

CONSTRUCTION AND USE OF CENTRAL FORCE MODELS FOR THE THEORY OF POLYATOMIC FLUIDS

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ABSTRACT

In order to avoid technical problems posed by nonspherical interactions in the statistical mechanics of liquids, central force models can be devised to describe polyatomic substances. In this approach separate spherical potentials exist for each type of atomic pair. In the case of water, three functions are necessary: $V_{OO}(r)$, $V_{HH}(r)$, and $V_{OH}(r)$; they can be selected so that proper molecules spontaneously form and engage in linear hydrogen bonds. In addition to conventional properties, central force models permit study of molecular vibration and dissociation. Details for NH_3 , H_2O , HF , and CH_4 are presented.

I. MOTIVATION

Although many chemically important liquids are polyatomic, most basic theory for the liquid state applies only to substances composed of spherical structureless particles [1, 2]. This disparity stems from severe technical difficulties that arise in the theory whenever noncentral forces must be considered. Probably the most interesting class of liquids is that with hydrogen bonds; for this class the noncentral character of the interactions seems to be especially pronounced. Thus theory appears most impotent where its application would be most useful.

To avoid this impasse, at least in part, a family of "central force models" has been proposed [3, 4]. The initial studies in this area have specifically concentrated on water. However these models have wider applicability, as we intend to illustrate.

The basic idea behind the central-force-model approach is to regard the separate atoms comprising the molecules as components of a liquid mixture. Judicious choice of central forces acting between atom pairs ensures spontaneous formation of the molecules in the required geometry. Pairs of molecules subsequently interact according to the sum of central forces acting between atoms in the different molecules. No distinction is drawn between atoms in the same or in different molecules; the central forces used for given atomic species are the same.

We show below that specific central forces can be selected to model NH_3 , H_2O , HF , and CH_4 . These details are supplemented by some general formulas that should be useful for making quantitative calculations with the central force models.

Beside reducing polyatomic substances to a description solely in terms of central forces, the present approach enjoys other advantages. Individual molecules possess vibrational modes as their constituent atoms move about in the central-force potential wells. Furthermore the molecules can dissociate, and the resulting fragments solvate. Quantitative theoretical study of these phenomena in the liquid state thus seems closer to fruition.

II. SPECIFIC POTENTIAL SETS

A. Ammonia

Although it undergoes tunnelling inversions, NH_3 is pyramidal in its lowest-energy nuclear configuration. This configuration exhibits bond lengths 1.0124 Å and 1.6243 Å for NH and HH respectively. The corresponding angles are 106.68° for HNH, and 67.86° for the angle between each NH bond and the symmetry axis [5].

Three central potentials are required, $V_{\text{NN}}(r)$, $V_{\text{NH}}(r)$, and $V_{\text{HH}}(r)$. By arranging for the latter two to have minima at the cited distances, separate molecules will adopt the desired shape. V_{NN} can subsequently be varied so as to achieve proper interaction between pairs of NH_3 "complexes".

The molecular dipole moment of ammonia is 1.47 D [6]. That suggests each H should bear charge 0.2674 e, and each N should bear charge -0.8022 e. This assignment reproduces the given moment at the stable molecular geometry. If each of V_{NN} , V_{NH} , and V_{HH} reduces to Coulombic form at large r with magnitude consistent with the charges, the proper dipole-dipole form for the ammonia intermolecular pair interaction will ensue.

A specific set of central potentials which satisfies the stated requirements is the following (expressed in kcal/mole, and Å):

$$V_{\text{NN}}(r) = \frac{213.759}{r} - \frac{3087.203}{r^6} + \frac{2738398}{r^{12}}; \quad (1)$$

$$V_{\text{NH}}(r) = -\frac{71.253}{r} + \frac{9.709081}{r^8} - \frac{1}{1 + \exp[10(r-2.4)]} - 9.13525 \exp[-25(r-1.0124)^2]; \quad (2)$$

$$V_{\text{HH}}(r) = \frac{23.751}{r} + \frac{10}{1 + \exp[20(r-2)]} - 7.610432 \exp[-25(r-1.6)^2]. \quad (3)$$

These functions are plotted in Fig. 1. It is obvious from the Figure that although V_{NH} has an absolute minimum at the desired bond length, V_{HH} has only a *relative* minimum. Nevertheless overall molecular stability obtains, due to the great depth of V_{NH} .

