

CHEMICAL ASSOCIATION IN SIMPLE MODELS OF MOLECULAR AND
IONIC FLUIDS: III. THE CAVITY FUNCTION

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April 11, 1991

CEAS Report # 602, April 1991

ABSTRACT

Exact equations which relate the cavity function to excess solvation free energies and equilibrium association constants are rederived by using a thermodynamic cycle. A zeroth-order approximation, derived previously by us as a simple interpolation scheme, is found to be very accurate if the associative bonding occurs on or near the surface of the repulsive core of the interaction potential. If the bonding radius is substantially less than the core radius, the approximation overestimates the association degree and the association constant. For binary association, the zeroth-order approximation is equivalent to the first-order thermodynamic perturbation theory (TPT) of Wertheim. For n-particle

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association, the combination of the zeroth-order approximation with a “linear” approximation (for n -particle distribution functions in term of the 2-particle function) yields the first-order TPT result. Using our exact equations to go beyond TPT, near-exact analytic results for binary hard-sphere association are obtained. Solvent effects on binary hard-sphere association and ionic association are also investigated. A new rule which generalizes Le Chatelier’s principle is used to describe the three distinct forms of behaviours involving solvent effects that we find. The replacement of the dielectric-continuum solvent model by a dipolar hard-sphere model leads to improved agreement with an experimental observation. Finally, an equation of state for an n -particle flexible linear-chain fluid is derived on the basis of a one-parameter approximation that interpolates between the generalized Kirkwood superposition approximation and the linear approximation. A value of the parameter that appears to be near optimal in the context of this application is obtained from comparison with computer-simulation data.

I. INTRODUCTION

This is the third in a series of studies by us on association in simple models of molecular and ionic fluids. The first¹ paper in the series considered a family of models (shielded sticky-shell and sticky-point models in both ionic and non-ionic versions) for which we introduced as simple interpolation scheme (SIS) in order to obtain association constant. In the second paper² of the series, we extended our results in the SIS to the general thermodynamic properties of our models, via the Helmholtz free energy. Here we consider in more detail the central role of the cavity function in our work, using it to further extend our treatment by going beyond the SIS on the basis of certain simple exact identities. We also extend our modeling to the associating pearl necklace model of polymer chains and related n -particle models, $n > 2$.

The cavity function $y_{ij}(r)$ for a pair of particles i and j is defined as $\exp[\beta u_{ij}(r)]g_{ij}(r)$ where $T = 1/k_B\beta$ is the absolute temperature, $u_{ij}(r)$ is the pair potential and $g_{ij}(r)$ is the radial distribution function. It has been shown that the cavity function at $r = 0$ is related to thermodynamic quantities according to zero-separation theorems for an important class of potentials (e.g., hard-sphere potentials³ and hard-core potentials with various tails^{4,5}). More recently, the cavity function has been exactly related to the excess solvation free energy for any type of pair potential.⁶ This new exact relation provides a way to calculate the cavity function easily and accurately if the equation of state for a relevant mixture is accurately known.⁶ The cavity function has also been found to be useful and important in investigating chemical association and molecular fluids.⁷⁻¹⁰

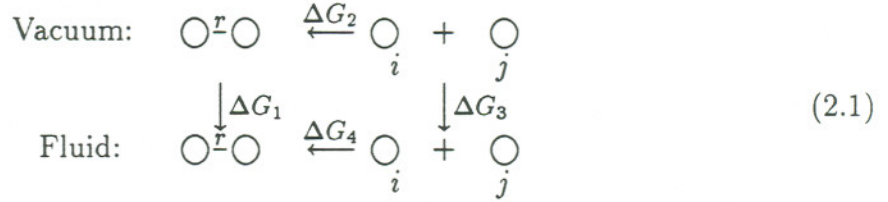
In this paper, we show that recent exact results⁶ for the cavity function can be simply obtained by using the thermodynamic cycle introduced earlier in our own work with Friedman¹² (Section II). Applying a generalized form of the exact result to binary chemical

association, we derive a new exact result which relates the cavity function to the chemical association constant (Section III). This result generalizes an earlier expression due to one of us¹³ and subsequent related results.¹⁰ It turns out that a zeroth-order approximation (in which the cavity function for two nonassociated particles in the presence of both nonassociated and associated particles)⁸⁻¹⁰ is approximated by the cavity function is nearly exact if the association occurs on the surface of the repulsive core of the interactive potential. (For certain special purposes, it is convenient to consider models in which the bonding occurs above the repulsive core surface, and these models are well described by the zeroth-order approximation. We include some representative results here for such cases.) If the bonding is inside the hard core, the zeroth-order approximation tends to overestimate the association degree and association constant. Near-exact analytic results for hard-sphere association are obtained. Solvent effects on hard-sphere association and ionic association are also investigated. A new rule is used to describe the three distinct forms of behaviour involving solvent effects that we find. In Section IV, n -particle association is investigated. We show that the zeroth-order approximation, when combined with a “linear” approximation for higher order cavity functions,¹⁴ yields the result of Wertheim’s first-order thermodynamic perturbation theory (TPT)⁸⁻⁹ when $n > 2$. While the zeroth-order approximation is very accurate for dimerization of hard-core monomers when the association occurs on the surface of the hard core, the first-order TPT is only highly accurate for n -mers ($n \geq 3$) for the association of atoms into a linear molecule, as has been noticed by others.^{8,9} Under the zeroth-order approximation, the thermodynamic properties of the mixture of atoms and molecules, which consists of n atoms, are fully determined by the thermodynamic properties of atomic fluids and the solvation free energy of a single n -atom molecule in the atomic fluid. A recent simulation study has verified this prediction.¹⁵ The approximation appears to be potentially very useful in investigating thermodynamic properties of polymer molecules. Finally a one-parameter equation of

state for a fluid of n -particle flexible chains is obtained that interpolates between the Kirkwood superposition and linear approximation result and compared with simulation data¹⁶ to obtain a near-optimal value of the parameter.

II. THE EXACT EQUATION

We consider a thermodynamic cycle introduced earlier¹²



where ΔG_2 and ΔG_4 are the reversible work needed to bring two particles of species i and j from infinity to distance r apart in a vacuum and in a fluid respectively, ΔG_1 is the Gibbs free-energy change of moving the fixed pair of particles from the vacuum to the fluid, and ΔG_3 is simply the sum of two single-particle excess chemical potentials. As a result, we have

$$\Delta G_3 = \mu_i^{ex} + \mu_j^{ex} \tag{2.2}$$

and

$$\Delta G_1 = \Delta G_4 + \Delta G_3 - \Delta G_2, \tag{2.3}$$

where μ_i^{ex} is the excess chemical potential of particles of species i (over the ideal chemical potential). Note that ΔG_1 can also be regarded as the solvation-free energy of a single pair of particles, one of species i and one of species j , a distance r apart, and can be identified with $\mu^{ex}(r)$, the excess chemical potential associated with such a pair

$$\Delta G_1 = \mu_{ij}^{ex}(r). \tag{2.3b}$$

This $\mu_{ij}^{ex}(r)$ can also be regarded as the excess chemical potential associated with a single diatomic molecule consisting of a pair of particles of different species rigidly held a distance

r apart. This in turn can be thought of as the zero-density limit of the excess chemical potential associated with a species M of such diatomics

$$\mu_{ij}^{ex}(r) = \mu_M^{ex}(r)|_{\rho_M=0} \quad (2.3c)$$

Further, it is easy to see that¹²

$$\Delta G_2 = u_{ij}(r) \quad (2.4)$$

and^{12,17}

$$\Delta G_4 = -k_B T \ln g_{ij}(r). \quad (2.5)$$

Then, from eq.(2.3), we immediately have, according the definition of $y_{ij}(r)$,

$$\ln y_{ij}(r) = \beta[\mu_i^{ex} + \mu_j^{ex} - \mu_M^{ex}(r)|_{\rho_M=0}]. \quad (2.6)$$

For a high-order and angular-dependent cavity function, a similar derivation yields

$$\ln y_{s_1 \dots s_n}^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \beta \left[\sum_{i=1}^n \mu_{s_i}^{ex} - \mu_M^{ex}(s_1 \dots s_n)(\mathbf{r}_1, \dots, \mathbf{r}_n)|_{\rho_M=0} \right] \quad (2.7)$$

where $\mu_{s_i}^{ex}$ is the excess chemical potential for species s_i and $\mu_M^{ex}(s_1 \dots s_n)(\mathbf{r}_1, \dots, \mathbf{r}_n)$ is the excess chemical potential for molecular species $M(s_1 \dots s_n)$, which consists of particles species s_1, s_2, \dots, s_n with the fixed distance and orientation between s_i and s_j , $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $1 \leq i, j \leq n$. Here, $y^{(n)}$ is defined as

$$y_{s_1 \dots s_n}^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \exp \left[\beta \sum_{1 \leq k \leq l \leq n} u_{s_k s_l}(\mathbf{r}_{k,l}) \right] g_{s_1 \dots s_n}^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \quad (2.8)$$

In this section, we have provided a new way to obtain the exact results⁶ (2.6) and (2.7). In the next section, we shall generalize these results to show how the cavity function is related to chemical association.

