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New Microscopic Approach to the Statistical Mechanics of Chemical Association

Kåre Olaussen[1,2] **and George Stell**[1,3]

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We consider a new approach to the statistical mechanics of chemical association, $A + B \rightleftharpoons AB$. In principle it is exact, and its thermodynamic basis goes back to Gibbs, but its statistical mechanical implementation in terms of molecular models does not appear to have been given before. For practical computations the success of the method hinges on our ability to calculate the free energy for a mixture of A, B, and AB species, where the species concentrations are regarded as independent. We illustrate the method by analysis of some simple limiting cases.

KEY WORDS: Chemical association; thermodynamic equilibrium condition; law of mass action; sticky spot models; fused-sphere virial coefficients.

1. INTRODUCTION

The problem of chemical association

$$A + B \rightleftharpoons AB$$

in systems dense enough to be out of the law-of-mass-action regime has been investigated in some detail in terms of molecular models during the last two decades.$^{(1-12)}$ Here we develop a new approach. Its thermodynamic basis was given by Gibbs,$^{(13)}$ but its implementation as a recipe for making quantitative predictions in terms of molecular models does not appear to have been previously carried out. In a fundamental statistical mechanical description this system can be viewed as consisting of two atomic species of densities ρ_A^0 and ρ_B^0 (which are independent of what fraction of A and

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[1] Department of Chemistry, State University of New York, Stony Brook, New York 11794.

[2] Permanent address: Institutt for Fysikk, UNIT, N-7034 Trondheim-NTH, Norway.

[3] Department of Mechanical Engineering, State University of New York, Stony Brook, New York 11794.

B atoms we regard as being associated), while for our purposes it is more convenient to view it as a three-species system[14] of densities ρ_A, ρ_B, and ρ_{AB} (which refer to unassociated A and B atoms and associated AB pairs) with

$$\rho_A^0 = \rho_A + \rho_{AB}, \qquad \rho_B^0 = \rho_B + \rho_{AB} \tag{1}$$

In this latter case, however, the densities cannot be varied arbitrarily, but are related through a constant of chemical association,

$$K \equiv \frac{\rho_{AB}}{\rho_A \rho_B} \tag{2}$$

which is among the quantities we want to determine from statistical mechanics. (Actually, K is not a constant, but a temperature-dependent and density-dependent function.) Following Gibbs, we shall determine K by maximizing the Helmholtz free energy. To do this quantitatively, one must have at hand a quantitative assessment of the independent thermodynamics of the three-species system over a whole range of densities ρ_A, ρ_B, and ρ_{AB} for given ρ_A^0 and ρ_B^0. It is the paucity of such input for Hamiltonian models of interest that has probably inhibited the prior development of this approach.

The first obstacle one encounters in approaching the problem is to distinguish—in the many-particle environment—between an AB molecule and two atoms A, B that happen to be close together. From the point of view of chemical binding, these two situations differ with respect to the internal electronic configurations of the atoms involved. This essentially quantum mechanical effect can be mimicked in simple classical terms by the "sticky-spot"[6,7] and related[1,5] models. (Remarkably, the sticky-spot model was already introduced by Boltzmann,[15] long before the advent of atomic physics.) In these models the atoms are given an internal degree of freedom of 4π times an angular orientation $\hat{n}$, and there is an attractive binding energy only when the two atoms are at binding distance, and also are oriented with (say) their internal north poles pointing toward each other to within a certain solid angle. If the region of attraction so defined is made small enough, and if the atoms are otherwise given a hard-core repulsion of sufficient range, only two-atom molecules can be formed. To be precise, we may define a *region of relative attraction* (Boltzmann calls this the *reduced critical space*) as the set where the characteristic function

$$\begin{aligned}\chi_S(\mathbf{r}_i, \hat{n}_i; \mathbf{r}_j, \hat{n}_j) \equiv {} & \Theta(L_+ - r)\, \Theta(r - L_-) \\ & \times \Theta(\hat{n}_i \cdot \hat{r}_{ij} - \cos\theta_0)\, \Theta(\hat{n}_j \cdot \hat{r}_{ji} - \cos\theta_0) \end{aligned} \tag{3}$$

is nonzero. Here $r=|\mathbf{r}_i-\mathbf{r}_j|$, $\hat{r}_{ij}=-\hat{r}_{ji}=(\mathbf{r}_i-\mathbf{r}_j)/r$, with $\mathbf{r}_i$ the center position of atom i. Further, $\hat{n}_i$ is the angular orientation of atom i, and

$$\Theta(x)=\begin{cases}1 & \text{for} \quad x>0\\ 0 & \text{for} \quad x<0\end{cases}$$

With the center position of one atom kept fixed, χ_S is nonzero on a region of volume

$$V_S=(4\pi/3)(L_+^3-L_-^3)(4\pi\sin^2\theta_0/2)^2\equiv(4\pi)^2\,v_S \tag{4}$$

By shrinking V_S to zero in appropriate ways one may obtain the sticky-spot or sticky-point models.

In these models we may thus give a precise definition of an AB molecule as a configuration of atoms A and B that are in their region of relative attraction. There is then no ambiguity problem with respect to what we mean by an AB particle. Of course, the important question is whether the essential physics has been modeled correctly. We believe that this is the case as far as association of monovalent atoms is concerned.