The ammonia inversion barrier can be calculated from V_{NH} and V_{HH} . During the

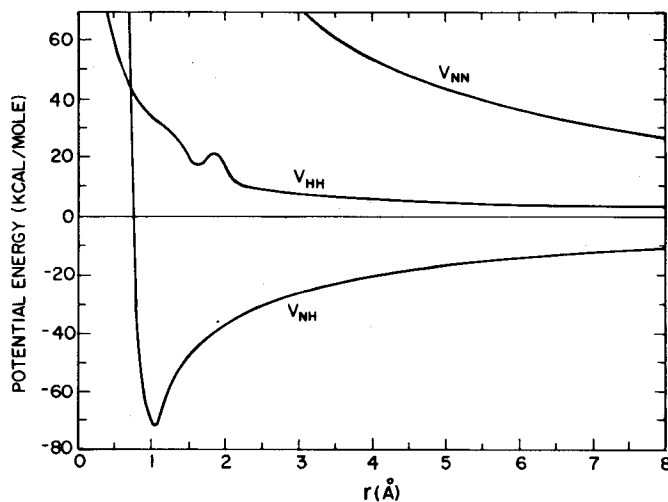


FIG. 1. Set of central potentials for NH_3 . Specific functional forms appear in Eqs. (1)–(3).

inversion process, the molecule passes through a symmetric planar configuration, which represents a saddle point on the multidimensional intramolecular potential hypersurface. This saddle-point configuration has slightly shortened NH bonds (0.9787\AA), and sits atop a 4.112 kcal barrier. Although this is somewhat lower than the value 5.78 kcal that has been inferred from spectroscopically observed frequencies [7], only rather small changes in V_{NH} and V_{HH} would be required to produce agreement.

Under the condition that the individual molecules remain at their minimum-energy geometries, one finds that the most stable structure for $(\text{NH}_3)_2$ implied by Eqs. (1)–(3) is the one shown in Fig. 2. A single nearly-linear hydrogen bond forms with strength 3.507 kcal/mole. The NN distance in this dimer, 3.200\AA , is a bit smaller than the corresponding distance, 3.4\AA , observed in the crystal [8]. However, it is likely that steric hindrance in neighbor shells in the crystal acts to hold pairs of molecules apart.

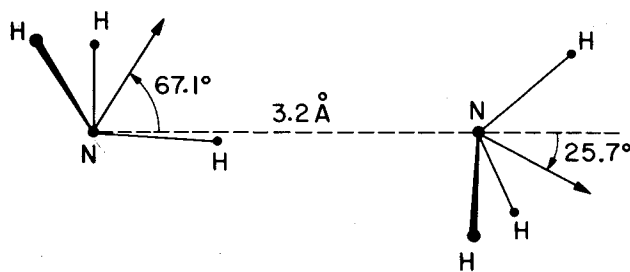


FIG. 2. Structure of ammonia dimer implied by interactions (1)–(3). Monomers have been frozen in their own stable geometries. Symmetry axes (arrows) are coplanar.

With potentials (1)–(3) it is energetically unfavorable for one ammonia molecule to transfer a proton to another forming ions NH_4^+ and NH_2^- ; the energy increase for widely separated NH_3 's would be V_{HH} (1.6243). Nevertheless, the central force model predicts a tetrahedral structure for the ammonium cation, and a nonlinear structure for the amide anion, both of which are the proper forms.

Of course the central force model assigns only the partial charges $\pm 0.2674 e$ to the NH_4^+ and NH_2^- ions, which seems unrealistically small. But the model has a compensating feature, namely its neglect of polarization. The mean electrostatic field surrounding an ion in the model liquid consequently is closer to the true value than would otherwise have been the case.

B. Water

Considerations similar to those used for ammonia are applicable for selection of the three central potentials V_{OO} , V_{OH} , and V_{HH} . The equilibrium internuclear distances in H_2O are 0.9584 Å for OH, and 1.5151 Å for HH (the bond angle is 104.45°). From the molecular dipole moment 1.86 D, charge 0.32983 e is required for each H, $-0.65966 e$ for each O [4]. The following set of functions satisfies these criteria (again using kcal/mole, and Å):

$$V_{\text{OO}}(r) = \frac{144.538}{r} + \frac{26758.2}{r^{8.8591}} - 1.5 \exp[-4(r - 3.4)^2]; \quad (4)$$

$$V_{\text{OH}}(r) = -\frac{72.269}{r} + \frac{6.23403}{r^{9.19912}} - \frac{10}{1 + \exp[40(r - 1.05)]} - \frac{5}{1 + \exp[5.49305(r - 2.2)]}; \quad (5)$$

$$V_{\text{HH}}(r) = \frac{36.1345}{r} + \frac{18}{1 + \exp[40(r - 2.05)]} - 17 \exp[-7.62177(r - 1.45251)^2]. \quad (6)$$

Graphically, this set has an appearance similar to that shown in Fig. 1, with O playing the role of N. In particular V_{HH} now has a relative minimum at 1.5151 Å, and V_{OH} a deep absolute minimum at 0.9584 Å.