III. BINARY CHEMICAL ASSOCIATION

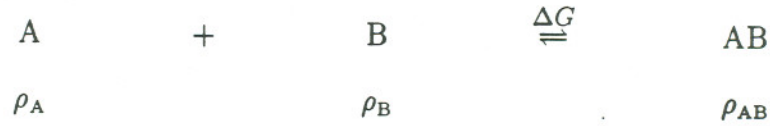
A. General Results

We can immediately generalize (2.6) to the case in which $\rho_M \neq 0$. Following the same reasoning as before we have simply

$$\ln y_{ij}(r) = \beta[\mu_i^{ex} + \mu_j^{ex} - \mu_M^u(r)]. \quad (3.1)$$

where $y_{ij}(r)$ refers to a cavity function for a particle of species i and a particle of species j in the presence of all the other particles of species i , j , and M . We shall now use (3.1) and the equilibrium conditions for the three-component system to which it refers to describe chemical association in a related two-species system consisting of particles of species I and species J that associate into rigid diatomics of species M consisting of pairs of I and J particles rigidly held a distance L apart. The IJ pair potential is to be regarded as identical to the ij pair potential except that it includes an extra associating term that leads to the binding between I and J particles into rigid dimers, indistinguishable from the rigid dimers of i and j particles considered above. We shall designate free (unbound) I particles as A particles, free J particles as B particles and M dimers as AB molecules. Equilibrium configurations of the two-species system consisting of free A particles of density ρ_A , free B particles of density ρ_B and AB dimers of density ρ_{AB} will be indistinguishable from equilibrium configurations of the three-component system of particles of species i density ρ_A , particles of species j of density ρ_B and ij dimers of density ρ_{AB} . This result, which follows immediately from the thermodynamics of association developed by Gibbs, has recently been discussed and rederived by Olaussen and Stell¹⁷ from the standpoint of statistical mechanical models such as those considered here. It was also obtained in the language of associating interaction-site models by Pratt and Chandler.¹¹

For a chemical-association reaction, we have



where ρ_A and ρ_B are the number densities of the unbounded atoms A and B, respectively and ρ_{AB} is the number density of the molecular AB.

Since $\mu_M - \mu_A - \mu_B = 0$ in chemical equilibrium, we have the exact result

$$K/K_0 = y_{AB}(L) \quad (3.2)$$

where we have used the equations

$$\mu_A \equiv \mu_A^\circ + k_B T \ln \rho_A + \mu_A^{ex} \quad (3.3a)$$

$$\mu_B \equiv \mu_B^\circ + k_B T \ln \rho_B + \mu_B^{ex} \quad (3.3b)$$

$$\mu_M \equiv \mu_M^\circ + k_B T \ln \rho_{AB} + \mu_M^{ex} \quad (3.3c)$$

$$-k_B T \ln K_0 \equiv \mu_{AB}^\circ - \mu_A^\circ - \mu_B^\circ \quad (3.3d)$$

$$K \equiv \frac{\rho_{AB}}{\rho_A \rho_B} \quad (3.3e)$$

Here, K is the equilibrium association constant and K_0 is its ideal limiting value. Equation (3.2), which was obtained earlier for some special cases,^{7a,10,13} is an exact equation for chemical reactions when the molecular AB is rigid.

For the equimolar association, we have $\rho_A = \rho_B = \rho_0(1 - \alpha) = \rho_B$, $\rho_{AB} = \alpha\rho_0$ where ρ_0 is total number density of particles A or B (including those associated and unassociated) and α is the association degree. Thus, eq.(3.2) becomes [cf.(3.3e)]

$$K = \frac{\alpha}{\rho_0(1 - \alpha)^2} = K_0 y_{AB}(L) \quad (3.4)$$

where $y_{AB}(L)$ is evaluated for $\rho_A = \rho_B = \rho_0(1 - \alpha)$ and $\rho_{AB} = \alpha\rho_0$. Eq.(3.4) represents an exact equation for the association degree α when K_0 and ρ_0 are given and $y_{AB}(L)$ is known as a function of ρ_A , ρ_B and ρ_{AB} .

Eq.(3.2) can be expanded in terms of the density ρ_{AB} at constant ρ_0

$$K/K_0 = y_{AB}(L)|_{\rho_{AB}=0} + \frac{\partial y_{AB}(L)}{\partial \rho_{AB}}|_{\rho_{AB}=0} \rho_{AB} + \dots \quad (3.5a)$$

The zeroth-order result is

$$K/K_0 \approx y_{AB}(L)|_{\rho_{AB}=0} = y_{AB}^{ref}(L), \quad (3.5b)$$

which is an approximation considered by Chandler and Pratt,¹⁰ and is also the first-order TPT result of Wertheim⁸ as well as the result of our own simple interpolation scheme (SIS).^{1,2} It has been extensively used.⁸⁻¹⁰ Here, *ref* denotes the reference system which contains only fully dissociated non-associative particles.

The following observations may be helpful in connection with (3.5b). Consider a two-species (A and B) mixture. The radial distribution function $g_{AB}^{ref}(r)$ is the equilibrium constant¹⁹ of the process of equilibration involving particles of species A in the bulk and particles of species A found a distance r away from those of species B. Consider next the addition of a third species [molecular $AB(L)$] into the mixture and the removal of pairs of A and B particles such that each pair are approximately a distance L apart. For each such pair removed, insert an AB dimer in its place. (Don't ask about details — this is a heuristic argument.) One expects that $g_{AB}(L)$ will be almost unchanged since each dimer $AB(L)$ is almost indistinguishable from an unassociated pair of atoms A and the atom B that are approximately a distance L apart,²⁰ assuming L is greater than or equal to the sum of atomic radii. Thus one expects the zeroth-order approximation (3.5b) to be accurate if the binding occurs on or above the surface of the hard-core region. And so it proves to be. (If soft-core potentials such as the Lennard-Jones potential are used, one expects that the zeroth-order approximation (3.5b) is accurate as long as L is not small compared to the effective diameter of the repulsive core of the potential.) This

illuminates why Wertheim obtained such excellent results for hard dumbbells for which a “sticky point” is located at contact, when using the first-order TPT.⁸

When the zeroth-order approximation (3.5b) is valid, we also have the following results^{8,2} for the Helmholtz free energy $A(\alpha)$ and the pressure $p(\alpha)$ for the equal binary association

$$\beta[A(\alpha) - A(\alpha = 0)]/N_0 = \frac{\alpha}{2} + \ln(1 - \alpha) \quad (3.6)$$

$$\beta[p(\alpha) - p(\alpha = 0)] = -\alpha\rho_0\left[1 + \rho_0 \frac{d\ln y_{AB}(L, \alpha = 0)}{d\rho_0}\right] \quad (3.7)$$

where $N_0 = 2\rho_0 V^{tot}$. Eq.(3.6) is simply the ideal limit of the excess Helmholtz free energy (over the Helmholtz free energy of the reference system).²¹ Since the Helmholtz free energy $A = G - PV^{tot}$, we have

$$A(\alpha) = \frac{1}{2}N_0(1 - \alpha)(\mu_A + \mu_B) + \frac{1}{2}N_0\alpha\mu_{M_{AB}} - p(\alpha)V^{tot} \quad (3.8)$$

or [cf.(3.3)]

$$\begin{aligned} \beta[A(\alpha) - A(\alpha = 0)]/N_0 = & \ln(1 - \alpha) + \frac{1}{2}\beta[\mu_A^{ex}(\alpha) + \mu_B^{ex}(\alpha) - \mu_A^{ex}(\alpha = 0) - \mu_B^{ex}(\alpha = 0)] \\ & - \frac{\beta[p(\alpha) - p(\alpha = 0)]}{2\rho_0} \end{aligned} \quad (3.9)$$

Eq.(3.9) is an exact equation. When (3.6) is accurate, we should also have

$$\beta[\mu_A^{ex}(\alpha) + \mu_B^{ex}(\alpha) - \mu_A^{ex}(\alpha = 0) - \mu_B^{ex}(\alpha = 0)] - \frac{\beta[p(\alpha) - p(\alpha = 0)]}{2\rho_0} - \frac{\alpha}{2} = 0 \quad (3.10)$$

or [cf.(3.7)]

$$\beta[\mu_A^{ex}(\alpha) + \mu_B^{ex}(\alpha) - \mu_A^{ex}(\alpha = 0) - \mu_B^{ex}(\alpha = 0)] = -\alpha\rho_0 \frac{d\ln y_{AB}(L, \alpha = 0)}{d\rho_0} \quad (3.11)$$

B. Hard-Sphere Association

When $L = \sigma_{AB}$, the zeroth-order approximation of (3.5b) should be very accurate. In Table I, we compare the exact virial coefficients²² for homonuclear hard-dumbbells with the virial coefficients obtained from eq.(3.7) when the exact virial coefficients for hard-spheres is used as input. It turns out that eq.(3.7) indeed gives very accurate B_3 , B_4 , and B_5 .