If all aspects of this classical model are taken dead seriously, the contribution to the partition function from the internal degrees of freedom $\hat{n}_i$ that give rise to the atomic association should show up as an additional term in, e.g., the entropy per atom and the specific heat per atom. If the atoms in our model are structureless, however, such contributions will not be present. To compensate for this, the integration over the internal angular variables $\hat{n}_i$ in the partition function should be normalized as

$$\prod_i \frac{1}{4\pi}\int d^2\hat{n}_i$$

and the remaining normalizations should be done in terms of the standard de Broglie thermal wavelengths for structureless particles,

$$\Lambda_{\mathrm{dB}}=\hbar(2\pi/mk_{\mathrm{B}}T)^{1/2}$$

with $\hbar$ Planck's constant (divided by 2π), m the particle mass, and $k_{\mathrm{B}}T$ Boltzmann's constant times temperature.

We may now continue. We must still decide on a reasonable region of attraction, as well as a binding potential in this region. A limiting case is obtained when the region of attraction shrinks to a point, $V_S\to 0$. This leads to a molecule of fixed interatomic distance, which is often a reasonable approximation. However, to get a finite possibility of binding, we then (for entropic reasons) have to scale the binding energy to infinity at the same time. This will in turn lead to a very singular temperature dependence, with all atoms dissociated above a certain temperature, and all associated below that temperature.

At this point it is probably wise to realize that a purely classical approach in any event is bound to be inaccurate. Since the binding of two atoms for accuracy must be described quantum mechanically, the thermodynamics of the resulting molecules is determined by the number of available bound states, their level spacings, and so on. As an example, the specific heat for a two-atomic molecule is typically $\frac{5}{2}k_B$ at room temperature, which means that of the six velocity degrees of freedom in the two bound atoms, one has been frozen out. It is very difficult to account for that in a completely classical model. The conclusion is that we should in any case model the (short-range binding part of the) Boltzmann factor directly, instead of via a classical interatomic binding potential. Thus we let

$$e^{-V(Ai;Bj)/k_B T}\chi_S(Ai;Bj) \to K_0(T)\,\chi_S(Ai;Bj)/v_S \tag{5}$$

where Ai and Bj represent short-hand notation for the coordinates of atoms A and B. Here the factor $K_0(T)$ can be found from quantum mechanical analysis of a single AB molecule. A worthwhile consistency requirement is that it should lead to the correct specific heat, and heat of reaction, in the dilute-gas limit. A reasonable approximation at room temperatures would be of the form

$$K_0(T) = C_0 T^{-1/2} e^{\Delta E/k_B T} \tag{6}$$

where C_0 is temperature independent, with dimensions such that $K_0(T)$ has dimension of volume. (The temperature dependence of the preexponential is chosen such that the specific heat per molecule becomes $\frac{5}{2}k_B$.)

2. MODEL, AND BASIC IDEA OF APPROACH

The considerations in the Introduction lead us to study models of atoms A and B with interactions defined by the Mayer f function,

$$\begin{aligned} f(Ii;Jj) = {} & (1-\delta_{IJ})\,\chi_S(Ii;Jj)\,K_0(T)/v_S \\ & + \begin{cases} -1 & \text{for} \quad r \equiv |\mathbf{r}_i - \mathbf{r}_j| < d/2 \\ \exp[-V_{IJ}(r)/k_B T] & \text{for} \quad r > d/2 \end{cases} \end{aligned} \tag{7}$$

where I, J = A, B. The canonical partition function for this system may now be decomposed according to the number N_{AB} of AB pairs which are in the region of relative attraction. This gives

$$\begin{aligned}
Z(N_A^0, N_B^0) &= \exp\frac{-F_2(N_A^0, N_B^0)}{k_B T} \\
&= \frac{1}{N_A^0!\,N_B^0!}\int \prod_{i=1}^{N_A^0} d^5 z_{Ai} \prod_{j=1}^{N_B^0} d^5 z_{Bj} \prod_{IJi'j'} [1 + f(Ii', Jj')] \\
&= \sum_{N_{AB}} \frac{1}{N_A!\,N_B!\,N_{AB}!}\int \prod_{i=1}^{N_A} d^5 z_{Ai} \prod_{j=1}^{N_B} d^5 z_{Bj} \prod_{k=1}^{N_{AB}} d^{10} z_{ABk} \\
&\quad \times \prod_{IJi'j'} [1 + f^{\text{eff}}(Ii', Jj')] \\
&= \sum_{N_{AB}} Z(N_A^0 - N_{AB}, N_B^0 - N_{AB}, N_{AB}) \\
&= \sum_{N_{AB}} \exp\frac{-F_3(N_A, N_B, N_{AB})}{k_B T}
\end{aligned} \tag{8}$$

where $N_A = N_A^0 - N_{AB}$, $N_B = N_B^0 - N_{AB}$. The combinatorics of the prefactors work out as follows: There are

$$\binom{N_A^0}{N_{AB}} \quad \text{resp.} \quad \binom{N_B^0}{N_{AB}}$$

ways to pick out the reacting atoms, and $N_{AB}!$ ways to combine them into molecules. The Mayer function f^{eff} differs from f in that $f^{\text{eff}}(Ai; Bj) = -1$ when the (unreacted) atoms Ai, Bj are in their region of relative attraction. By this definition we avoid double counting of such configurations.

