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Long-Range Many-Molecule Interactions in an Extended van der Waals Equation of State

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Distinction between the effects of pairwise and nonadditive interactions on thermodynamic functions can be made only in an approximate sense and then only for the long-range part of the interaction. Within such an approximation the entire contributions of all long-range many-body interactions to the free energy and pressure are obtained in closed form. These appear as simple extensions of the well known long-range terms of the van der Waals equations. Using a simple harmonic oscillator model for the molecule it is found that the relative contributions of the entire nonadditive to additive interactions to the free energy and pressure are functions only of a reduced polarizability of the molecule. Taking actual values of polarizabilities and densities of the noble gases it is found that the nonadditive effects contribute at most about 7% to the pressure and 4% to the free energy even at the liquid densities. Using van der Waals' expression for the short-range part of the pressure, the corrections to the critical constants are also estimated. As a rule inclusion of nonadditive effects improves the agreement between calculated and experimental values of all thermodynamic functions.

I. INTRODUCTION AND SUMMARY

The extent to which nonadditive intermolecular interactions can be neglected when determining the thermodynamic properties of a system of interacting molecules has been questioned time and again.¹ However, it seems that an answer to this question can be given only within a certain approximate treatment of the system.

Consider first the definition of nonadditive interactions. It is based on the possibility to express the quantum mechanically calculated interaction energy of a system of N molecules at fixed positions $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N$ as a sum of terms

$$U = \sum_{k \geq 2} U_k \quad (1.1)$$

with

$$U_k \equiv \sum_{1 \leq i_1 < \dots < i_k \leq N} U^{(k)}(\mathbf{R}_{i_1}, \dots, \mathbf{R}_{i_k}), \quad (1.2)$$

where by definition the potentials $U^{(k)}$ cannot be decomposed into a sum of potentials of lower order. By nonadditive interactions we understand all terms in U_k with $k > 2$, since the force on a molecule derived from the potential cannot be decomposed into a sum of $k-1$ independent forces acted by the other molecules.

Now it appears that since all potentials $U^{(k)}$ are given or can be calculated, at least in principle, from quantum mechanics,² the thermodynamic functions can be fully determined from these potentials through the partition function given by the classical form

$$Q = (\Lambda^{3N} N!)^{-1} \int \exp[-\beta U(\mathbf{R}^N)] d\mathbf{R}^N, \quad (1.3)$$

where $\Lambda = (2\pi\beta\hbar^2/m)^{1/2}$ is the thermal wavelength of a molecule and where we have used the shorthand notation $d\mathbf{R}^N = d\mathbf{R}_1 \dots d\mathbf{R}_N$, $(\mathbf{R}^N) = (\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$.

However, when examining the full quantum mechanical perturbation theory for a system of many interacting molecules³ it turns out to be far from obvious that

Q can be expressed solely as a functional of a set of potentials $U^{(k)}$. A detailed examination shows that only by assuming that the intermolecular interactions are weak can we obtain, keeping only low order terms in the perturbation expansion, an expression for Q which is a functional of suitably defined $U^{(k)}$.

On the other hand the assumption of weak intermolecular interactions cannot be justified even for a dilute gas, for although in the overwhelming part of molecular configurations only the weak long-range interactions are effective, the strong repulsion at short distances cannot be taken into account correctly in any finite order perturbation theory. Hence it follows that the decomposition of the interaction energy U as given in (1.1) and (1.2) can be used in an approximate way in (1.3) only when restricted to molecular configurations where U is small. Thus, we shall split U into two parts,

$$U = U_0 + U_d, \quad (1.4)$$

where U_0 represents the short-range repulsive interaction energy which has a high positive value at short intermolecular distances and decays rapidly to zero at larger separation between molecules. U_d is the weak long-range part of the interaction to which we shall apply the decomposition (1.1)

$$U_d = \sum_{k \geq 2} U_k, \quad (1.5)$$

where the U_k as before comprise the potentials $U^{(k)}$ as in (1.2), but where the $U^{(k)}$ are now understood to be nonzero only in an appropriate domain of molecular configurations where the intermolecular distances are sufficiently large. A precise specification of this domain will be given below. Substituting now (1.4) into (1.3) we obtain an approximate partition function for the system.

It follows that one can distinguish between effects

of pair, triple, etc., potentials on thermodynamic functions only in an approximate sense and only by restricting oneself to the weak long-range part of the interactions. Hence it is sufficient for this purpose to consider U_d in Eq. (1.3) as a small perturbation⁴ and estimate all derived thermodynamic functions only up to first order in U_d . Thus we get from (1.3) to first order

$$Q = (\Lambda^{3N} N!)^{-1} \int \exp(-\beta U_0) (1 - \beta U_d) d\mathbf{R}^N, \quad (1.6)$$

and for the free energy

$$F = F^0 - \beta^{-1} \log(1 - \beta \langle U_d \rangle_0)$$

to first order

$$F = F^0 + \langle U_d \rangle_0, \quad (1.7)$$

where F^0 is the free energy of the unperturbed system and $\langle U_d \rangle_0$ is the average of U_d in this system. Namely,

$$\langle U_d \rangle_0 = Z_0^{-1} \int U_d \exp(-\beta U_0) d\mathbf{R}^N, \quad (1.8)$$

where Z_0 is the configurational integral of the unperturbed system:

$$Z_0 = \int \exp(-\beta U_0) d\mathbf{R}^N. \quad (1.9)$$

Substituting from (1.3) and (1.1) into (1.8) we obtain

$$\langle U_d \rangle_0 = \sum_{2 \leq k \leq N} (k!)^{-1} \int n_0^{(k)}(\mathbf{R}^k) U^{(k)}(\mathbf{R}^k) d\mathbf{R}^k, \quad (1.10)$$

where $n_0^{(k)}$ is the k -molecules distribution function of the unperturbed system

$$n_0^{(k)}(\mathbf{R}^k) = (N)_k Z_0^{-1} \int \exp(-\beta U_0) d\mathbf{R}^{N-k}. \quad (1.11)$$

If in addition one introduces the approximation

$$n_0^{(k)} = \rho^k, \quad (1.12)$$

where ρ is the molecular density of the system, which is based on the assumption that because of the long-range interaction U_d , the main contribution to the integral in (1.8) comes from configurations where the molecules are sufficiently far apart for the short-range interactions to have no effect. Thus substituting from (1.12) into (1.10) and from there into (7) we obtain

$$F = F^0 + \sum_{k \geq 2} \rho^k / k! \int U^{(k)}(\mathbf{R}^k) d\mathbf{R}^k. \quad (1.13)$$

Equation (1.13) represents a straightforward generalization of the van der Waals (vdW) equation as obtained by Ornstein,⁵ who considered only the ρ^2 term in the sum on the rhs of (1.13), to include all higher order potentials. We conclude that this extended vdW equation represents a natural model system for which the effects of all orders of nonadditive long-range interactions on the thermodynamic properties can be estimated. One has only to calculate the $U^{(k)}$ explicitly

and evaluate the integrals in (1.13) in order to obtain the contribution of long-range interactions to the free energy of the system.