For the hard-sphere association, $\mu_{M_{AB}}^{ex}$, μ_A^{ex} and μ_B^{ex} can be calculated from the Boublík equation of state^{23,5} and then $y_{AB}(L)$ can be calculated from the exact eq.(3.1) analytically with very high accuracy. In Figs.1-8 we compare the association degree obtained in (3.2) with those obtained in the zeroth-order approximation (3.5b). The figures show that for $L < \sigma_{ij}$, the zeroth-order approximation overestimates the association degree α and the association constant K . When K_0 increases, α increases but K/K_0 decreases. The figures also show that the association degree α appears to be largest when $L = 0$ if K_0 is fixed.

In Fig.9, we investigate the hard-sphere solvent effects on association between hard-spheres with surface attraction at infinite dilution of reacting species. It turns out that there are three distinct regimes of solvent effects as the solvent density is increased: 1) the association constant increases, 2) the association constant decreases, 3) the association constant first increases and then decreases. Chandler and Pratt¹⁰ argued that the increase of the association constant is due to the tendency to save space under the influence of the steric repulsive core effects that lead to attractive potentials of mean force in liquids. However, this cannot explain the other two sorts of solvent effects we observe. All three types of behaviour can be explained in terms of a generalized Le Chatelier's principle:

the chemical equilibrium will shift to the side in which the reacting species is most like the solvent.

When the solvent hard-sphere is smaller than or equal to the reacting hard-spheres in size, one expects $K/K_0 > 1$ since the dumbbell is relatively less like the solvent sphere than the reacting hard sphere. On the other hand, when the solvent hard sphere is much bigger than the reacting hard sphere, one has $K/K_0 < 1$ since the reacting hard sphere is relatively less like the solvent hard-sphere than the dumbbell. Between these two extremes, we have the third kind of behaviour. (At low density, the solvent is more like of fluid of reacting hard spheres, but at the liquid density, the solvent is more like a collection of dumbbells because of the greater number of solvent sphere pairs nearly at contact.) Fig.9 also shows that the reduced association constant K/K_0 is very sensitive to the diameter ratio of the solvent to the reacting sphere. This makes the quantitative comparisons with experiments difficult due to the lack of an accurate means of estimating the diameter of our model molecules when comparing with experimental systems. Some qualitative comparisons have been made elsewhere.^{7,10}

C. Ionic Association: Solvent Effects

The zeroth-order approximation has been applied to the ionic association for the bonding length equal to the closest distance of approach between ions.² According to the arguments in subsection A above, we know that the zeroth-order approximation is very accurate at that bonding length. In this paper we focus on the solvent effects on the charged hard-sphere association.

Consider ionic association in a solvent in the infinitely dilute limit of reacting species. We have [cf.(3.2)]

$$K/K_0 = y_{AB}(L) = y_{AB}^{HS}(L) \exp[\beta(\mu_A^{ele} + \mu_B^{ele} - \mu_M^{ele}(L))] \quad (3.12)$$

where K_0 is the association constant in the ideal gas limit, y_{AB}^{HS} is the hard-core contribution to the cavity function for ionic species A and B, μ_A^{ele} , μ_B^{ele} , and $\mu_{AB}^{ele}(L)$ are the Born

solvation free energy (BSFE)²⁴ for species A, B, and ionic pair AB at a fixed distance L apart, respectively. The single ionic BSFE μ_A^{ele} for a dielectric continuum solvent model is well known.²⁵ It is

$$\mu_A^{ele} = -\frac{q_A^2}{\sigma_A}(1 - 1/\epsilon) \quad (3.13)$$

where q_A and σ_A is the charge and hard-core diameter of ionic species A, respectively, and ϵ is the dielectric constant of the solvent. When $L \geq \sigma_{AB} = (\sigma_A + \sigma_B)/2$, the BSFE of ionic pair at a fixed distance L apart is also well known.²⁵ It is

$$\mu_{MAB}^{ele}(L) = -\left[\frac{q_A^2}{\sigma_A} + \frac{q_B^2}{\sigma_B} + \frac{q_A q_B}{L}\right](1 - 1/\epsilon) \quad (3.14)$$

Therefore, for a continuum solvent model, we have,²⁵

$$\ln\{K/[K_0 y_{AB}^{HS}(L)]\} = \frac{\beta q_A q_B}{L}(1 - 1/\epsilon), \quad L \geq \sigma_{AB} \quad (3.15)$$

From (3.15), $\ln K$ is linearly dependent on $1/\epsilon$.²⁵ For a dipolar hard-sphere solvent model^{12,26-29} and a dipolar dumbbell solvent model,^{12,27-29} the single ionic BSFE^{26,27} and the BSFE for an ionic pair^{12,28} at a fixed distance apart under the mean-spherical approximation have also been obtained analytically for $L \geq \sigma_{AB}$.²⁸ One has

$$\begin{aligned} \mu_{MAB}^{ele}(L) = & -\frac{(1 - 1/\epsilon)}{(\sigma_A + \Delta_s)(\sigma_B + \Delta_s) - [\sigma_A \sigma_B / (2L)]^2} \times \\ & \{[\sigma_A \sigma_B - (\frac{\sigma_A \sigma_B}{2L})^2] (\frac{q_A^2}{\sigma_A} + \frac{q_B^2}{\sigma_B} + \frac{q_A q_B}{\sigma_{AB}}) + [q_A^2 + q_B^2 + \frac{2q_A q_B \sigma_{AB}}{L} + \frac{q_A^2 \sigma_B^2 + q_B^2 \sigma_A^2}{4L^2}] \Delta_s \} \end{aligned} \quad (3.16)$$

where Δ_s reflects the solvent properties.^{12,26-29} For a dipolar hard-sphere solvent, we have³⁰

$$\Delta_s = \frac{3\sigma_s}{f^{1/3} + f^{-1/3} - 2} \quad (3.17a)$$

where σ_s is the diameter of the solvent particles and

$$f = g - \sqrt{g^2 - 1}, \quad g = 1 + 54\sqrt{\epsilon}. \quad (3.17b)$$

Using eq.(3.12), we have for the association constant in a dipolar hard-sphere solvent

$$\ln\{K/[K_0 y_{AB}^{HS}(L)]\} = \beta[\mu_M^{ele}(L = \infty) - \mu_M^{ele}(L)] \quad (3.18)$$

where $\mu_M^{ele}(L)$ satisfies eq.(3.16). When $\sigma_s/\sqrt{\sigma_A\sigma_B} \rightarrow 0$, eq.(3.18) reduces to (3.15) as expected. The $\ln K$ in (3.18) is not linearly dependent on $1/\epsilon$ anymore. However, it still can be approximated as linearly dependent when ϵ is not too large or not too small (Fig.10). When ϵ is large (or small), compared to 1, the linear dependence will underestimate $\ln K$ (or overestimate $-\ln K$, as in Fig.10). This has been observed experimentally.²⁵

When $\sigma/3 \leq L \leq \sigma = \sigma_A = \sigma_B$, the analytical expression for $\mu_M^{ele}(L)$ has also been obtained for dipolar dumbbell and dipolar hard-sphere solvents.²⁹

IV. n-PARTICLE ASSOCIATION

For an n-particle association reaction



it is easy to show that

$$K/K_0 = y_{ABC\dots}^{(n)}(\mathbf{L}_A, \mathbf{L}_B, \dots) = \exp\{\beta[\sum_{i=A,B,\dots}^n \mu_i^{ex} - \mu_{M\dots}^{ex}(\mathbf{L}_A, \mathbf{L}_B, \dots)]\} \quad (4.2)$$

where the n-point cavity function $y^{(n)}$ is evaluated at the locations $\mathbf{L}_A, \mathbf{L}_B, \dots$, of A, B, \dots , that yield the structure of the molecule $M \dots$. Again, $y_{ABC\dots}^{(n)}$ is the n-point cavity for unassociated particles A, B, C, \dots . Using an accurate equation of state for hard-body mixtures,²³ one is able to solve eq.(4.2) numerically to obtain the association degree and the association constant.