Further, in (8),

$$\begin{aligned}
d^5 z_{Ii} &= \frac{d^3 r_{Ii}}{\Lambda_{dB}(I)^3}\frac{d^2 \hat{n}_{Ii}}{4\pi}, \qquad I = \text{A, B} \\
d^{10} z_{ABk} &= \frac{d^3 r_{Ak}}{\Lambda_{dB}(A)^3}\frac{d^3 r_{Bk}}{\Lambda_{dB}(B)^3}\frac{d^2 \hat{n}_{Ak}}{4\pi}\frac{d^2 \hat{n}_{Bk}}{4\pi}
\end{aligned} \tag{9}$$

denotes integration over center positions and angular orientations of the particles, with $\Lambda_{dB}(I)$ the de Broglie thermal wavelengths of atoms I = A, B. The ten-dimensional integration over each z_{ABk} can be factorized into an unrestricted three-dimensional integration over the center-of-mass position and a remaining seven-dimensional integration restricted to the region of relative attraction.

In the thermodynamic limit we may approximate the sum in (8) by its largest term, found by differentiating the summand with respect to N_{AB} with fixed N_A^0, N_B^0. This leads to the relation

$$F_2(N_A^0, N_B^0) \simeq F_3(N_A, N_B, N_{AB}) \tag{10}$$

where the densities in the three-species system is determined by the equilibrium condition

$$\mu_{\mathrm{AB}} = \mu_{\mathrm{A}} + \mu_{\mathrm{B}} \tag{11}$$

with

$$\mu_I = \left(\frac{\partial F_3}{\partial N_I}\right)_{T, N_J \neq N_I} \tag{12}$$

The μ_I is the chemical potential of species $I = \mathrm{A, B, AB}$. Thus, the models defined by (7) may really be analyzed as if consisting of three independent species, provided that in the end we impose the condition (11). Furthermore, this approach is exact (for the models considered) to the extent that we are able to compute the free energy $F_3(N_{\mathrm{A}}, N_{\mathrm{B}}, N_{\mathrm{AB}})$ exactly. Of course, in practice we must rely on approximations at this last point.

Equation (12) is also the true chemical potential for the species A, B when we view the system as a two-species system. We have

$$\left(\frac{\partial F_2}{\partial N_I^0}\right) = \left(\frac{\partial F_3}{\partial N_I}\right) - \left(\frac{\partial N_{\mathrm{AB}}}{\partial N_I^0}\right)\left[\left(\frac{\partial F_3}{\partial N_{\mathrm{A}}}\right) + \left(\frac{\partial F_3}{\partial N_{\mathrm{B}}}\right) - \left(\frac{\partial F_3}{\partial N_{\mathrm{AB}}}\right)\right]$$

where the last bracket is zero due to (11). However, variations with respect to the bare densities are not in general that simple. We have that

$$\frac{\partial}{\partial \rho_I^0} = \frac{\partial}{\partial \rho_I} - \frac{\partial \rho_{\mathrm{AB}}}{\partial \rho_I^0}\left(\frac{\partial}{\partial \rho_{\mathrm{A}}} + \frac{\partial}{\partial \rho_{\mathrm{B}}} - \frac{\partial}{\partial \rho_{\mathrm{AB}}}\right) \tag{13}$$

where $(\partial \rho_{\mathrm{AB}}/\partial \rho_I^0)$ can be found by differentiating (11):

$$\left(\frac{\partial \rho_{\mathrm{AB}}}{\partial \rho_I^0}\right) = \frac{(\partial/\partial \rho_I)(\mu_{\mathrm{A}} + \mu_{\mathrm{B}} - \mu_{\mathrm{AB}})}{(\partial/\partial \rho_{\mathrm{A}} + \partial/\partial \rho_{\mathrm{B}} - \partial/\partial \rho_{\mathrm{AB}})(\mu_{\mathrm{A}} + \mu_{\mathrm{B}} - \mu_{\mathrm{AB}})} \tag{14}$$

The extension of this method to systems with more than two species of atoms (as well as reduction to the case of $\mathrm{A} = \mathrm{B}$) is straightforward. The basic equation is

$$\mu_{IJ} = \mu_I + \mu_J \tag{15}$$

for all IJ, if only diatomic molecules can be formed. Actually, Eq. (15) is just a consequence of the thermodynamic fact that the reaction $I + J \rightleftharpoons IJ$ will proceed until the free energy is minimized, and must be true in general (to the extent that it is possible to distinguish between molecules and individual atoms). This viewpoint goes back to Gibbs$^{(13)}$, and was recently enunciated by Pratt and Chandler$^{(2b)}$ as a basis for their interaction-site formalism of association[2a]. The method used in (8) to evaluate the partition function gives a general statistical mechanical justification of this viewpoint, and shows how the relevant thermodynamic potentials can be evaluated outside of chemical equilibrium.

As a further extension, the method may also be refined by considering molecules with different internal degrees of freedom (e.g., different interatomic distances) as being different. This latter viewpoint is in spirit close to the approach taken in ref. 3b.

3. THE LOW-DENSITY LIMIT

As a consistency requirement, our approach must reproduce the law of mass action in the low-density limit. The lowest order free energy per volume unit[4] becomes

$$\frac{f_3^{(0)}}{k_B T} = \rho_A\{\ln[\rho_A \Lambda_{dB}(A)^3] - 1\} + \rho_B\{\ln[\rho_B \Lambda_{dB}(B)^3] - 1\}$$
$$+ \rho_{AB}\{\ln[\rho_{AB}\Lambda_{dB}(A)^3\,\Lambda_{dB}(B)^3/K_0(T)] - 1\} \tag{16}$$

Thus, the equilibrium condition (11) becomes

$$\rho_{AB} = K_0(T)\,\rho_A\,\rho_B \tag{17}$$

which is precisely the law of mass action.