Presently we shall examine the perturbation expansion of the logarithm of the grand partition function Ξ as described in Ref. 3. At first we select from the expansion all terms which are of lowest order in the intermolecular interaction. Then we separate out from these terms the long-range part by introducing a certain diameter σ characterizing the limit of approach of molecules still affected by long range interactions. Considering this part as a small perturbation to an ideal gas, we obtain then the long-range contribution to the free energy. The resulting expression can be identified term by term with the sum on the rhs of (1.13). Choosing a simple harmonic oscillator (Drude) model² for the molecule we find that the corresponding $U^{(k)}$ are identical with calculated⁶ dispersive interaction energies for this model.

In Sec. V we make use of experimental data for noble gases in order to evaluate numerically the effects of nonadditivity (due to $U^{(k)}$, $k \geq 3$) on the free energy and pressure. They are found to depend parametrically only on the reduced polarizability $\alpha^* = \alpha \rho_0$ of the molecule (where $\rho_0^{-1} = 2\pi\sigma^3/3$). We find that the change in pressure and free energy at constant ρ and temperature T , due to nonadditive interactions, exhibit monotonic increase with increasing α^* .

Finally we use the simple expression due to van der Waals for the short-range repulsive part of the free energy F^0 and pressure P^0 [see (4.12) and (4.11), respectively], in order to obtain an expression for the total pressure of the gas. This enables us to estimate the effects of nonadditive interactions on the critical constants P_c , T_c , ρ_c .

In principle the relative effects can become very large but for physically relevant values of α^* our results confirm previous calculations^{7,8} considering only three-body potentials, showing no dramatic change in the properties of the gas due to nonadditive interactions. It should be noted that the nonadditive corrections to the thermodynamic functions considered improve the agreement with the experimental values.

It should be kept in mind that the simple vdW equation of state as well as the extended equation (1.13), which result from a combination of a first order perturbation theory of the long-range interactions with a crude representation of a short-range repulsive effect, ignore completely the higher order contributions of the long-range interactions. However these have a pronounced effect at short distances which cannot be incorporated into the repulsive part. For example they are responsible for the physical clustering property of molecules which as we know leads to very pronounced effects near the critical point of the gas. Thus our reasonable agreement of numerical values of critical constants with experiment is a consequence of compen-

sating errors and cannot be regarded as a test of validity of our approximations.

II. PERTURBATION THEORY

We shall review here briefly the main features of the perturbation theory to be used.³ Most details are given in Ref. 3(b), but we have slightly altered notation and nomenclature in the present discussion.

The basic elements in the perturbation theory are the intramolecular particle correlations of the isolated molecules. These relate to correlations among particles, i.e., electrons and nuclei, inside the molecule at different positions \mathbf{r} in space and at variable imaginary times $t = -i\tau$, where $0 \leq \tau \leq \beta$. Thus the s -particle intramolecular correlation function is given by

$$\begin{aligned} \bar{f}_{\alpha\beta\cdots\sigma}(\mathbf{r}_1, \tau_1, \mathbf{r}_2, \tau_2, \cdots, \mathbf{r}_s, \tau_s) \\ = \bar{z} \text{Tr}[\exp(-\beta\bar{H})\bar{n}_\alpha(\mathbf{r}_1, \tau_1)\bar{n}_\beta(\mathbf{r}_2, \tau_2)\cdots\bar{n}_\sigma(\mathbf{r}_s, \tau_s)], \\ \tau_1 > \tau_2 > \cdots > \tau_s \end{aligned} \quad (2.1)$$

where $\alpha, \beta, \cdots, \sigma$ are the species to which the particles 1, 2, \cdots, s belong respectively, \bar{z} is the activity of the molecule, \bar{H} its Hamiltonian, and $\bar{n}_\alpha(\mathbf{r}, \tau)$ is the Heisenberg representation of the particle density operator⁹ $\bar{n}_\alpha(\mathbf{r})$ thus:

$$n_\alpha(\mathbf{r}, \tau) = \exp(\tau\bar{H})\bar{n}_\alpha(\mathbf{r}) \exp(-\tau\bar{H}). \quad (2.2)$$

Implicit in (2.1) is the omission of the scattering states of the molecule,^{3a} which holds for the molecular model which will be adopted presently.

Multiplying (2.1) by the particles' charges and summing over all particle species, we obtain the intramolecular charge correlation function

$$\begin{aligned} \bar{f}(\mathbf{r}_1, \tau_1, \cdots, \mathbf{r}_s, \tau_s) \\ = \bar{z} \text{Tr}[\exp(-\beta\bar{H})\bar{p}(\mathbf{r}_1, \tau_1)\cdots\bar{p}(\mathbf{r}_s, \tau_s)], \\ \tau_1 > \tau_2 > \cdots > \tau_s, \end{aligned} \quad (2.3)$$

where

$$\bar{p}(\mathbf{r}) = \sum_{\alpha} e_{\alpha}\bar{n}_{\alpha}(\mathbf{r}) \quad (2.4)$$

is the charge density operator, with e_{α} the charge of the particle of type α and the summation extended over all particle species.