Using a similar argument as that already given in Section III, we expect that the zeroth-order approximation

$$K/K_0 = y_{ABC\dots}^{(n)}(\mathbf{L}_A, \mathbf{L}_B, \dots)|_{\rho_{ABC\dots}=0} = [y_{ABC\dots}^{(n)}]^{ref} \quad (4.3)$$

will be very accurate as long as the bonding occurs on or outside the hard-core. We drop the arguments L_i of $y_{ABC\dots}^{(n)}$ for convenience. If the interaction is a soft potential, one expects that the zeroth-order approximation is accurate even when the bonding length is relatively small.

For equal-molar association [$\rho_A = \rho_0(1 - \alpha)$, $\rho_B = \rho_0(1 - \alpha)$, \dots , $\rho_{ABC\dots} = \rho_0\alpha$], the Helmholtz free energy is given by

$$A(\alpha) = \frac{1}{n}N_0(1 - \alpha)(\mu_A + \mu_B + \dots) + \frac{1}{n}N_0\alpha\mu_{ABC\dots} - p(\alpha)V^{tot} \quad (4.4)$$

or [cf.(3.3)]

$$\beta[A(\alpha) - A(\alpha = 0)]/N_0 = \ln(1 - \alpha) + \frac{1}{n}\beta \sum_{i=A,B,\dots} [\mu_i^{ex}(\alpha) - \mu_i^{ex}(\alpha = 0)] - \frac{\beta[p(\alpha) - p(\alpha = 0)]}{n\rho_0} \quad (4.5)$$

where $N_0 = n\rho_0V^{tot}$ is the total number of particles both associated and unassociated. Eq.(4.5) is an exact equation. Since the zeroth-order approximation for the cavity function corresponds to taking the ideal limit of excess Helmholtz free energy (over the Helmholtz free energy of the reference system) for binary association, we assume this is also true for n-particle association. Then, the zeroth-order approximation of eq.(4.5) is (after the ideal limit is taken)

$$\beta[A(\alpha) - A(\alpha = 0)]/N_0 = \ln(1 - \alpha) + \frac{n - 1}{n}\alpha \quad (4.6)$$

When $n = 2$, (4.6) reduces to (3.6). Since

$$p = n\rho_0^2 \frac{\partial(A/N_0)}{\partial\rho_0} \quad (4.7)$$

we find the pressure under the zeroth-order approximation to be

$$\beta[p(\alpha) - p(\alpha = 0)] = -\alpha\rho_0 \left[n - 1 + \rho_0 \frac{d \ln y_{ABC\dots}^{(n)}(\alpha = 0)}{d\rho_0} \right]. \quad (4.8)$$

When $n = 2$, (4.8) reduces to (3.7). It is worth noting that eq. (4.6) and (4.8) are different from the expressions of first-order TPT⁸⁻⁹ when $n \geq 3$. If one uses the “linear” approximation¹⁴ for $y^{(n)}$,

$$y_{ABC\dots}^{(n)} = y_{AB}^{(2)}(L_{AB})y_{BC}^{(2)}(L_{BC})\dots \quad (4.9)$$

eq.(4.8) yields the expression of first-order TPT^{8,9}

$$\beta[p(\alpha) - p(\alpha = 0)] = -\alpha\rho_0(n-1)\left[1 + \rho_0 \frac{d \ln y_{AB}^{(2)}(\alpha = 0)}{d\rho_0}\right] \quad (4.10)$$

when $A = B = C = \dots$ and $L_{AB} = L_{BC} = \dots$. In eq.(4.9), A and B , B and C , etc, are nearest neighbours. For a hard-sphere chain of particles connected pairwise at the sphere surfaces [$(L_{ij} = \sigma_{ij})$, pearl necklace model], eq.(4.10) yields^{8,9} for $\alpha = 1$

$$\frac{\beta p}{n\rho_0} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{(n-1)}{n} \frac{1 + \eta - \eta^2/2}{(1 - \eta)(1 - \eta/2)} \quad (4.11)$$

The Kirkwood superposition approximation (SA)³¹ for $n = 3$ yields

$$y_{ABC}^{(3)} = y_{AB}^{(2)} y_{BC}^{(2)} y_{AC}^{(2)} \quad (4.12)$$

compared with the linear approximation

$$y_{ABC}^{(3)} = y_{AB}^{(2)} y_{BC}^{(2)} \quad (4.13)$$

where $L_{AC} \geq L_{AB}$ and L_{BC} . Since the exact 3-point cavity function can be expected to lie between the SA and the linear approximation¹⁴ in value for such configurations, one expects, for such L_{ij} , $y^{(3)} = [y^{(2)}]^f$ with $3 \geq f \geq 2$. More generally, for $n \geq 3$, one expects

$$y^{(n)} = [y^{(2)}]^{f(n)} \quad (4.14)$$

with $f(n) \geq n - 1$. Eq.(4.14) leads to

$$\frac{\beta p(\alpha)}{n\rho_0} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - \frac{1}{n} \left[n - 1 + f(n) \frac{\eta(5/2 - \eta)}{(1 - \eta/2)(1 - \eta)} \right] \quad (4.15)$$

We find that $f(n) = (8n - 9)/7$ gives a good fit to the available computer simulation data¹⁶ for flexible n-hard-sphere chain (Fig.11).

For the case of unequal molar association, derivations for the zero-order approximation are similar. For the Helmholtz free energy, we have

$$\beta A^{ex} = -N_{ABC\dots} \ln[y_{ABC\dots}^{(n)}]^{ref} + [\beta A^{ex}]^{ref} \quad (4.16)$$

where A^{ex} is the excess free energy over the ideal gas limit, the *ref* denotes the system when the full dissociation is achieved. For the pressure, we have

$$p^{ex} - [p^{ex}]^{ref} = -\rho_{ABC\dots} \rho_0 \frac{d \ln[y_{ABC\dots}^{(n)}]^{ref}}{d \rho_0} \quad (4.17)$$

when ρ is the total number density of system at the full dissociation limit.

Under the zeroth-order approximation (4.3), the thermodynamic properties of atomic and molecular mixtures can be obtained from the thermodynamic properties of atomic mixtures and the solvation free energy of one molecule in the atomic mixture [cf. eqs.(4.6), (4.8) and (2.7)]. This property of the zeroth-order approximation greatly simplifies the calculation of thermodynamic properties of larger molecules such as polymers when the bonding region is on or outside a the hard-core.

Finally, using an accurate equation of state for hard-body mixtures,²² we find that the zeroth-order approximation (4.6) and (4.8) is nearly exact for $n = 3$ for the bonding length $L_{ij} \geq \sigma_{ij}$.

ACKNOWLEDGMENTS

Y. Z. acknowledges the support of the National Science Foundation and G. S. acknowledges the support of the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

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Table I. Comparisons of the exact virial coefficients, the virial coefficients of the Boublík-Nezbeda (BN) equation of state, and the virial coefficients obtained from eq.(3.7) using exact hard-sphere virial coefficients as input for $\alpha = 1$ at $L = \sigma$. Here V_M is the volume of a homonuclear dumbbell.