Further, due to (11), the equation of state becomes just the ideal gas result,

$$\frac{p^{(0)}}{k_B T} = -\frac{1}{k_B T}\left(\frac{\partial F}{\partial V}\right)_{T, N_A^0, N_B^0} = \rho_A + \rho_B + \rho_{AB} \tag{18}$$

as does the specific heat,

$$\frac{c_V^{(0)}}{k_B} = -\left(\frac{\partial}{\partial T} T^2 \frac{\partial}{\partial T}\frac{f}{k_B T}\right)_{V, N_A^0, N_B^0}$$
$$= \frac{3}{2}(\rho_A + \rho_B) + \left[3 + \frac{\partial}{\partial T} T^2 \frac{\partial}{\partial T} \ln K_0(T)\right]\rho_{AB} \tag{19}$$

even though the composition of the system changes with temperature and volume.

Although these results are trivial to derive from the point of view of the three-species system, in terms of the bare densities ρ_A^0, ρ_B^0 a rather

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[4] From now on f denotes the free energy per unit volume, not the Mayer f function.

elaborate perturbation expansion is needed.[3a] The reason is that even though all densities are small, the ratios (ρ_A/ρ_A^0), etc., may still be of order 1 if the attractive potential ΔE is strong enough or the temperature is low enough. Thus, to obtain a density expansion which is valid uniformly in temperature, this must be accounted for by an infinite resummation of the perturbation expansion in the bare densities ρ_A^0, ρ_B^0. The present method leads to a density expansion where this resummation is done automatically through use of the equilibrium condition (2).

4. SYSTEMATIC DENSITY EXPANSION

If the potentials $V_{IJ}(r)$ are of short range, so that the integration over the Mayer f bonds converges, we may proceed with a regular density expansion. In terms of the virial expansion for the excess pressure

$$\left(\frac{p}{k_B T} - \sum_I \rho_I\right) = \sum_{IJ} B_2^{IJ}\rho_I\rho_J + \sum_{IJK} B_3^{IJK}\rho_I\rho_J\rho_K + \cdots \tag{20}$$

(where the sums run over I, J, $K =$ A, B, AB), we have the corresponding expansion for the excess free energy

$$\left(\frac{f - f^{(0)}}{k_B T}\right) = \sum_{IJ} B_2^{IJ}\rho_I\rho_J + \frac{1}{2}\sum_{IJK} B_3^{IJK}\rho_I\rho_J\rho_K + \cdots \tag{21}$$

Solving the equilibrium condition (11) now leads to a perturbation expansion for the association constant

$$K = \frac{\rho_{AB}}{\rho_A\rho_B} = K_0 \exp\left[-2\sum_{IJ}(-1)^{[I]} B_2^{IJ}\rho_J - \frac{3}{2}\sum_{IJK}(-1)^{[I]} B_3^{IJK}\rho_J\rho_K + \cdots\right] \tag{22}$$

where the sums again run over I, J, $K =$ A, B, AB, and $[I] = (1, 1, 2)$ for $I = (\text{A, B, AB})$. This expansion shows how the association constant acquires density dependence. The exponential factor is just a perturbative expression for the quantity

$$e^{(\Delta\mu_A + \Delta\mu_B - \Delta\mu_{AB})/k_B T}$$

where the $\Delta\mu_I$ are the excess chemical potentials (i.e., the deviations from the ideal-gas mixture values).

Explicit evaluation of the virial coefficients in general is cumbersome, since, e.g., the computation of $B_2^{AB,AB}$ has about the same complexity as calculating B_4 in a monatomic system. But there is no way to avoid evaluating all three types of virial coefficients (atom–atom, atom–molecule,

molecule–molecule) if we want to have a truly systematic expansion. For a system of hard spheres A and B of diameters

$$d_A = (1+y)d, \qquad d_B = (1-y)d, \qquad -1 \leqslant y \leqslant 1$$

reacting to form fused-sphere diatomic particles AB with center–center distance

$$a = xd, \qquad 0 \leqslant x \leqslant 1$$

it is straightforward to calculate the virial coefficients

$$B_2^{A,A} = \frac{\pi}{6} d^3 (2+2y)^3, \qquad B_2^{A,B} = \frac{\pi}{6} d^3 2^3, \qquad B_2^{B,B} = \frac{\pi}{6} d^3 (2-2y)^3 \tag{23}$$

and

$$\begin{aligned} B_2^{A,AB} &= \frac{\pi}{6} d^3 [1+y+r(x,y,1+y)]^3 \\ B_2^{B,AB} &= \frac{\pi}{6} d^3 [1-y+r(x,y,1-y)]^3 \end{aligned} \tag{24}$$

where $r(x, y, z)$ is defined by the equation

$$[r(x,y,z)+z]^3 = \begin{cases} (1+|y|+z)^3 + \dfrac{1}{2}\left[\dfrac{3}{x}(1+z)^2 - (x+2|y|)\right](x-|y|)^2 \\ \quad \text{for} \quad |y| \leqslant x \leqslant 1 \\ (1+|y|+z)^3 \\ \quad \text{for} \quad 0 \leqslant x \leqslant |y| \end{cases}$$