Using monomers frozen at their equilibrium shapes, the most stable dimer structure implied by Eqs. (4)–(6) involves a nearly linear hydrogen bond, in the required plane-symmetric *trans* configuration [3]. The hydrogen bond has length $r_{\text{OO}} = 2.862 \text{ Å}$, and its strength is 6.762 kcal/mole. By allowing the monomer shapes to relax, only about 0.2 kcal/mole extra stabilization should be expected [4].

Central-force models for liquid water have been used to study structures of small clusters [4], to apply hypernetted-chain integral equations to molecular structure in water [9], and to simulate the liquid via computer using molecular dynamics [10].

These studies have been encouraging, but have suggested small changes in the earlier potential sets; those changes were incorporated in Eqs. (4)–(6).

The hydronium ion H_3O^+ implied by Eqs. (5) and (6) is pyramidal, in agreement with *ab initio* quantum mechanical calculations [11].

C. Hydrogen Fluoride

The HF bond length in the isolated molecule is 0.9170 Å, while the dipole moment is 1.82 D. Consequently, the separate H and F particles must be assigned charges $\pm 0.4132 e$. An appropriate set of central force interactions seems to be the following (in kcal/mole, and Å):

$$V_{\text{FF}}(r) = \frac{56.7232}{r} - \frac{6091.06}{r^6} + \frac{42774.5}{r^8}; \quad (7)$$

$$V_{\text{FH}}(r) = -\frac{56.732}{r} + \frac{3.86595}{r^8} - 18.58835 \exp[-25(r-0.917)^2] \\ - 0.7 \exp[-10(r-3)^2]; \quad (8)$$

$$V_{\text{HH}}(r) = \frac{56.7232}{r} + \frac{20}{1 + \exp[20(r-1.95)]} - 0.7 \exp[-12(r-2.7)^2] \\ - 21.65073 \exp[-4.5(r-1.41185)^2]. \quad (9)$$

The curvature of V_{FH} at its absolute minimum ($r = 0.9170 \text{ Å}$) has been forced to equal $1389.4 \text{ kcal/mole Å}^2$, to be consistent with observed vibrational frequencies for the molecule.

In accord with the previous cases, V_{HH} in Eq. (9) possesses a relative minimum, now at $r = 1.5446 \text{ Å}$. The reason for requiring this property is that the resulting fluoronium ion FH_2^+ will have a stable nonlinear structure with $\text{HFH} = 114.75^\circ$ to agree with quantum mechanical results [12].

Dyke, Howard, and Klemperer [13] have determined the structure of $(\text{HF})_2$ by radiofrequency and microwave spectroscopy. This dimer has a linear hydrogen bond with $r_{\text{FF}} = 2.79 \pm 0.05 \text{ Å}$, and the proton acceptor molecule rotated off the FF axis $\approx 70^\circ$. The dimer structure implied by Eqs. (7)–(9) (with frozen monomers) is similar; it has $r_{\text{FF}} = 2.711 \text{ Å}$, acceptor rotation angle 85.3° , and the strength of bonding is 6.212 kcal/mole .

D. Methane

The methane molecule is tetrahedral, with CH bond lengths equal to 1.0940 Å . A relative minimum in V_{HH} is not strictly necessary to ensure tetrahedral symmetry, since this arrangement would arise naturally as four hydrogens minimize their repulsions on a sphere surrounding an attracting carbon.

Since CH_4 is nonpolar, assignment of electrostatic charges is less crucial than

before. We can use theoretical Mullikan populations [14] to conclude that H's and C's should bear at most 0.1843 e and -0.7372 e, respectively. We have elected to use these values.

The following set describes methane adequately:

$$V_{CC}(r) = \frac{180.52}{r} + \frac{1.82473 \times 10^7}{r^{12}}, \quad (10)$$

$$V_{CH}(r) = -\frac{45.13}{r} + \frac{15.2564}{r^{12}} - 20 \exp[-25(r - 1.094)^2], \quad (11)$$

$$V_{HH}(r) = \frac{11.2825}{r} + \frac{100}{r^8}. \quad (12)$$

The minimum-energy dimer (with frozen monomers) has a linear CH...C axis, and staggered pendant protons. The r_{CC} distance is 4.200\AA , and the energy is -2.497 kcal/mole.

III. DISTRIBUTION FUNCTIONS

Molecular distribution functions play a basic role in liquid theory. The distribution functions that are relevant to the present circumstance are those for distinct nuclei H and X (= N, O, F, C). Since pairwise additive central forces alone are present, pair correlation functions $g_{XX}(r)$, $g_{XH}(r)$, and $g_{HH}(r)$ suffice to give the thermodynamic functions [3, 4].