	B_2/V_M	B_3/V_M^2	B_4/V_M^3	B_5/V_M^4
Exact	5.444	17.04 ± 0.06	34.52 ± 0.35	52.22 ± 1.05
BN	5.5	16.75	32.5	52.75
Eq. (3.7)	5.5	17.0676	34.37	53.62

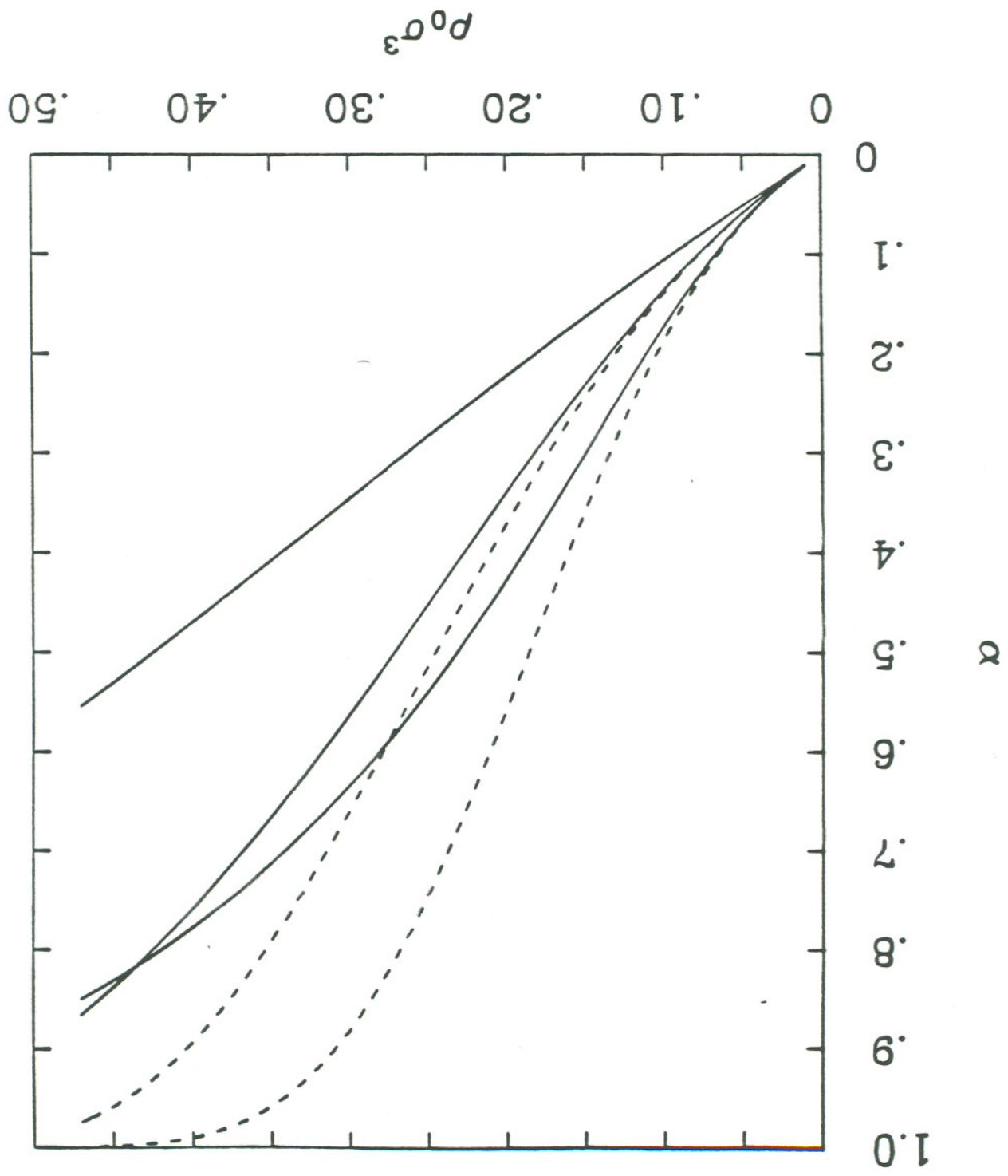
FIGURE CAPTIONS

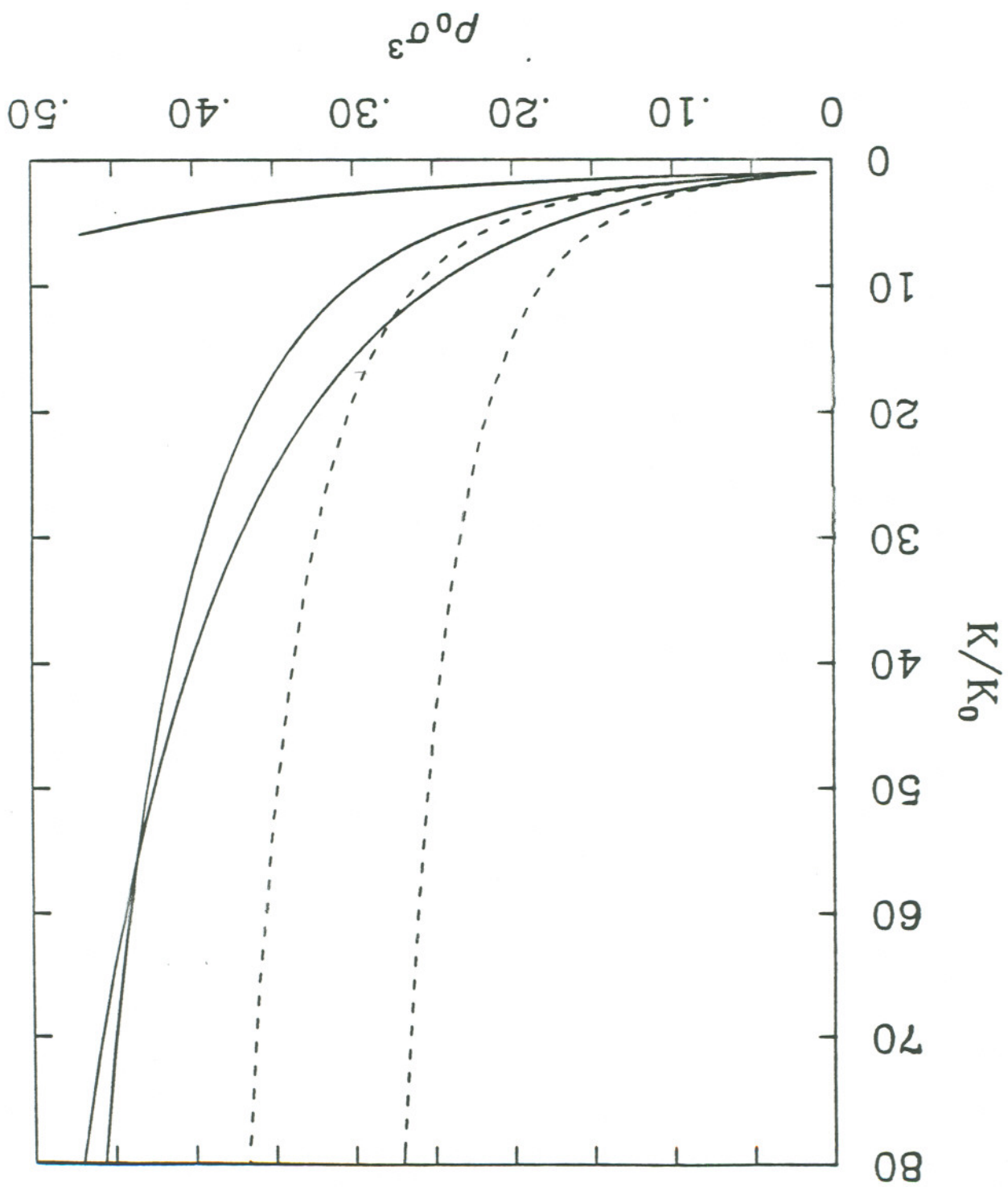
- Fig.1 The association degree α as a function of $\rho_0\sigma^3$ obtained by using Eq.(3.2) (—) and the zeroth-order approximation (- - -). $\sigma_A = \sigma_B = \sigma$, $K_0/\sigma^3 = 1$, $L/\sigma = 1$, 0.5 and 0 from bottom to top at $\rho_0\sigma^3 = 0.3$. For $L/\sigma = 1$, (3.2) and the zeroth-order approximation (3.5b) give indistinguishable results.
- Fig.2 The reduced association constant K/K_0 as a function of $\rho_0\sigma^3$. Symbols and parameters as in Fig.1.
- Fig.3 The association degree α as a function of $\rho_0\sigma^3$. $\sigma_A = \sigma_B = \sigma$, $L/\sigma = 0.5$ and $K_0/\sigma^3 = 1$ and 5 from bottom to top. Symbols as in Fig.1.
- Fig.4 The reduced association constant K/K_0 as a function of $\rho_0\sigma^3$. $K_0/\sigma^3 = 1$ and 5 from top to bottom. Other symbols and parameters as in Fig.3. For the zeroth-order approximation (3.5b) (- - -), K/K_0 is independent of K_0 .
- Fig.5 The association degree α as a function of $\rho_0\sigma_1^3$. $\sigma_A = \sigma_1$, $\sigma_B = 2\sigma_1$, $K_0/\sigma_1^3 = 1$ $L/\sigma_1 = 0$, 0.7 and 1.5 from top to bottom. Symbols as in Fig.1. For $L/\sigma_1 = 1.5$, (3.2) and the zeroth-order approximation (3.5b) give indistinguishable results.
- Fig.6 The reduced association constant K/K_0 as a function of $\rho_0\sigma_1^3$. Symbols and parameters as in Fig.5.
- Fig.7 The association degree α as a function of $\rho_0\sigma_1^3$ at $K_0/\sigma_1^3 = 1$ and $K_0/\sigma_1^3 = 5$ (top curve) respectively. $L/\sigma_1 = 0.7$. Other symbols and parameters as in Fig.5.
- Fig.8 The reduced association constant K/K_0 as a function of $\rho_0\sigma_1^3$ at $K_0/\sigma_1^3 = 1$ and $K_0/\sigma_1^3 = 5$ (bottom curve) respectively. Symbols and parameters as in Fig.7. For the zeroth-order approximation (3.5b) (- - -), K/K_0 is independent of K_0 .
- Fig.9 The reduced association constant K/K_0 as a function of $\rho_s\sigma_s^3$ in a hard-sphere solvent at infinite dilution of reacting species. Here ρ_s and σ_s is the number