We have written (24) in a form that suggests that the AB fused-sphere particle can be approximated by a hard sphere of effective diameter $d_{AB}^{\text{eff}} = r(x, y, z)d$. Due to the z dependence of r, the optimal choice for this effective diameter will depend on the situation. For a universal approximation one must decide on which value of z to use. Fortunately, within a reasonable range of parameters, r is rather insensitive to z. We have investigated the ratio $r(x, y, 1+y)/r(x, y, 1-y)$ over the allowed range of parameters $(0 \leqslant x \leqslant 1, -1 \leqslant y \leqslant 1)$, and found it to vary within the range (0.98, 1.02), the largest and smallest values being obtained at $x = 1$, with $y \approx 0.38$ and -0.38, respectively. This is illustrated by Fig. 1, where we plot $r(1, y, z)$ for $z = (1+y, 1, 1-y)$. This gives us confidence that the approximation

$$B_2^{AB,AB} \approx \frac{\pi}{6} d^3 [2r(x, y, 1)]^3$$

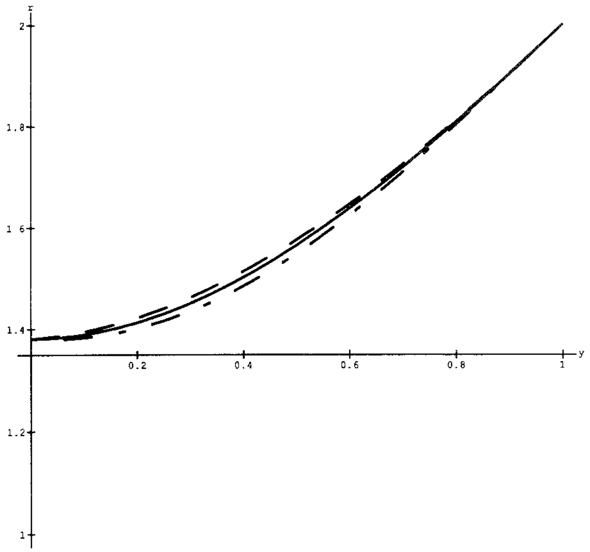

Fig. 1. This figure illustrates how the effective diameter $d_{\mathrm{AB}}^{\mathrm{eff}} = rd$ should vary with the physical situation to which the effective diameter approximation is applied. The ratio $r(x, y, z)$ is plotted for $x = 1$, with $z = 1 + y$ (– –), $z = 1$ (—), and $z = 1 - y$ (- - -). The curves for $r(1, y, 1 \pm y)$ are those which reproduce the correct second virial coefficients $B_2^{\mathrm{AB,A}}$ and $B_2^{\mathrm{AB,B}}$, respectively.

is accurate to the few-percent level. It may also be a reasonable approximation to treat the AB fused sphere as hard sphere of effective diameter

$$d_{\mathrm{AB}}^{\mathrm{eff}} = r(x, y, 1)d$$

throughout the range of fluidlike densities. For equal-diameter atoms the function $r(x, 0, 1)$ is plotted in Fig. 2.

5. FLUID REGIME IN THE HARD-SPHERE APPROXIMATION

The statistical mechanics of a hard-sphere fluid has been extensively studied, to the extent that for many purposes it can be regarded as an exactly known "reference system." We here make use of this knowledge by approximating the AB molecules by hard spheres of effective diameter d_{AB}. As a simple analytic approximation to thermodynamics we adopt the MCSL equation of state for a hard-sphere mixture,(16)

$$\left(\frac{p}{k_{\mathrm{B}} T \rho}\right)_{\mathrm{MSCL}} = \frac{1}{1-\eta} + \frac{3\eta\xi}{(1-\eta)^2} + \frac{(3-\eta)\,\eta^2\zeta}{(1-\eta)^3} \tag{25}$$

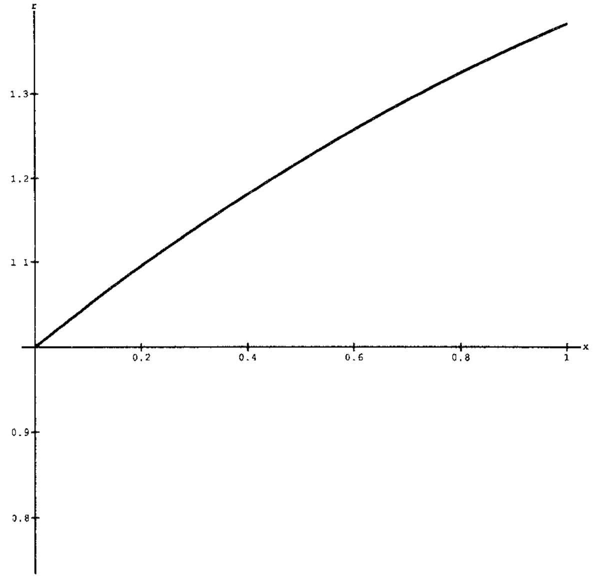

Fig. 2. The effective hard-sphere diameter $d_{\mathrm{AB}}^{\mathrm{eff}}$ for a molecule of equal-size atoms, plotted as a function of the interatomic distance a.