Noting that the Hamiltonian of the molecule can be split into a sum of K , the Hamiltonian of the motion of the center of mass, and H , the Hamiltonian of the internal motion of the molecule, we write

$$\bar{H} = K + H$$

in (2.3) and evaluate the partial trace over all states of K . Consequently the translational partition function factors out and we obtain in the particular case of the pair correlation

$$\bar{f}(\mathbf{r}_1, \mathbf{r}_2, \tau) = z f(\mathbf{r}_1, \mathbf{r}_2, \tau), \quad \tau = \tau_1 - \tau_2 \quad (2.5)$$

where the relative activity, or fugacity, z is given by

$$z = \bar{z}\Lambda^{-3} \exp(-\beta E_0) = \bar{z}q, \quad (2.6)$$

with q the molecular partition function for unit volume and E_0 the ground energy level of the internal motion of the molecule and where

$$\begin{aligned} f(\mathbf{r}_1, \mathbf{r}_2, \tau) = \int d\mathbf{R} \text{Tr}\{\exp[-\beta(H - E_0)] \\ \times \rho(\mathbf{r}_1 - \mathbf{R}, \tau)\rho(\mathbf{r}_2 - \mathbf{R})\}, \quad \tau > 0 \end{aligned} \quad (2.7)$$

with $\rho(\mathbf{s})$ [and its Heisenberg representation $\rho(\mathbf{s}, \tau)$] the charge density operator relative to the center of mass of the molecule. For the sake of simplicity we shall consider a molecule consisting only of a central structureless ion and one orbiting electron. In that case H is just the Hamiltonian of the motion of the electron relative to the center of the ion and the matrix elements of $\rho(\mathbf{r})$ become^{2b}

$$\rho_{mn}(\mathbf{r}) = e[\delta_{mn}\delta(\mathbf{r}) - \psi_m^*(\mathbf{r})\psi_n(\mathbf{r})], \quad (2.8)$$

where $\psi_m(\mathbf{r})$ etc. are the eigenfunctions of H and e is the elementary electric charge. In addition we shall restrict ourselves to moderate temperatures where β^{-1} is still sufficiently small compared to the excitation energy of the molecule. In that case we obtain for the integrand in (2.7)

$$f^M(\mathbf{s}_1, \mathbf{s}_2, \tau) = \sum_m \rho_{0m}(\mathbf{s}_1)\rho_{m0}(\mathbf{s}_2) \exp(-\tau E_{0m}) \quad (\tau > 0) \quad (2.9)$$

with

$$E_{0m} = E_m - E_0, \quad (2.10)$$

and we will rewrite (2.7) as

$$f(\mathbf{r}_1, \mathbf{r}_2, \tau) = \int d\mathbf{R} f^M(\mathbf{r}_1 - \mathbf{R}, \mathbf{r}_2 - \mathbf{R}, \tau). \quad (2.11)$$

The function $f^M(\mathbf{s}_1, \mathbf{s}_2, \tau)$ is the intramolecular pair correlation at the two points \mathbf{s}_1 and \mathbf{s}_2 relative to the center of mass of an isolated static molecule. We can split f^M into two terms

$$f^M = f^{0M} + f^{eM}, \quad (2.12)$$

where

$$f^{0M}(\mathbf{s}_1, \mathbf{s}_2) = \rho_{00}(\mathbf{s}_1)\rho_{00}(\mathbf{s}_2) \quad (2.13)$$

is independent of τ and depends only on the static charge density of the molecule, and

$$f^{eM}(\mathbf{s}_1, \mathbf{s}_2, \tau) = \sum_{m \neq 0} \rho_{0m}(\mathbf{s}_1)\rho_{m0}(\mathbf{s}_2) \exp(-\tau E_{0m}), \quad \tau > 0 \quad (2.14)$$

is dependent only on transition charge densities and is a fast decaying function of τ already at $|\tau| \ll \beta$. It is directly connected to the mutual polarizability¹⁰ inside the molecule at imaginary frequencies through its Fourier transform

$$\alpha(\mathbf{r}_1, \mathbf{r}_2, i\omega) = - \int_{-\infty}^{\infty} f^{eM}(\mathbf{r}_1, \mathbf{r}_2, \tau) \exp(i\hbar\tau\omega) d\tau. \quad (2.15)$$

The mutual polarizability is related in turn to the polarizability tensor at imaginary frequency as follows

$$\alpha(i\omega) = -\int \mathbf{r}_1 \mathbf{r}_2 \alpha(\mathbf{r}_1, \mathbf{r}_2, i\omega) d\mathbf{r}_1 d\mathbf{r}_2. \quad (2.16)$$

In the following we shall require also the decomposition of the function f

$$f = f^0 + f^e \quad (2.17)$$

corresponding to the decomposition (2.12) of f^M , in conformity with (2.11):

$$\begin{aligned} f^0(\mathbf{r}_1, \mathbf{r}_2) &= \int d\mathbf{R} f^{0M}(\mathbf{r}_1 - \mathbf{R}, \mathbf{r}_2 - \mathbf{R}), \\ f^e(\mathbf{r}_1, \mathbf{r}_2, \tau) &= \int d\mathbf{R} f^{eM}(\mathbf{r}_1 - \mathbf{R}, \mathbf{r}_2 - \mathbf{R}, \tau). \end{aligned} \quad (2.18)$$

We turn now to examine the perturbation expansion of $\log \Xi$ and pick up the lowest order term from each set of terms representing the interaction of n molecules. As mentioned previously^{3b} such a term is represented by the closed chain diagram for n molecules. The corresponding mathematical expression is

$$\begin{aligned} \frac{\bar{A}_n \bar{z}^n}{(2n)} &= \frac{(-1)^n z^n}{(2n)} \\ &\times \int_0^\beta \cdots \int_0^\beta d\tau_1 \cdots d\tau_n \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_{2n} \\ &\times f_1(\mathbf{r}_1, \mathbf{r}_2, \tau_1 - \tau_2) r_{23}^{-1} f_2(\mathbf{r}_3, \mathbf{r}_4, \tau_2 - \tau_3) r_{45}^{-1} \cdots \\ &\times f_n(\mathbf{r}_{2n-1}, \mathbf{r}_{2n}, \tau_n - \tau_1) r_{2n,1}^{-1}, \end{aligned} \quad (2.19)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Here we have numbered the intramolecular correlation functions as well as the connection points sequentially along the chain: The correlation functions f_i , represented by big circles (e.g., Fig. 1), have each a pair of connecting points \mathbf{r}_{2i-1} , \mathbf{r}_{2i} , and the factors $-r_{2i,2i+1}^{-1}$ represented by an interaction line, connect the two adjacent correlation functions f_i and f_{i+1} . (For $i = n$, put $i+1 = 1$.) The denominator $2n$ in front of (2.19) is the symmetry number of the closed chain diagram of n molecules.

Substituting now (2.17) into (2.19) we obtain a decomposition of \bar{A}_n into a sum of terms. One term contains only the factors f^e in the integrand:

$$\begin{aligned} (-1)^n \int_0^\beta \cdots \int_0^\beta d\tau_1 \cdots d\tau_n \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_{2n} \\ \times f^e(\mathbf{r}_1, \mathbf{r}_2, \tau_1 - \tau_2) r_{23}^{-1} f^e(\mathbf{r}_3, \mathbf{r}_4, \tau_2 - \tau_3) r_{45}^{-1} \cdots \\ \times f^e(\mathbf{r}_{2n-1}, \mathbf{r}_{2n}, \tau_n - \tau_1) r_{2n,1}^{-1}, \end{aligned} \quad (2.20)$$

while in all other terms some of the f^e factors in the integrand are replaced by f^0 . As seen from (2.13) and (2.14) in addition to (2.18), the first term (2.20) includes only transition charge densities and is due^{3b} to dispersion interactions among the n molecules, whereas all other terms include also static charge densities and are due to the static-induced charge interactions among the molecules.

