1-3]. The electronic fluctuations are essentially of quantal origin and at ordinary temperatures the dispersion and also the induction interactions are temperature independent. In contrast, the rotational fluctuations are essentially of thermal origin, and the orientation (or Keesom) potential is temperature dependent. The orientation potential is useful in the treatment of polar fluids; in fact, when the correlation time for rotational motion is much faster than the collision time the orientation potential is *the* appropriate potential for dipolar interaction.

In the present paper, we examine the effects on the interaction arising from vibrational fluctuations and treat explicitly the interaction of two linear dipolar molecules. As a model we choose the Morse oscillator whose potential is the Morse potential [4]. The reason for choosing this model is twofold:

- 1) The Morse potential is an excellent representation of the potential energy of a diatomic molecule over virtually the entire range of distances except the tail end;
- 2) The Morse potential is capable of yielding analytic expressions for the transition dipole moments of the oscillator.

In contrast to the electronic and rotational fluctuations, the vibrational fluctuations of many molecules are neither strictly classical nor strictly quantal, in which case the full quantum statistical formula given by Eq. (1) will be needed. The availability of an analytic expression for  $\boldsymbol{\alpha}(\omega)$  greatly facilitates the evaluation of the interaction potential.

## 2. The Morse Oscillator

The wave equation associated with the vibrational motion of a diatomic molecule, in which the rotational degrees of freedom are assumed frozen, can be written

$$\frac{d^2 S_{n,v}(r)}{dr^2} + \frac{2\mu}{\hbar^2} [E - U(r)] S_{n,v}(r) = 0 \quad (2)$$

where  $S_{n,v}(r) = rR_{n,v}(r)$  in which  $R_{n,v}(r)$  is the radial part of the wave-function, which depends on the internuclear separation  $r$  and the electronic and vibrational quantum numbers  $n$  and  $v$  respectively. (Since we are not interested in the electronic motion here, we shall henceforth suppress the indices  $n$ ). The potential chosen here is the Morse potential [4]

$$U(r) = D\{e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}\} \quad (3)$$

where  $r_0$  is the equilibrium position,  $D$  the potential minimum and  $a$  is a constant. ( $\mu$  and  $E$  are respectively the reduced mass and energy eigenvalue.) The parameters  $D$  and  $a$  are so chosen as to yield the classical vibration frequency

$$\nu_0 = \frac{a}{2\pi} (2D/\mu)^{1/2} \quad (4a)$$

in the limit of small displacements  $r - r_0$ . The exact solution of Eq. (2) gives

$$E_v = -D + \hbar a \left( \frac{2D}{\mu} \right)^{1/2} \left( v + \frac{1}{2} \right) - \frac{\hbar^2 a^2}{2\mu} \left( v + \frac{1}{2} \right)^2. \quad (4b)$$

It is noted that the reference state is the state of the dissociated molecule.

The differential equation (Eq. (2)) has been solved by means of

- 1) Laguerre polynomials;
- 2) confluent hypergeometric functions;
- 3) factorization.

The method of factorization [5] lends itself to producing analytic expressions for the transition dipole moments,

$$m_{vv'} \equiv qr_{vv'} = q \int_0^\infty S_v(r) r S_{v'}(r) dr \quad (5)$$

needed in the evaluation of the polarizability<sup>1</sup>. Infeld and Hull [5] have derived an expression for a transition moment of a quantity  $x$ , related to  $r$  as follows [6]

$$x = -a(r - r_0) + \ln [(8\mu D)^{1/2} / (a\hbar)]. \quad (6)$$

Using their results we obtain

$$|qr_{vv', v < v'}| = \frac{q}{a} \frac{2}{(v' - v)(2s - v - v')} \left[ \frac{v'! \Gamma(2s - v' + 1)}{v! \Gamma(2s - v + 1)} (s - v)(s - v') \right]^{1/2} \quad (7)$$

<sup>1</sup> The quantity  $q$  is an effective charge to be determined by equating  $qr_0$  to the experimental permanent dipole moment,  $\bar{m}$

where

$$s = \frac{(2\mu D)^{1/2}}{a\hbar} - \frac{1}{2}. \quad (8)$$

The polarizability, as noted before, is likely to be neither strictly classical nor strictly quantal. The general expression for  $\alpha(\omega)$  for positive frequencies, is [1]

$$\alpha(\omega) = \frac{1}{\hbar Q} \sum_{\substack{v,v' \\ v' > v}} [\exp(-E_v/kT) - \exp(-E_{v'}/kT)] |qr_{vv'}|^2 \\ \times \left[ \mathcal{P} \frac{2\omega_{v'v}}{\omega_{v'v}^2 - \omega^2} - i\pi\delta(\omega - \omega_{v'v}) \right] \quad (9)$$

where  $\mathcal{P}$  stands for the principal value when  $\omega_{v'v} = \omega$ ;  $\omega_{v'v} = (E_{v'} - E_v)/\hbar$ , and  $Q = \sum_v \exp(-E_v/kT)$ . Along the imaginary axis,

$$\alpha(-iy_l) = \frac{2}{\hbar Q} \sum'_{v,v'} (e^{-E_v/kT}) \frac{\omega_{v'v} |qr_{v'v}|^2}{\omega_{v'v}^2 + (2\pi kT\hbar^{-1}l)^2}. \quad (10)$$