where $\rho = \sum_i \rho_i$ is the total density, and $\eta = (\pi/6) \sum_i \rho_i d_i^3 = (\pi/6)\, \rho \langle d^3 \rangle$ is the filling fraction (with ρ_i the density and d_i the hard-sphere diameter of species i). The remaining dependence upon composition and geometry is encoded in the parameters

$$\xi = \frac{\langle d \rangle \langle d^2 \rangle}{\langle d^3 \rangle}, \qquad \zeta = \frac{\langle d^2 \rangle^3}{\langle d^3 \rangle^2}$$

with

$$\langle d^n \rangle = \sum_i x_i d_i^n, \qquad x_i = \rho_i \Big/ \sum_j \rho_j$$

Equation (25) gives the correct low-density behavior up to (and including) the third virial coefficients. The corresponding expression for the excess free energy is

$$\left(\frac{\Delta f}{k_{\mathrm{B}} T_\rho} \right)_{\mathrm{MSCL}} = (\zeta - 1) \ln(1 - \eta) + \frac{3\eta\xi}{1-\eta} + \frac{\eta\zeta}{(1-\eta)^2} \tag{26}$$

from which the excess chemical potentials can be found to be

$$\left(\frac{\Delta\mu_i}{k_\mathrm{B}T}\right)_\mathrm{MSCL}=\left(1+a_i\eta\frac{\partial}{\partial\eta}+b_i\xi\frac{\partial}{\partial\xi}+c_i\zeta\frac{\partial}{\partial\zeta}\right)\left(\frac{\Delta f}{k_\mathrm{B}T_\rho}\right)_\mathrm{MSCL}$$

$$=-A_i\ln(1-\eta)+\frac{B_i\eta-C_i\eta^2+D_i\eta^3}{(1-\eta)^3}\tag{27}$$

where

$$a_i=\frac{d_i^3}{\langle d^3\rangle},\quad b_i=\frac{d_i}{\langle d\rangle}+\frac{d_i^2}{\langle d^2\rangle}-\frac{d_i^3}{\langle d^3\rangle}-1,\quad c_i=3\frac{d_i^2}{\langle d^2\rangle}-2\frac{d_i^3}{\langle d^3\rangle}-1$$

and

$$\begin{aligned}
A_i&=1-(1+c_i)\zeta\\
&\to\begin{cases}(0,\,1-3r^2+2r^3) & \text{as}\quad x_\mathrm{AB}\to 0\\ (1-3r^{-2}+2r^{-3},\,0) & \text{as}\quad x_\mathrm{AB}\to 1\end{cases}\\
B_i&=a_i+3(1+a_i+b_i)\xi+(1+c_i)\zeta\\
&\to\begin{cases}(8,\,3r+6r^2-r^3) & \text{as}\quad x_\mathrm{AB}\to 0\\ (3r^{-1}+6r^{-2}-r^{-3},\,8) & \text{as}\quad x_\mathrm{AB}\to 1\end{cases}\\
C_i&=2a_i+(6+3a_i+6b_i)\xi+(1-3a_i+c_i)\zeta\\
&\to\begin{cases}(9,\,6r+9r^2-6r^3) & \text{as}\quad x_\mathrm{AB}\to 0\\ (6r^{-1}+9r^{-2}-6r^{-3},\,9) & \text{as}\quad x_\mathrm{AB}\to 1\end{cases}\\
D_i&=a_i+3(1+b_i)\xi-a_i\zeta\\
&\to\begin{cases}(3,\,3r+3r^2-3r^3) & \text{as}\quad x_\mathrm{AB}\to 0\\ (3r^{-1}+3r^{-2}-3r^{-3},\,3) & \text{as}\quad x_\mathrm{AB}\to 1\end{cases}
\end{aligned}\tag{28}$$

Here the limiting cases refer to $i=(\mathrm{A},\mathrm{AB})$, under the assumption that $x_\mathrm{A}=x_\mathrm{B}$, $d_\mathrm{A}=d_\mathrm{B}$, with $r=d_\mathrm{AB}^\mathrm{eff}/d_\mathrm{A}$. To proceed, one must generally resort to numerical calculations. What can be said without numerical work, using the assumptions and results above, is that the association constant is renormalized by a factor

$$\kappa\equiv K/K_0=\exp[(\Delta\mu_\mathrm{A}+\Delta\mu_\mathrm{B}-\Delta\mu_\mathrm{AB})/k_\mathrm{B}T]$$

which varies between asymptotes κ_0 and κ_1, where

$$\begin{aligned}
\ln(\kappa_0)=&\,(1-3r^2+2r^3)\ln(1-\eta_0)\\
&+[(16-3r-6r^2+r^3)\,\eta_0-(18-6r-9r^2+6r^3)\,\eta_0^2\\
&+(6-3r-3r^2+3r^3)\,\eta_0^3]/(1-\eta_0)^3
\end{aligned}\tag{29}$$

and

$$\begin{aligned}\ln(\kappa_1) = {} & (-2 + 6r^{-2} - 4r^{-3}) \ln(1 - \eta_1) \\ & - [(8 - 6r^{-1} - 12r^{-2} + 2r^{-3}) \eta_1 \\ & - (9 - 12r^{-1} - 18r^{-2} + 12r^{-3}) \eta_1^2 \\ & + (3 - 6r^{-1} - 6r^{-2} + 6r^{-3}) \eta_1^3]/(1 - \eta_1)^3 \end{aligned} \tag{30}$$