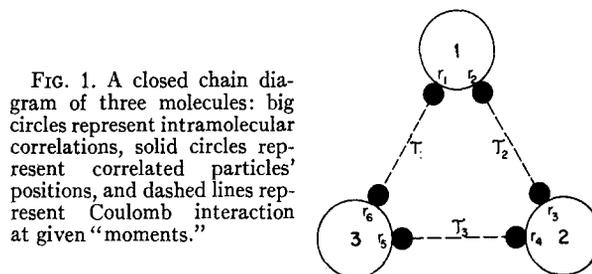


FIG. 1. A closed chain diagram of three molecules: big circles represent intramolecular correlations, solid circles represent correlated particles' positions, and dashed lines represent Coulomb interaction at given "moments."

III. LONG-RANGE INTERACTIONS

Returning to (2.19) and substituting (2.11) into it and using the notation

$$\mathbf{s}_{2i} = \mathbf{r}_{2i} - \mathbf{R}_i, \quad \mathbf{s}_{2i-1} = \mathbf{r}_{2i-1} - \mathbf{R}_i, \quad 1 \leq i \leq n \quad (3.1)$$

we obtain

$$\begin{aligned} A_n &= (-1)^n \int_0^\beta \cdots \int_0^\beta d\tau \cdots d\tau_n \int \cdots \int d\mathbf{R}_1 \cdots d\mathbf{R}_n \\ &\times \int \cdots \int d\mathbf{s}_1 \cdots d\mathbf{s}_{2n} f_1^M(\mathbf{s}_1, \mathbf{s}_2, \tau_1 - \tau_2) r_{23}^{-1} \cdots \\ &\times f_n^M(\mathbf{s}_{2n-1}, \mathbf{s}_{2n}, \tau_n - \tau_1) r_{2n,1}^{-1}, \end{aligned} \quad (3.2)$$

where now

$$r_{2i,2i+1} = |\mathbf{s}_{2i} - \mathbf{s}_{2i+1} + \mathbf{R}_i - \mathbf{R}_{i+1}|, \quad 1 \leq i \leq n. \quad (3.3)$$

In this form the integration over the centers of the molecules is displayed in a way which enables to separate out from \bar{A}_n the long-range contribution. This is done by restricting the domain of integration of the coordinates $\mathbf{R}_1, \cdots, \mathbf{R}_n$ so that the distances $R_{i,i+1} = |\mathbf{R}_i - \mathbf{R}_{i+1}|$ between two interacting molecules shall not be smaller than some fixed length σ . The choice of σ is somewhat arbitrary but must ensure that for $R_{i,i+1} > \sigma$ no appreciable overlap of the wavefunctions of the two molecules occurs. Within the restricted domain of integration of the \mathbf{R}_i we introduce now the dipole approximation for the Coulomb interaction factors $r_{2i,2i+1}^{-1}$ in (3.2). Both this approximation and the restriction on the domain of integration can be combined in the following representation:

$$r_{2i,2i+1}^{-1} = \mathbf{s}_{2i} \cdot T(\mathbf{R}_{i,i+1}) \cdot \mathbf{s}_{2i+1}, \quad (3.4)$$

where the tensor T is given by

$$\begin{aligned} T(\mathbf{R}) &= R^{-3}(I - 3\hat{\mathbf{R}}\hat{\mathbf{R}}), \quad R \geq \sigma \\ &= 0, \quad R < \sigma \end{aligned} \quad (3.5)$$

with I the unit tensor and $\hat{\mathbf{R}}$ the unit vector in the direction of \mathbf{R} . Substituting (3.4) into (3.2) we obtain the long range part of \bar{A}_n :

$$\begin{aligned} A_n &= (-1)^n \int_0^\beta \cdots \int_0^\beta d\tau_1 \cdots d\tau_n \int \cdots \int d\mathbf{R}_1 \cdots d\mathbf{R}_n \\ &\times \text{Tr}[K_1(\tau_1 - \tau_2) T(\mathbf{R}_{12}) \cdots K_n(\tau_n - \tau_1) T(\mathbf{R}_{n1})], \end{aligned} \quad (3.6)$$

where the tensors $K_i(\tau_i - \tau_{i+1})$ are defined by

$$K(\tau) = \iint \mathbf{s}_1 \mathbf{s}_2 f^M(\mathbf{s}_1, \mathbf{s}_2, \tau) d\mathbf{s}_1 d\mathbf{s}_2. \quad (3.7)$$

Noting (2.13) we have, because of the spherically symmetric charge distribution of our simplified molecular model,

$$\int \mathbf{s} \rho_{00}(\mathbf{s}) d\mathbf{s} = 0, \quad (3.8)$$

i.e., the molecule has zero average dipole moment in its ground state. Consequently

$$\iint \mathbf{s}_1 \mathbf{s}_2 f^{0M}(\mathbf{s}_1, \mathbf{s}_2, \tau) d\mathbf{s}_1 d\mathbf{s}_2 = 0, \quad (3.9)$$

and we can equally write instead of (3.7)

$$K(\tau) = \iint \mathbf{s}_1 \mathbf{s}_2 f^{eM}(\mathbf{s}_1, \mathbf{s}_2, \tau) d\mathbf{s}_1 d\mathbf{s}_2. \quad (3.10)$$

Substituting this into (3.6) we obtain the well known result that for spherically symmetric molecules and within the dipole approximation for the Coulomb interaction, the many-molecules-long range interactions are due only to dispersion forces.