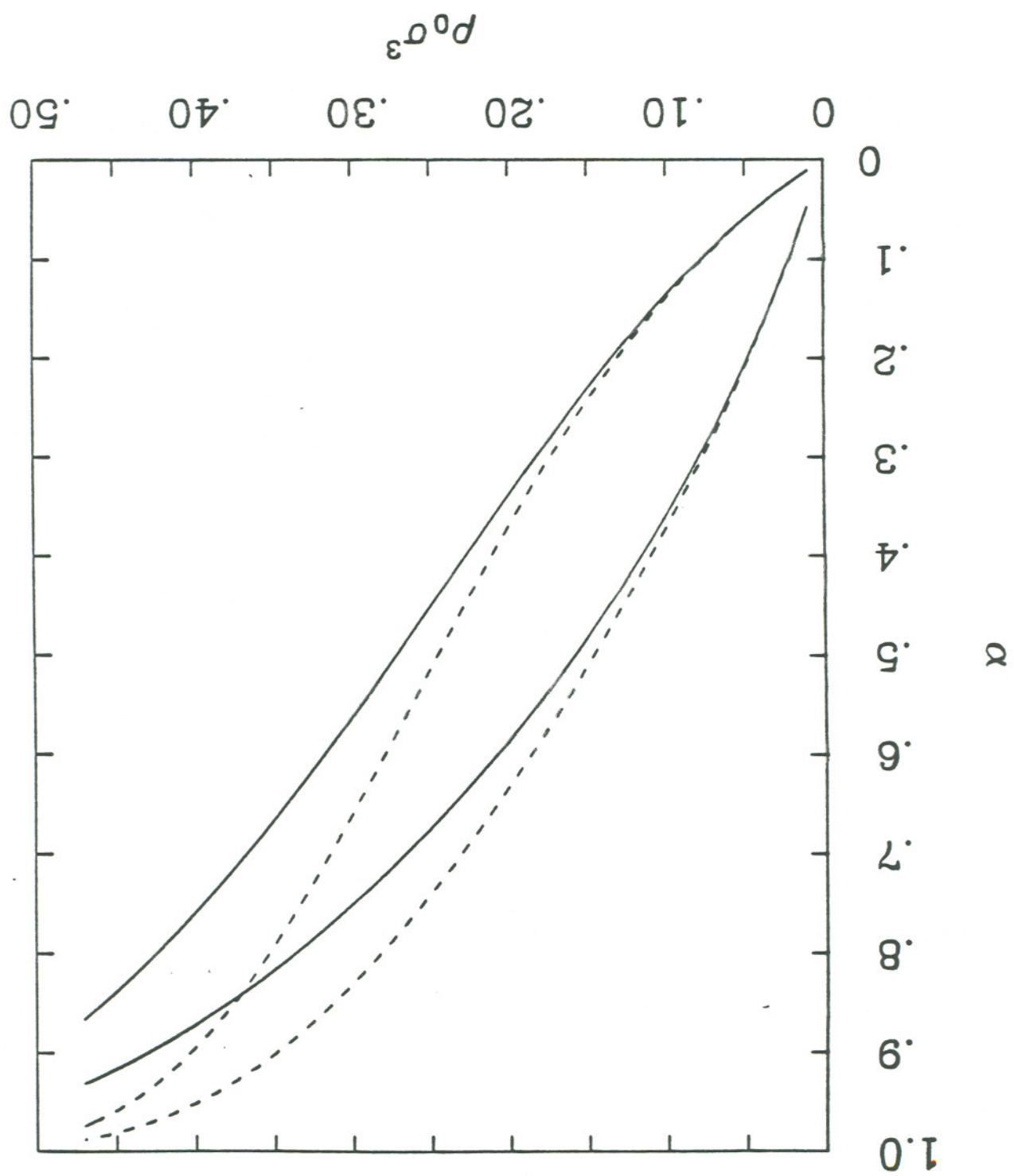
density of solvent and the solvent diameter respectively. $\sigma_A = \sigma_B$, $L/\sigma_A = 0.5$.
 From top to bottom, $\sigma_s/\sigma_A = 1.2, 1.3$, and 2 .

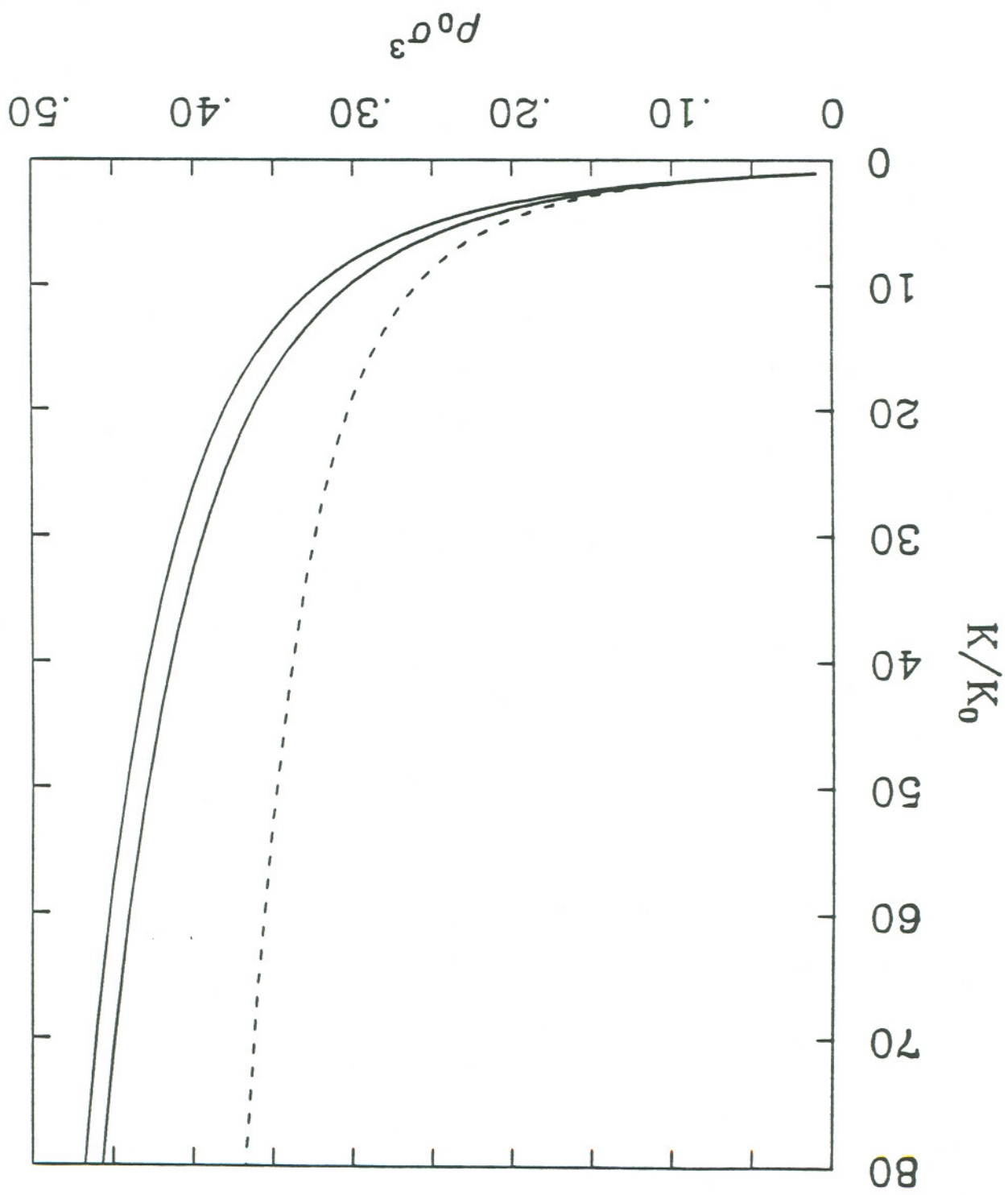
Fig.10 The logarithm of the ionic association constant, $-k_B T \sigma_A / q_A^2 \ln[K/K_0 y^{\text{HS}}(\sigma_{AB})]$, as a function of the inverse of the solvent dielectric constant $1/\epsilon$. Here $\sigma_A = \sigma_B$, $L = \sigma_{AB} = (\sigma_A + \sigma_B)/2$, and the solvent diameter $\sigma_s = \sigma_A/2$. The continuum solvent model (- - -) and the dipolar hard-sphere solvent (—). The solvent diameter has been kept in constant for convenience.