### 3. The Vibrational Interaction Potential

Since the Morse oscillators are linear oscillators we must adapt Eq. 1 to the interaction between such oscillators. Let us assume that the line connecting the centers of the two molecules coincides with the  $Z$ -axis of the space-fixed coordinate systems and the orientations of the molecular axes with respect to this frame are

$$\mathbf{S}_1 = ix_1 + jy_1 + kz_1 \quad \text{and} \quad \mathbf{S}_2 = ix_2 + jy_2 + kz_2. \quad (11)$$

With respect to the space-fixed frame, the  $r$  appearing in the expression for the polarizability  $\alpha_i$  should be replaced by  $r_i = r_i \mathbf{S}_i$  and  $\alpha_i$  by  $\alpha_i = \alpha_i \mathbf{S}_i \mathbf{S}_i$ . Accordingly,

$$\text{tr}(\alpha_1 \cdot \mathbf{T}_{12} \cdot \alpha_2 \cdot \mathbf{T}_{21}) = \alpha_1 \alpha_2 \text{tr}(\mathbf{S}_1 \mathbf{S}_1 \cdot \mathbf{T}_{12} \cdot \mathbf{S}_2 \mathbf{S}_2 \cdot \mathbf{T}_{21}). \quad (12)$$

The expression for  $\mathbf{T}_{12}$  in the chosen frame is

$$\mathbf{T}_{12} = R^{-3} [ii + jj - 2kk]. \quad (13)$$

Combining Eqs. (11), (12) and (13) gives

$$\text{tr}(\alpha_1 \cdot \mathbf{T}_{12} \cdot \alpha_2 \cdot \mathbf{T}_{21}) = \frac{\alpha_1 \alpha_2}{R^6} [x_1 x_2 + y_1 y_2 - 2z_1 z_2]^2 \\ = \frac{\alpha_1 \alpha_2}{R^6} \{ [\sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) - 2 \cos \theta_1 \cos \theta_2]^2 \} \\ = \frac{\alpha_1 \alpha_2}{R^6} f(\theta_1, \theta_2, \phi_1 - \phi_2) \quad (14)$$

where  $(\theta_1, \phi_1)$  and  $(\theta_2, \phi_2)$  are the orientation angles of the two molecules.

Finally, substitution into Eq. (1b) yields

$$\phi^{(2)} = -\frac{kT}{R^6} \sum_{l=0}^{\infty} \alpha_l(-iy_l) f(\theta_1, \theta_2, \phi_1 - \phi_2) \quad (15)$$

which is explicit angle-dependent, as it should be since the rotational degrees of freedom are assumed frozen. [If averaged over the angles,  $f(\theta_1, \theta_2, \phi_1 - \phi_2) = 2$ ]. The  $\alpha_l(-iy_l)$  are the polarizabilities given by Eq. (10), and by virtue of Eq. (7) can be formulated in terms of the parameters  $q$ ,  $a$  and  $s$ , and thus in terms of  $\nu_0$ ,  $r_0$ ,  $\bar{m}$ ,  $D$  and  $\mu$ . In the final analysis the evaluation of the interaction potential requires knowledge of the fundamental vibration frequency, equilibrium distance, permanent moment, dissociation energy, and reduced mass, all of which are readily available from experimental data for most diatomic molecules.

The potential given by Eq. (15) has the appearance of a dispersion potential, and might be called appropriately 'vibrational dispersion' potential. However, the  $C_6$ -coefficient of this potential, i.e.

$$\phi^{(2)} = -C_6 R^{-6} f(\theta_1, \theta_2, \phi_1 - \phi_2) \quad (15a)$$

will generally be temperature-dependent not only because of its explicit dependence on  $T$  but also because of the  $T$ -dependence of the polarizabilities.

#### 4. Application to NaCl

As an illustration of the method we apply the theory to the interaction between two NaCl molecules. The calculations are based on the following set of data [7]:  $r_0 = 2.361 \times 10^{-8}$  cm,  $\bar{m} = 9.002$  Debye,  $\nu_0 = 1.0930343 \times 10^{13}$  sec $^{-1}$ ,  $\mu = 2.3164407 \times 10^{-23}$  g,  $D = 6.8451334 \times 10^{-12}$  erg, yielding the values  $q = 3.8127911 \times 10^{-10}$  esu,  $a = 8.9334315 \times 10^7$  cm $^{-1}$  and  $s = 188.54808$ .

Table 1 lists the values of  $C_6$  as a function of temperature. It is seen that  $C_6$  varies rather strongly with temperatures which is a manifestation that in NaCl there is a substantial classical contribution to the vibrational dispersion potential. At room temperature ( $T = 298.1$ )  $C_6 = 3.788 \times 10^{-62}$  erg cm $^6$ . This value, when multiplied by  $f(\theta_1, \theta_2, \phi_1 - \phi_2)$  which ranges from 0 to 4, is about two to three orders of magnitude smaller than typical (electronic) dispersion energy coefficients and about one to two orders of magnitude smaller than typical orientation and induction energies.

Thus, it would appear that the vibrationally produced Van der Waals forces are much smaller than the dispersion forces and also smaller than the orientation

**Table 1.** Values of  $C_6$  for NaCl as a function of temperature

$T$ (K)	100	200	298.1	400	500	600	700
$C_6 \times 10^{62}$ erg cm $^6$	1.734	2.622	3.788	5.083	6.392	7.729	9.093

forces. Nonetheless, in large molecules there are many degrees of vibrational freedom and if the molecules contain a large number of polar bonds or polar groups the cumulative effect of their vibrational interaction could conceivably overshadow the contribution from the orientation interaction.

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