The τ integrations can be performed now as done in Ref. 3b, by carrying out one integration from 0 to β and replacing all other integration limits by infinities. The convolution integral is then expressed in terms of Fourier transforms of the integrands. From (3.10), (2.15), and (2.16) it is seen at once that the Fourier transform of $K(\tau)$ is the polarizability tensor at imaginary frequency $\alpha(i\omega)$. Hence we obtain

$$A_n = (-1)^n \beta \frac{\hbar}{2\pi} \int \cdots \int d\mathbf{R}_1 \cdots d\mathbf{R}_n \int_{-\infty}^{\infty} d\omega \times \text{Tr}[\alpha_1(i\omega) T(\mathbf{R}_{12}) \alpha_2(i\omega) T(\mathbf{R}_{23}) \cdots \alpha_n(i\omega) T(\mathbf{R}_{n1})]. \quad (3.11)$$

Because of the isotropy of the molecular model $\alpha(i\omega)$ is a scalar. Hence we can write

$$A_n = (-1)^n \beta \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega [\alpha(i\omega)]^n \int \cdots \int d\mathbf{R}_1 \cdots d\mathbf{R}_n \times \text{Tr}[T(\mathbf{R}_{12}) T(\mathbf{R}_{23}) \cdots T(\mathbf{R}_{n1})]. \quad (3.12)$$

The two expressions, with the integration over molecular centers omitted and without the proportionality constant β , are equal to well known expressions for the long range interaction of n molecules. For the harmonic oscillator (Drude) model of a molecule they coincide with the expression of Bader.⁶ When $n=2$ we have the London dispersion interaction^{2,11} and for $n=3$ we have the famous nonadditive long-range interaction of Axilrod and Teller.^{2,12}

Finally we apply a Fourier transformation from \mathbf{R} to \mathbf{k} variables to the integrand in (3.12). Putting

$$\tilde{T}(\mathbf{k}) = \int T(\mathbf{R}) \exp(i\mathbf{k}\mathbf{R}) d\mathbf{R} \quad (3.13)$$

we have indeed

$$\int \cdots \int d\mathbf{R}_1 \cdots d\mathbf{R}_n \text{Tr}[T(\mathbf{R}_{12}) T(\mathbf{R}_{23}) \cdots T(\mathbf{R}_{n1})] = V / (2\pi)^3 \int d\mathbf{k} \text{Tr}\{\tilde{T}(\mathbf{k})\}^n. \quad (3.14)$$

Taking the z axis to be along the vector \mathbf{k} it follows from (3.13) that all nondiagonal elements of \mathbf{T} vanish and the diagonal elements are given by

$$\tilde{T}_{xx} = \tilde{T}_{yy} = -\frac{1}{2} \tilde{T}_{zz} = -\frac{1}{2} f(k\sigma), \quad (3.15)$$

where $k = |\mathbf{k}|$ and

$$f(x) = (8\pi/x^2) [(\sin x/x) - \cos x] = (8\pi/x) j_1(x), \quad (3.16)$$

with $j_1(x)$ the spherical Bessel function of order 1. Thus we have

$$\text{Tr}[\tilde{T}(\mathbf{k})]^n = [1 + (-1)^n / 2^{n-1}] [f(k\sigma)]^n, \quad (3.17)$$

and substituting this into (3.14) and then into (3.12) we obtain

$$A_n = 2\beta \hbar V (2\pi\sigma)^{-3} \int_{-\infty}^{\infty} d\omega \int_0^{\infty} x^2 dx [(-1)^n + 1/2^{n-1}] \times [\alpha(i\omega) f(x)]^n. \quad (3.18)$$

IV. THE EXTENDED VAN DER WAALS EQUATION

The contribution of all long-range interactions to $\log \bar{Z}$ (or to the pressure) is given by

$$\beta(P - P^0)V = \sum_{n \geq 2} A_n z^n / (2n), \quad (4.1)$$

where P^0 is the contribution of all the remaining terms to the pressure. Assume now that A_n are independent of all other terms contributing to the pressure. Consequently one can view the rhs of (4.1) as a first order correction to $\beta P^0 V$, due to the perturbation of long range interactions. P^0 can be the pressure of any gas where long range interactions are absent. In particular we can take the ideal gas as the unperturbed system. In that case using the thermodynamic relation

$$\rho = z(\partial \beta P / \partial z), \quad (4.2)$$

we obtain from (4.1) (with $\beta P^0 = z$)

$$\rho = z + (2V)^{-1} \sum_{n \geq 2} A_n z^n, \quad (4.3)$$

or, inverting (4.3) into a power series in ρ ,

$$z = \rho - (2V)^{-1} \sum_{n \geq 2} A_n \rho^n \quad (4.4)$$

to first order in the long-range interactions. Substituting (4.4) into (4.1) we have

$$\beta P = \rho - V^{-1} \sum_{n \geq 2} [(n-1)/2n] A_n \rho^n \quad (4.5)$$

to the same order. Similarly we obtain the free energy, to the same order, from the thermodynamic relation

$$\beta F / V = \rho \log \bar{z} - \beta P, \quad (4.6)$$

leading to

$$\beta(F - F^0) / V = -(1/V) \sum_{n \geq 2} (A_n / 2n) \rho^n, \quad (4.7)$$

where, noting (2.6), the ideal gas free energy is given by

$$\beta F^0 / V = \rho(\log \rho - 1 - \log q). \quad (4.8)$$

By our assumption of the independence of the A_n , (4.7) holds for any F^0 not including the long-range interactions.

We can compare now (4.7) with (1.13) and identify the corresponding terms in the power series in the two equations, we have then

$$\beta/(n!) \int U^{(n)}(\mathbf{R}^n) d\mathbf{R}^n = -A_n/(2n). \quad (4.9)$$

Moreover, substituting (3.12) into the rhs of (4.9) we shall identify the integrands on both sides. This leads to the relation

$$U^{(n)}(\mathbf{R}_1, \dots, \mathbf{R}_n) = (-1)^{n+1} \frac{n!}{2n} \text{Tr}\{T(\mathbf{R}_{12}) \dots T(\mathbf{R}_{n1})\} \\ \times \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} [\alpha(i\omega)]^n d\omega. \quad (4.10)$$

Essentially the expression on the rhs is the lowest order (nonadditive) free energy of interaction of n molecules at positions $\mathbf{R}_1, \dots, \mathbf{R}_n$ [note that $n!/(2n)$ is the number of arrangements of the n molecules in a closed chain], where the Coulomb interaction is taken in the dipole approximation. Since we have taken already the zero temperature limit ($\beta^{-1} \ll E_{01}$), (4.10) coincides with the ground state energy of interaction. As mentioned before this expression has been checked in the particular cases $n=2, 3$ and for arbitrary n harmonic oscillators.