These functions specify nuclear order both within and between molecules. On account of the distances involved, prominent and fully-resolved intramolecular peaks exist in g_{XH} and g_{HH} at small r , due to intramolecular geometry. At least at low temperature, where dissociation is negligible, one has the stoichiometric condition

$$C_H \int_{\ell-\epsilon}^{\ell+\epsilon} g_{XH}(r) dr = \nu, \quad (13)$$

where C_H is the number density of H's, ν is the number of H's per molecule (formula XH_ν), and the integration spans sufficient width about the nominal XH bond length ℓ to accommodate vibrational broadening. Similarly we have

$$C_H \int_{\ell'-\epsilon'}^{\ell'+\epsilon'} g_{HH}(r) dr = \mu, \quad (14)$$

where μ represents the number of intramolecular HH pairs, whose lengths cluster around ℓ' [Eq. (14) is not applicable to HF].

A variety of integral equation techniques is available for determination of the $g_{\alpha\beta}$

analytically. One approach is based on the Born-Green-Yvon integrodifferential equation [15]; it relates the $g_{\alpha\beta}$ to the interactions $V_{\alpha\beta}$ and to the triplet correlation functions $g_{\alpha\beta\gamma}^{(3)}$ for sets of three nuclei. In order to construct numerical solutions to these equations, closure is usually achieved through the Kirkwood superposition approximation [15]:

$$g_{\alpha\beta\gamma}^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13}) \cong g_{\alpha\beta}(\mathbf{r}_{12}) g_{\alpha\gamma}(\mathbf{r}_{13}) g_{\beta\gamma}(\mathbf{r}_{23}). \quad (15)$$

One should note that even if the pair correlation functions satisfy stoichiometric conditions (13) and (14), the superposition approximation (15) generally will *not* be consistent with the underlying stoichiometry. As an example, consider water at low temperature. Since two H's are bonded to any given O,

$$C_H^2 \int_{\Omega} g_{\text{OHH}}^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13}) d\mathbf{r}_{12} d\mathbf{r}_{13} = 2, \quad (16)$$

where the integration only spans the intramolecular region Ω . To ensure that (16) obtain, one must revise (15) within the intramolecular region to:

$$g_{\text{OHH}}^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13}) \cong K g_{\text{OH}}(\mathbf{r}_{12}) g_{\text{OH}}(\mathbf{r}_{13}) g_{\text{HH}}(\mathbf{r}_{23}),$$

$$K = 8\pi C_O r_{\text{OH}}^2 r_{\text{HH}} \quad (17)$$

($C_O = C_H/2$ is the oxygen number density).

According to the general Kirkwood-Buff solution theory [16], the isothermal compressibility κ_T of a binary mixture can be written in terms of pair correlation function integrals

$$G_{\alpha\beta} = G_{\beta\alpha} = \int [g_{\alpha\beta}(r) - 1] dr. \quad (18)$$

In this expression, the $g_{\alpha\beta}$ must be infinite-system limit functions, and after making that interpretation the integration limits in (18) may be allowed to go to infinity. In the current view, each substance XH_ν can be treated as a binary mixture, so its κ_T formally would seem to follow from [16]:

$$k_B T \kappa_T = \frac{1 + C_H G_{\text{HH}} + C_X G_{\text{XX}} + C_H C_X (G_{\text{HH}} G_{\text{XX}} - G_{\text{HX}}^2)}{C_H + C_X + C_H C_X (G_{\text{HH}} + G_{\text{XX}} - 2G_{\text{HX}})} \quad (19)$$

Since the particles treated by the central force models are charged, the $G_{\alpha\beta}$ must obey local electroneutrality conditions:

$$C_H (G_{\text{XH}} - G_{\text{HH}}) = 1,$$

$$C_X (G_{\text{XH}} - G_{\text{XX}}) = 1. \quad (20)$$

These relations render Eq. (19) indeterminate, with both numerator and denominator collapsing to zero.

One way to remove the indeterminacy is to make a careful analysis of charge fluctuations in the grand ensemble, with the system confined to a finite box. This analysis reveals that correct evaluation of (19) proceeds by replacing

$$\begin{aligned} G_{HH} &\rightarrow G_{HH} + \eta \\ G_{XH} &\rightarrow G_{XH} - \eta \\ G_{XX} &\rightarrow G_{XX} + \eta, \end{aligned} \quad (21)$$

then permitting η to go to zero. The result can be put into several alternative forms, using Eqs. (20):

$$\begin{aligned} k_B T \kappa_T &= G_{HH} + (1/C_H) \\ &= G_{XX} + (1/C_X) \\ &= G_{XH}. \end{aligned} \quad (22)$$

The response of these substances to incident electromagnetic radiation can be expressed in terms of $\epsilon(k, \omega)$, the wavelength- and frequency-dependent dielectric function. Formulas are available for this quantity within the central-force-model context [4]. Since a large body of infrared and Raman spectral information is available for the liquids discussed here, central-force models may offer a vital tool for molecular interpretation of that information.

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