as the equilibrium shifts between the limits $x_{\mathrm{AB}} = 0$ and $x_{\mathrm{AB}} = 1$. Here we have, in terms of the bare densities, $\eta_0 = (\pi/6)(\rho_{\mathrm{A}}^0 + \rho_{\mathrm{B}}^0)\, d_{\mathrm{A}}^3$ and $\eta_1 = (\pi/6)\, \rho_{\mathrm{A}}^0 (d_{\mathrm{AB}}^{\mathrm{eff}})^3 = \frac{1}{2} r^3 \eta_0$. It should be noted that the two asymptotes cross each other at a sufficiently high density, $\eta_0 = \eta_{0,\mathrm{crit}}$, and that this critical density seems to decrease with increasing effective diameter of the molecule (cf. Figs. 3 and 4).

We can see from Fig. 4 that the two asymptotes κ_0 and κ_1 are essentially equal at lower densities, and that the overlap range may become rather large when the effective diameter of the molecule is appropriate. (In that respect the choice $x = 0.8$ is about optimal; the dependence of K on how far the reaction has proceeded becomes larger again when x is

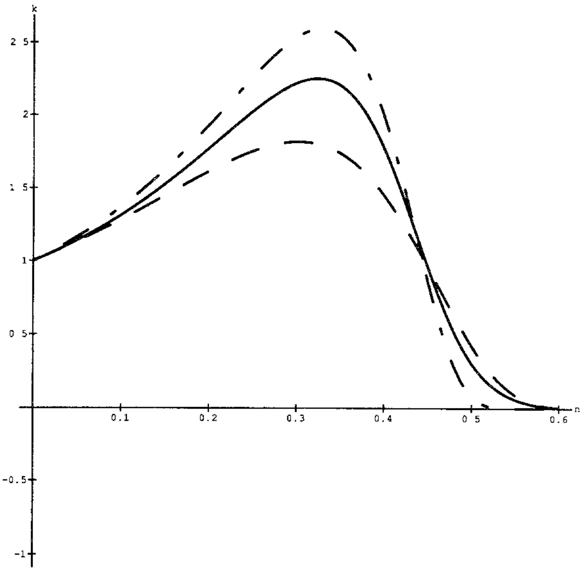

Fig. 3. The renormalization $\kappa = K/K_0$ of the association constant as function of bare density η_0, for a molecule of equal-size atoms, with interatomic distance $a = d$. (—) The behavior at a fixed temperature (for $K_0 d^3 = 14$). (– –) The limiting behavior when the equilibrium is shifted toward $x_{\mathrm{AB}} = 1$; (– – –) the behavior when $x_{\mathrm{AB}} = 0$.

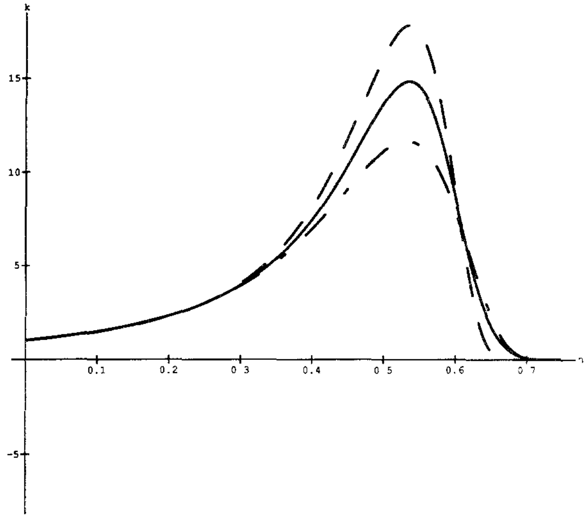

Fig. 4. The same quantities as in Fig. 3, but with interatomic distance $a = 0.8d$.

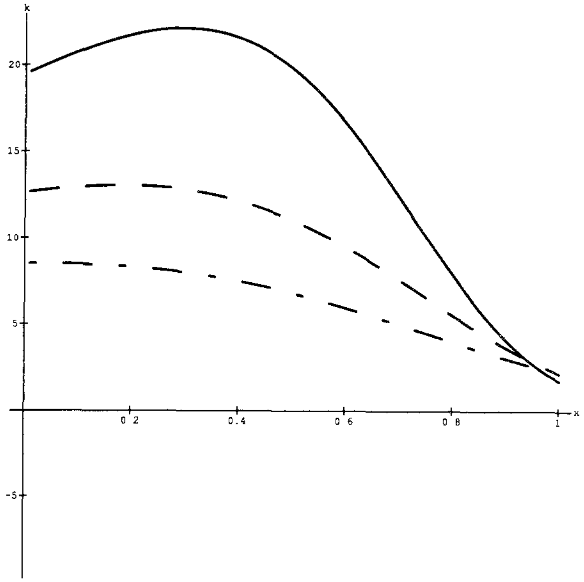

Fig. 5. The renormalization $\kappa = K/K_0$ of the association constant as function of the interatomic distance $a = xd$ of the molecule, at a bare density $\eta_0 = 0.4$ (—), 0.35 (– –), and 0.3 (– – –).

decreased still further.) Such a behavior was essentially built into the approximation used in ref. 12 (cf. ref. 12, Fig. 2). By comparing Figs. 3 and 4, we find that the association constant is rather sensitive to the interatomic distance a. This is due to its exponential dependence on the excess chemical potentials, and the potentially large cancellation which may occur between $\Delta\mu_{\mathrm{A}} + \Delta\mu_{\mathrm{B}}$ and $\Delta\mu_{\mathrm{AB}}$. When $a = d$, this cancellation is essentially complete. The a dependence of K/K_0 is shown in Fig. 5 for $\eta_0 = (0.4, 0.35, 0.3)$. We note the possibility of a phase transition (an "unbinding transition") in our model, of a sort discussed in Ref. 18. We reserve its consideration for a future report.