In the following section we shall restrict ourselves to the harmonic oscillator (Drude) model and consider mainly the numerical evaluation of the sums in (4.7) and (4.5) and their comparison with the additive interactions contributions—the ρ^2 terms. However, in order to estimate the over-all effect of the nonadditive interactions on the equation of state, we shall adopt van der Waals⁵ approximation for the repulsive part of the pressure, namely

$$\beta P^0 = \frac{\rho}{1 - \rho/\rho_0} \quad (4.11)$$

and correspondingly replace (4.8) by

$$\beta F^0/V = \rho \left[\log \left(\frac{\rho}{1 - \rho/\rho_0} \right) - 1 - \log q \right]. \quad (4.12)$$

Thus we obtain an extended van der Waals equation of state

$$\beta P = \frac{\rho}{1 - \rho/\rho_0} - V^{-1} \sum_{n \geq 2} \frac{n-1}{2n} A_n \rho^n. \quad (4.13)$$

Truncation of the sum at the $n=2$ term reproduces van der Waals' equation, with the same vdW coefficient

$$a = \frac{1}{2} \pi (\hbar \omega_0 / \sigma^3) \alpha^2 \quad (4.14)$$

derived by London¹¹ from his famous formula

$$U^{(2)}(R) = -\frac{3}{4} (\hbar \omega_0 \alpha^2 / R^6). \quad (4.15)$$

V. NUMERICAL RESULTS

Throughout the following we shall take the harmonic oscillator (Drude) model as our molecular model and apply it to the noble gas molecules. Turning first to evaluation of the free energy we substitute (3.18) into (4.7) and carrying out the summation we obtain

$$\frac{\beta(F - F^0)}{V} = \frac{\beta \hbar}{(2\pi\sigma)^3} \int_{-\infty}^{\infty} d\omega \int_0^{\infty} dx x^2 \\ \times \log \{ [1 + \rho \alpha(i\omega) f(x)] [1 - \frac{1}{2} \rho \alpha(i\omega) f(x)] \}, \quad (5.1)$$

with $f(x)$ defined in (3.16) and F^0 given by (4.12). Substituting now the polarizability of the harmonic oscillator model

$$\alpha(i\omega) = \alpha \omega_0^2 / (\omega^2 + \omega_0^2), \quad (5.2)$$

enables us to carry out the ω integration, leading to

$$(F - F^0)/V = -[\hbar \omega_0 / (2\pi)^2 \sigma^3] K(\rho \alpha_0), \quad (5.3)$$

where

$$K(\lambda) = \int_0^{\infty} dx x^2 \{ 3 - [1 + \lambda f(x)]^{1/2} - 2[1 - \frac{1}{2} \lambda f(x)]^{1/2} \}. \quad (5.4)$$

The pressure can be obtained with the aid of the thermodynamic relation

$$P = \rho^2 \frac{\partial [F/(\rho V)]}{\partial \rho},$$

giving

$$P = \frac{\rho k T}{1 - \rho/\rho_0} - \frac{\hbar \omega_0}{(2\pi)^2 \sigma^3} L(\rho \alpha_0), \quad (5.5)$$

where

$$L(\lambda) = \int_0^{\infty} dx x^2 \left(\frac{1 + \frac{1}{2} \lambda f(x)}{[1 + \lambda f(x)]^{1/2}} \right. \\ \left. + 2 \frac{1 - \frac{1}{4} \lambda f(x)}{[1 - \frac{1}{2} \lambda f(x)]^{1/2}} - 3 \right). \quad (5.6)$$

Equations (5.3) and (5.5) contain four constants (in addition to the constants in F^0) whose values must be taken from experiment. Values for the static polarizability α are well known, $\hbar \omega_0$ is usually chosen to be the ionization potential, but there is some arbitrariness in choosing ρ_0 and σ .

Since we are dealing with vdW and "extended" vdW equations the "natural" choice for ρ_0 is N_0/b , where N_0 is the Avogadro number and b is the usual vdW constant. σ is some critical distance, measuring the molecular diameter and such that for larger distances there is no appreciable overlap between two molecules. Its precise value has no effect on the contribution of the nonadditive interactions relative to the additive interactions, to the thermodynamic properties of gases. Consequently we have chosen σ to be the so called vdW

TABLE I. Molecular constants.^a

	$\alpha \times 10^{24}$ (cm ³)	$\hbar\omega_0 \times 10^{12}$ (erg)	$\rho_0 \times 10^{-22}$ (cm ⁻³)	σ (Å)	α^*
Ne	0.39	42.1	3.54	2.38	0.0138
Ar	1.63	28.0	1.88	2.94	0.0306
Kr	2.46	23.5	1.51	3.16	0.0372
Xe	4.00	19.5	1.17	3.44	0.0468

^a Values of the polarizability α and the ionization potential, equated to $\hbar\omega_0$, are taken from H. Margenau and N. R. Kestner, Ref. 2, p. 32. The value of ρ_0 is equal to N_0/b where N_0 is Avogadro's number and b is the vdW constant. For values of b see, e.g., J. R. Partington, *An Advanced Treatise on Physical Chemistry* (Longmans, London, 1949), Vol. 1.

diameter which is defined by

$$\rho_0 = 3/(2\pi\sigma^3). \quad (5.7)$$

Equations (5.3) and (5.5) can be written in a reduced form, with less molecular parameters, by transforming to the reduced variables

$$P^* = P/(\hbar\omega_0\rho_0), \quad F^* = F/(V\rho_0\hbar\omega_0), \\ \rho^* = \rho/\rho_0, \quad T^* = kT/(\hbar\omega_0), \quad \alpha^* = \alpha\rho_0. \quad (5.8)$$

Thus, for the reduced pressure we have

$$P^* = [\rho^*T^*/(1-\rho^*)] - (6\pi)^{-1}L(\alpha^*\rho^*), \quad (5.9)$$

and for the reduced free energy (having omitted E_0 from F^0)

$$F^* = \rho^*T^* \log\{(A/T^{*3/2})[\rho^*/(1-\rho^*)]\} - (6\pi)^{-1}K(\alpha^*\rho^*) \quad (5.10)$$

where

$$A = (2\pi\hbar^2/m\hbar\omega_0)^{3/2}(\rho_0/e)$$

The corresponding vdW equations, which follow from (5.9) and (5.10) by taking the first term in the expansion

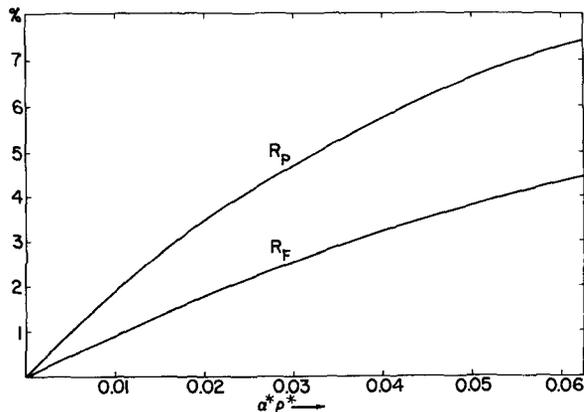


FIG. 2. The relative contribution of nonadditive long-range interactions to the pressure (R_p) and free energy (R_f) of a gas as functions of the reduced polarizability times the reduced density.