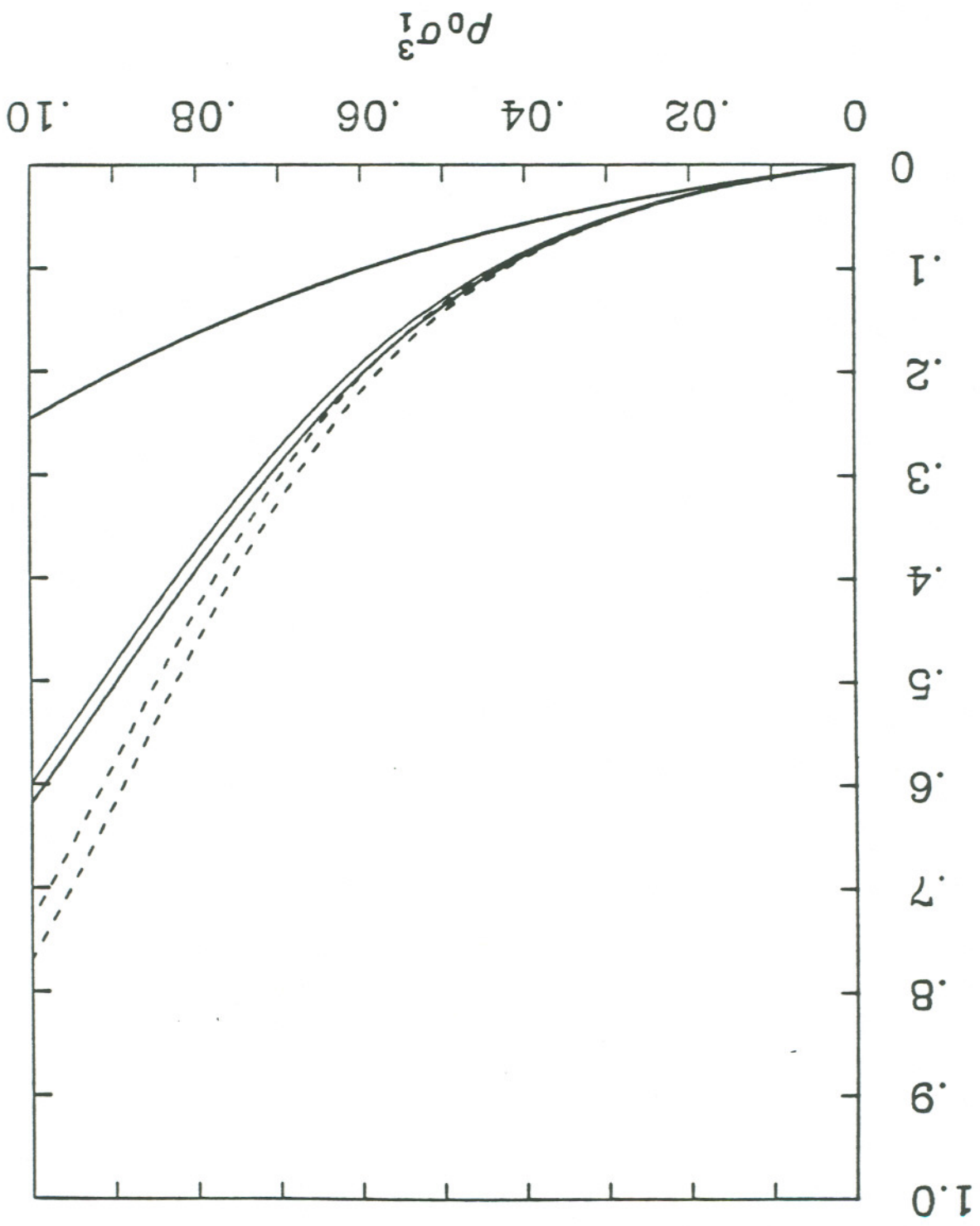
Fig.11 The reduced pressure $\beta p / n \rho_0$ as a function of the volume fraction $\eta = n \pi \rho_0 \sigma^3 / 6$ for chains of $n = 4, 8, 16$ hard spheres. eq.(4.12) (- - -), (4.15) (—), and simulation (Ref.) (●).