5. EFFECT OF COULOMB FORCES

If the pair interaction is such that the integrals over the Mayer f bonds fail to converge at large distances, the density corrections become qualitatively different. The canonical example is the case of Coulomb interactions,

$$V_C(\mathbf{r}_i - \mathbf{r}_j) = \frac{Z_i Z_j}{\varepsilon_r} \frac{q^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

with $Z_{i,j}$ the (opposite sign) atomic charges in units of the electron charge, ε_r the relative dielectric constant, and q proportional to the electron charge. [The expression for q^2 is a potential source of confusion, since it depends on the choice of electromagnetic units. It is $q^2 = e^2/4\pi\varepsilon_0$ ($q^2 = e^2$) in SI (CGS) units. Bypassing the necessity of any choice of electromagnetic units, one can write $q^2 = \hbar c/137.04\ldots$, with c the speed of light.] The lowest order density correction to the free energy is then given by (minus) the sum of the ring diagrams,[17]

$$\frac{f^{(\mathrm{R})}}{k_{\mathrm{B}} T} = -\frac{1}{12\pi}\left[\frac{4\pi q^2}{\varepsilon_r k_{\mathrm{B}} T} \sum_I Z_I^2 \rho_I\right]^{3/2} \tag{31}$$

where the sum runs over $I = \mathrm{A}, \mathrm{B}, \mathrm{AB}$, with $Z_{\mathrm{AB}} = Z_{\mathrm{A}} + Z_{\mathrm{B}}$. From this it follows that the density corrections to the constant of chemical association are more dramatic than in the case of short-range forces,

$$K = K_0(T) \exp\left\{-\frac{1}{8\pi}(Z_{\mathrm{A}}^2 + Z_{\mathrm{B}}^2 - Z_{\mathrm{AB}}^2)\left[\left(\frac{4\pi q^2}{\varepsilon_r k_{\mathrm{B}} T}\right)^3 \sum_I Z_I^2 \rho_I\right]^{1/2}\right\} \tag{32}$$

since the suppression is proportional to the square root of density at low densities. This behavior is clearly visible in the numerical results of ref. 12 (cf. ref. 12, Fig. 6). However, its authors analyze a parameter range that is beyond the validity of the ring diagrams. The effect embodied in (32) is an effect that is not accounted for in the Bjerrum theory of electrolytes[19] or in any other theory with an association constant given *a priori*. A simple consequence of this effect is that ρ_{AB} no longer has to increase monotonically with the bare densities. Consider the symmetric case, with $Z_{\mathrm{A}} = -Z_{\mathrm{B}} = Z$ and $\rho_{\mathrm{A}}^0 = \rho_{\mathrm{B}}^0$. Using (14), we then find that

$$\left(\frac{\partial}{\partial \rho_{\mathrm{A}}^0} + \frac{\partial}{\partial \rho_{\mathrm{B}}^0}\right) \rho_{\mathrm{AB}} = 0$$

when the densities of unassociated ions are

$$\rho_{\mathrm{A}} = \rho_{\mathrm{B}} = \frac{8}{\pi} \left(\frac{\varepsilon_r k_{\mathrm{B}} T}{q^2 Z^2}\right)^3 \tag{33}$$

which moves rapidly to lower densities with increasing charge, due to the Z^{-6} factor. However, this must be taken only as a qualitative indication, since we expect contributions beyond the ring diagrams at the densities (33). The reason is that the Coulombic part of the Boltzmann factors is large up to a distance of order the Bjerrum length,

$$b \equiv \left(\frac{q^2 Z^2}{\varepsilon_r k_{\mathrm{B}} T}\right)$$

while in the ring diagrams the approximation

$$e^{\pm b/r} - 1 \approx \pm \frac{b}{r}$$

is made. Thus, the average distance between unassociated particles should be (much) larger than b for this approximation to be good. A quantitative measure is the average number z of particles inside a sphere of radius b. In the case of (33) we find

$$z = \frac{4\pi}{3} (\rho_{\mathrm{A}} + \rho_{\mathrm{B}})\, b^3 = \frac{64}{3}$$

which clearly is not small. We expect results based on (16) and (31) to be reliable in the region where $z \ll 1$ and $(\pi/6)(\rho_{\mathrm{A}}^0 + \rho_{\mathrm{B}}^0)\, d^3 \ll 1$. Since the first condition is based on the density of unassociated ions, which goes to zero as $T \to 0$, it only leads to an additional constraint at intermediate temperatures. Note that the Coulomb interaction between an associated pair must be included in the zeroth-order association constant,

$$K_0(T) \to K_0(T)\, e^{b/a}$$

Also, atoms A and B may now associate without being in their region of relative nonionic attraction (e.g., their "sticky" region), due to their Coulomb attraction.

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