of K and L in powers of ρ^* are

$$P^* = [\rho^*T^*/(1-\rho^*)] - (\pi^2/3)(\alpha^*\rho^*)^2, \quad (5.11)$$

$$F^* = \rho^*T^* \log\{(A/T^{*3/2})[\rho^*/(1-\rho^*)]\} - \frac{1}{3}\pi^2(\alpha^*\rho^*)^2. \quad (5.12)$$

The integrals K and L were calculated numerically, for a range of $\alpha^*\rho^*$ sufficiently large to cover all relevant densities including those of the liquid, gas, and critical states of the gases Ne, Ar, Kr, and Xe. The molecular constants for these gases are listed in Table I.

We define relative deviations of nonadditive from additive contributions to the pressure and free energy as

$$R_p(\alpha^*\rho^*) = 1 - [L(\alpha^*\rho^*)/2\pi^3(\alpha^*\rho^*)^2], \quad (5.13)$$

$$R_f(\alpha^*\rho^*) = 1 - [K(\alpha^*\rho^*)/2\pi^3(\alpha^*\rho^*)^2]. \quad (5.14)$$

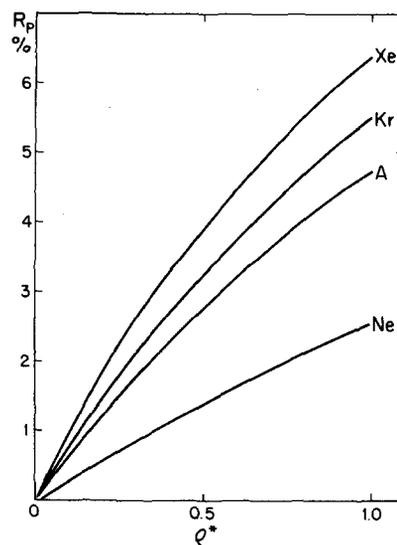


FIG. 3. The relative contribution of nonadditive long-range interactions to the pressure of the noble gases as a function of the reduced density.

For all densities consider L and K are positive¹³ but their values are smaller than that of the vdW term, i.e., R_p and R_f are positive. Hence, the sign of the nonadditive contribution is opposite to that of the additive (vdW) contributions. This qualitative result is in agreement with other results⁷ obtained in an entirely different way which takes into account only three body interactions.

The values of R_f and R_p are plotted (Fig. 2) as functions of $\alpha^*\rho^*$ and for each gas as functions of ρ^* (Fig. 3). It shows that the relative nonadditive effects on the pressure are approximately twice the effects on the free energy. In fact, taking from the sums in (4.5) and (4.7) only the terms corresponding to $n=2$ and 3, it follows from Eqs. (5.13) and (5.14) that $R_p/R_f=2$. The smallness of the deviations from this value, especially for low values of $\alpha^*\rho^*$, may indicate that the

TABLE II. Critical constant for the noble gases.

	T_c (°K)			P_c (atm)			$\rho_c \times 10^{-22}$ (cm ⁻³)		
	Exptl	vdW	Extended vdW	Exptl	vdW	Extended vdW	Exptl	vdW	Extended vdW
Ne	44.5	56.6	54	26	34.2	29.1	1.44	1.18	1.18
Ar	151	185.6	180	48	59.4	56.5	0.80	0.63	0.63
Kr	210	229.0	221	54	59.1	54.9	0.56	0.50	0.50
Xe	290	301.4	290	58	60.2	56.9	0.53	0.39	0.38

nonadditive effects are due mainly to three-body forces. From Figs. 2 and 3 we may estimate the nonadditive effects at various densities for different gases. (The dependence on the kind of gas is only through the reduced polarizability α^* .) Thus, for example, for low densities, i.e., the normal densities of the gases where $\rho^* < 0.01$, the nonadditive effects are negligible (0.2%). Thus in this range the pairwise additivity assumption for the potential energy $U = U_2$ is an excellent approximation. For larger densities, such as the critical density ($\rho^* \sim 1/3$) the effects are of the order of a few percent. [$R_p(\alpha^* \rho_c^*)$ varies from $\sim 1\%$ for Ne to $\sim 3\%$ for Xe.]

These results are of the same order of magnitude as those of Graben and Fowler.⁷

Another fact worth mentioning is that R_F and R_p , i.e., the relative nonadditive effects, increase with increasing reduced polarizability of the gas.

Figure 4 shows some isotherms of Xe, from which one can estimate the nonadditivity effects on the critical constants. Such an estimation is very crude, but qualitatively correct. Table II presents a collection of results obtained from such isotherms for the noble gases, based on equations (5.9) and (5.11).¹⁴

We have no pretence to be able to fit our results to the experimental data, and we think that the similarity between our and the experimental results for T_c and P_c of Xe is only a coincidence.

A comparison may be made with Barker, Henderson, and Smith's⁸ calculations for the effects of three body interactions on critical constants. Their results, which are based on much more sophisticated techniques, agree qualitatively with our results. These show that the addition of nonadditive terms to the additive term in the pressure cause a decrease in ρ_c , P_c , and T_c by a few percent.

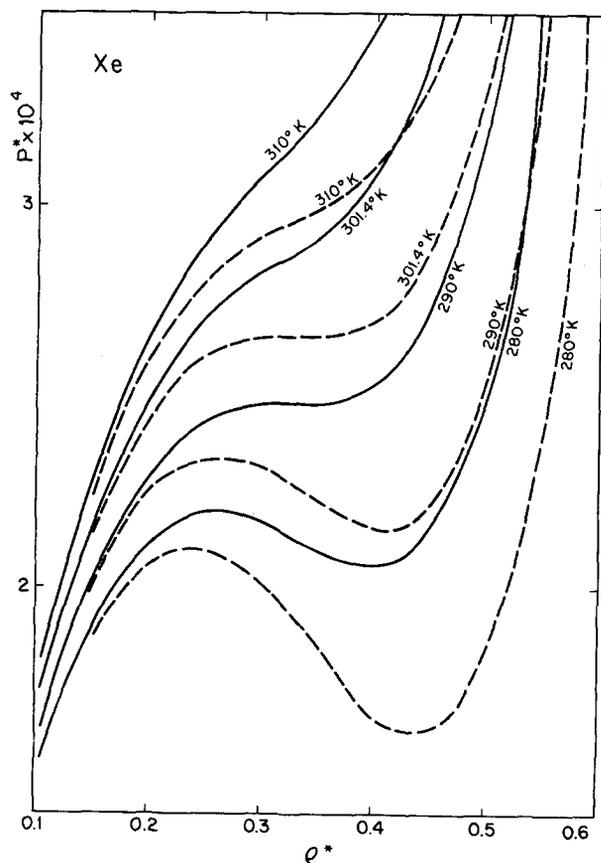


FIG. 4. Isotherms of reduced pressure of Xe vs reduced density according to the vdW (dashed lines) and extended vdW (solid line) equations of state.