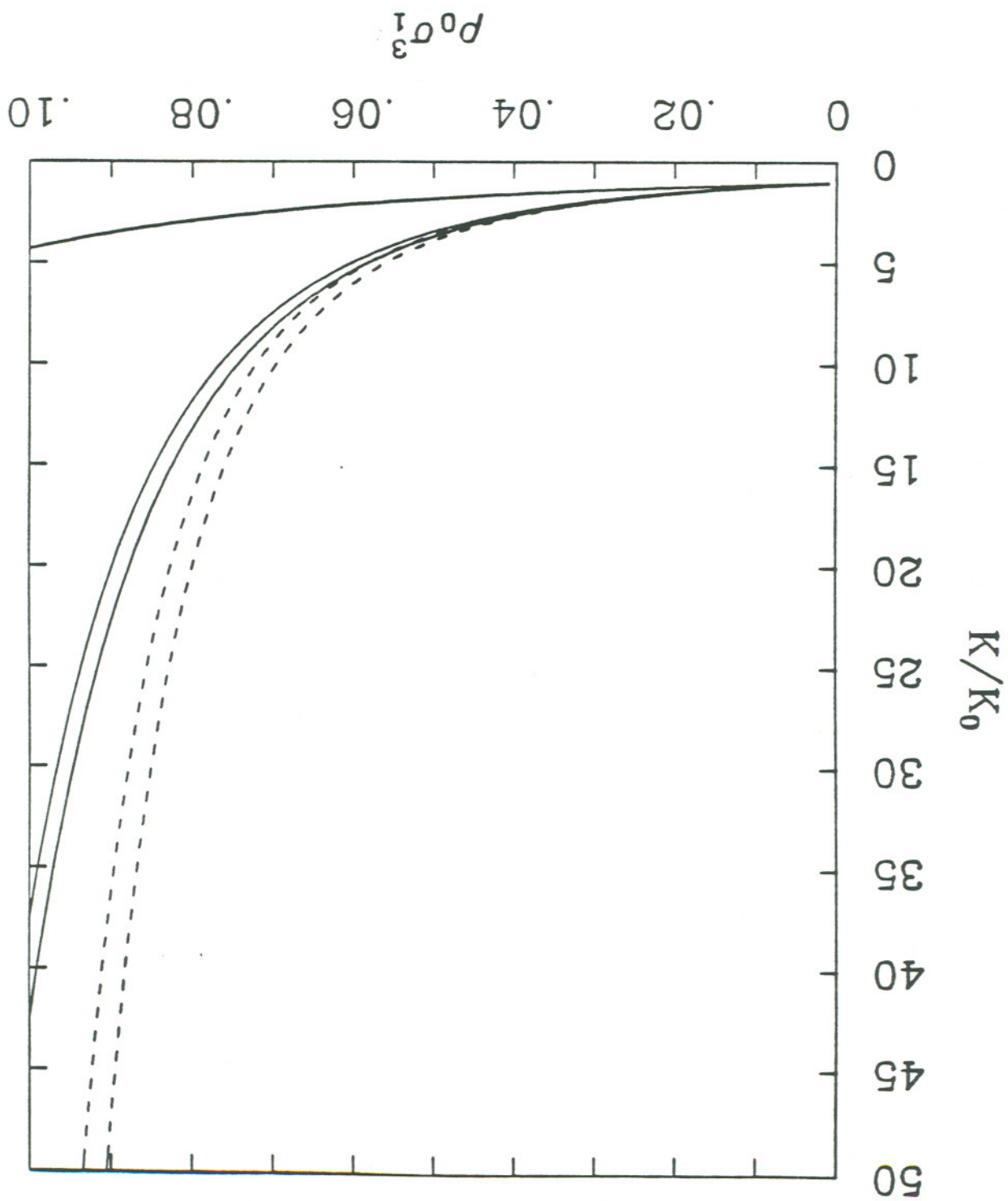


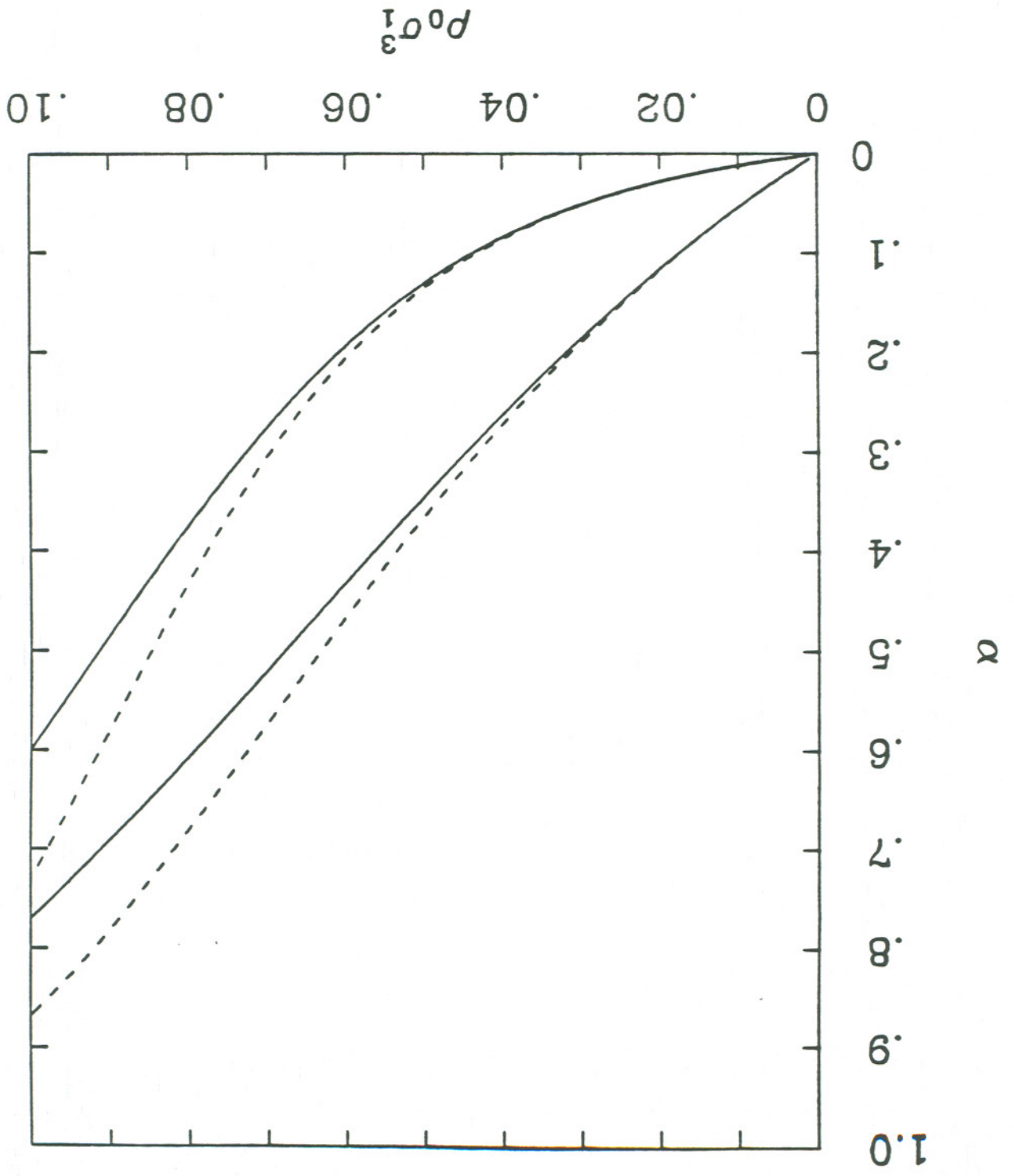


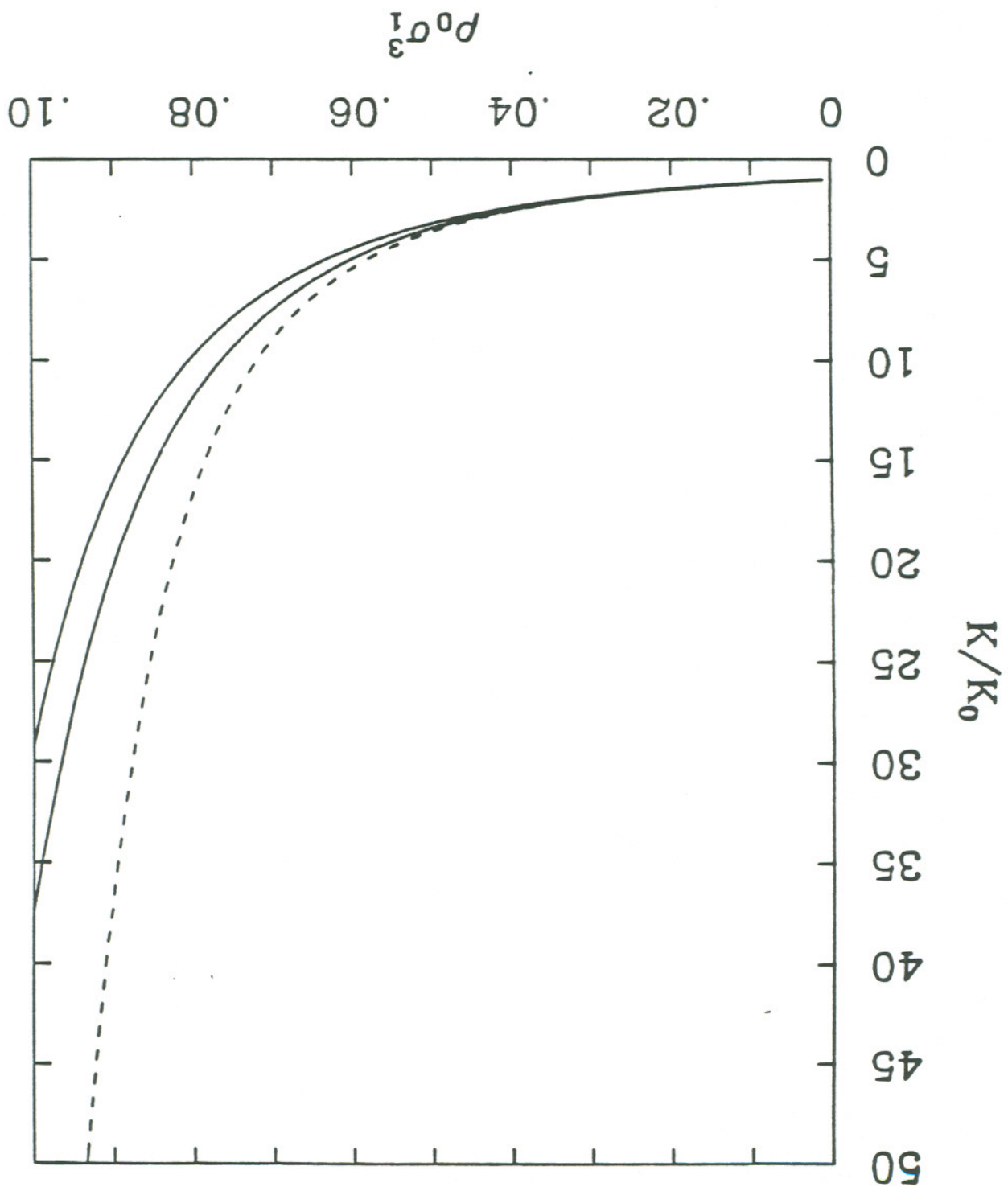












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