¹ Significant contributions of three-body forces to the third virial coefficient were first computed by S. Koba, S. Kaneko, and T. Kihara, *J. Phys. Soc. (Japan)* **11**, 1050 (1956), H. W. Graben and R. D. Present, *Phys. Rev. Letters* **9**, 247 (1962). Conflicting views on the effect of these forces on the structure factor are reported in P. G. Mikolaj and C. J. Pings, *Phys. Rev. Letters* **16**, 4 (1966) and D. Levesque and L. Verlet, *Phys. Rev. Letters* **20**, 905 (1968). The effect of three-body forces on noble gas crystal energies and lattice stability was considered by B. M. Axilrod, *J. Chem. Phys.* **17**, 1349 (1949); **19**, 719, 724 (1951); L. Jansen, *Phys. Rev.* **125**, 1798 (1962); **A135**, 1292 (1964); L. Jansen and E. Lombardi, *Discussions Faraday Soc.* **40**, 78 (1965), but questioned by J. H. Dymond and B. J. Alder, *Chem. Phys. Letters* **2**, 54 (1968) who have fitted solid and gaseous (including third virial coefficient) A data into a pair potential. Many-body potentials were found to contribute significantly to linear lattices by W. L. Bade and J. G. Kirkwood, *J. Chem. Phys.* **27**, 1285 (1957), but are claimed to converge rapidly by S. Doniach, *Phil. Mag.* **8**, 129 (1963).

² See e.g., H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces* (Pergamon, New York, 1969); J. O. Hirschfelder, C. F. Curtiss, and R. B. Byrd, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967).

³ S. Baer, *J. Chem. Phys.* (a) **47**, 2889 (1967); (b) **49**, 3632 (1968).

⁴ This approach had been considered by R. Zwanzig, *J. Chem. Phys.* **22**, 1420 (1954). See also J. A. Barker and D. Henderson, *J. Chem. Phys.* **47**, 2856 (1967).

⁵L. S. Ornstein, dissertation, Leiden, 1908. See also G. E. Uhlenbeck, in *Brandeis Lectures in Theoretical Physics*, 1962, (Benjamin, New York, 1962), Vol. 3.

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⁸J. A. Barker, D. Henderson, and W. R. Smith, *Phys. Rev. Letters* **21**, 134 (1968).

⁹H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* **A235**, 537 (1956).

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¹¹F. London, *Trans. Faraday Soc.* **33**, 8 (1937).

¹²B. M. Axilrod and E. Teller, *J. Chem. Phys.* **11**, 299 (1943); Y. Muto, *Proc. Phys. Soc. (Japan)* **17**, 629 (1943); A. D. McLachlan, *Mol. Phys.* **6**, 423 (1963).

¹³The density for which the integrands in K and L become imaginary is greater even than the solid density.

¹⁴The difference between vdW curves (5.10) and extended vdW curves (5.12) for the free energy is very small.

Interactions between Oppositely Charged Nonspherical Ions. I. Potential Energy Function

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In this paper we apply the theory of Steele to the problem of determining the pairwise interactions between oppositely charged nonspherical ions imbedded in a vacuum. The diatomic model of Sweet and Steele was extended by superimposing at either end of each linear, symmetric rod a Coulombic center characterized by a r^{-1} distance dependence. With respect to the consequent charge-charge interactions, a value of the Onsager coupling parameter was chosen which allowed a more detailed study of the relative importance of Lennard-Jones versus Coulombic forces; in effect, the ions were assumed to be only partially charged. Coefficients in the expansion of the potential energy function were calculated numerically, and changes in the profiles of the resulting curves [$U_{i,v,m}(r)$ as a function of interionic distance] were noted for different values of R/σ (where R is the length of the rod and σ is the usual Lennard-Jones range parameter). The trends observed were compared with those found by Sweet and Steele in their study of the diatomic model.

I. INTRODUCTION

Recently, several authors have drawn attention to the importance of short-range forces in determining the properties of electrolyte solutions.^{1,2} Martynov, in particular, has suggested that in the intermediate-concentration region, the thermodynamic properties of ionic solutions are determined primarily by repulsive forces, with the long-range attractive forces playing a secondary role. In support of this hypothesis, it was pointed out that those theories which fail to take the repulsive forces into account in a proper way (e.g., the Debye-Huckel theory) fail to give a satisfactory description of the thermodynamic properties in this concentration regime. As the first step in a program to investigate the importance of repulsive forces in ionic solutions of intermediate concentration, we have undertaken here a study of pairwise interactions between oppositely charged nonspherical ions. In Sec. II, we introduce the model studied in this paper, making essential use of the theory developed by Steele,³ and using as a guide in the over-all formulation of the problem, the diatomic model of Sweet and Steele.⁴ The general expression for the coefficients which appear in the expansion of the potential energy function is given in this section, as well as a brief discussion

of the methods used in the evaluation of these coefficients. The detailed, rather technical discussion of the various elliptic integrals which arise when Coulombic interactions are considered is relegated to Appendix A. In Sec. III, we present the results of our numerical studies in which the behavior of a number of these coefficients as a function of interionic distance was characterized for different rod lengths. Differences and similarities between our results and those obtained by Sweet and Steele in their numerical study of the diatomic model are indicated. Finally, in Sec. IV, we summarize how the results presented in this paper will be used in developing a theory of ionic solutions in the intermediate concentration region.

II. SPECIFICATION OF THE MODEL

As noted in the Introduction, we shall draw rather extensively on the work of Steele³ and Sweet and Steele.⁴ Accordingly, the reader is referred to these papers for details, and we proceed at once with the specification of the model studied in this paper. Recalling the diatomic model studied in Ref. 4, we superimpose on each of the Lennard-Jones centers at either end of each linear symmetric molecule a Coulombic center. More precisely, to study the pairwise inter-