Chemical association in simple models of molecular and ionic fluids.

IV. New approximation for the cavity function and an application to the theory of weak electrolytes.

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ABSTRACT

A multiplicative interpolation scheme (MIS) for the cavity function of associating hard-core particles is proposed and applied to the case of our shielded sticky-point model in which the particles associate into fused hard-sphere diatomic molecules (hard dumbbells). The results indicate that the MIS is a significant improvement over the simple interpolation scheme (SIS) of our earlier paper when the bonding length is much less than the hard-core diameter. The MIS is also applied to the case of a weak electrolyte modelled by shielded sticky-point particles that are charged, which associate into hard dipolar dumbbells. Using a near-exact hard-sphere cavity function along with the mean spherical approximation (MSA) for the electrostatic part of the activity coefficient, we find that the resulting version of the MIS is already in reasonable agreement with the experimental data for monochloroacetic acid, despite the equal-diameter restriction of the simple version of the model that we are using.

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I. INTRODUCTION

In our previous paper[1] of this series, the chemical-association constant was found to be directly proportional to the cavity function for particles associating via shielded sticky shell or shielded sticky point interactions. In the zeroth-order approximation the cavity function of the associating particles in the presence of both free and bound particles is approximated by the cavity functions of free particles. This approximation was considered earlier by Chandler and Pratt,[2] and it also follows from the Wertheim's first-order thermodynamic perturbation theory[3] as well as our own simple interpolation scheme (SIS).[4] We have found in previous work that the SIS is nearly exact when the bonding length L is greater than or equal to the hard-core diameter σ. We also found that the SIS is quantitatively useful only if L/σ is greater than about 0.8.

In a recent paper by Rasaiah and Zhu, a different approximation was given for the cavity function.[5] However, we find here that the approximation they suggested is not quantitatively useful since it yields inappropriate asymptotic behaviour of the association constant K relative to the constant in the ideal limit, K_0. Amos and Jackson[6] have also suggested an approximation to improve the cavity function when the bonding length L is less than σ. However, their approximation is only applicable to the fully-associated case such as a dumbbell fluid and we have not compared our new results with theirs.

Changing the reference density so that the cavity function approaches the correct limits at $L = 0$ and $L = \sigma$, is the bases of another approximation that was recently suggested by Kalyuzhnyi, Holovko, and Duda (the KHD approximation).[7] In this paper, we extend their approximation to the unequal-size case, in which the diameters of the particles of the associating species A and B are different, as well as develop new approximations.

In Section II of this paper, the exact limit of cavity function for the binary hard-sphere association when $L \to 0$ is discussed. Two approximations which interpolate between the SIS and the exact limit are developed. One of them is an additive interpolation scheme (AIS) and one of them is a multiplicative interpolation scheme (MIS). In Section III, the two approximations are applied to the shielded sticky-point hard-sphere model. While both approximations significantly improve the SIS, the multiplicative version is found to be more accurate than the additive version. A comparison between these approximations and the KHD approximation[7] indicates that the MIS is somewhat more accurate than the latter, which in turn is a bit more accurate than the AIS. In Section IV, the MIS is applied to ionic association of weak electrolytes. Theoretical results are compared with experimental data for monochloroacetic acid.

II. BINARY CHEMICAL ASSOCIATION

There are two different ways to deal with binary chemical association for our model particles. One way is to consider the system as a hypothetical three-component mixture of nonassociating particles A, particles B, and molecules AB, in thermodynamic equilibrium. Another way is to consider the system as a two-component mixture in which particle A and particle B associate into rigid diatoms of species M consisting of pairs of particle A and B rigidly held a distance L apart. In this paper, we will use the three-component approach only.

For a chemical-association reaction, we have

$$ \mathrm{A} \quad + \quad \mathrm{B} \quad \overset{\Delta G}{\rightleftharpoons} \quad \mathrm{AB} \qquad (2.1) $$
$$ \rho_{\mathrm{A}} \qquad\qquad \rho_{\mathrm{B}} \qquad\qquad \rho_{\mathrm{AB}} $$

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

At chemical equilibrium, we have the exact result[1]

$$K/K_0 = y_{AB}(L) \tag{2.2}$$

where $y_{AB}(L)$ is the cavity function of free particles A and B, K is the association constant defined as

$$K = \frac{\rho_{AB}}{\rho_A \rho_B} \tag{2.3}$$

and K_0 is the association constant at the infinite dilution of reacting species. We note that the y_{IJ} of ref. [1] is the y_{AB} of this one, and is $(1-\alpha)^2$ times the y_{AB} of ref. [4]. We also note that the phrase "in the linear approximation" in footnote [18] of [1] referring to the relation among the y's is unnecessary.

For simplicity, we shall consider only equimolar association where we have $\rho_A = \rho_B = \rho_0(1-\alpha)$ and $\rho_{AB} = \alpha\rho_0$. Here ρ_0 is the total number for particle A or B (both free and bound particles) and α is the association degree. Then, we have [cf eq.(2.3) and eq.(2.2)]

$$K = \frac{\alpha}{\rho_0(1-\alpha)^2} = K_0 y_{AB}(L) \tag{2.4}$$

where y_{AB} is evaluated for $\rho_A = \rho_B = \rho_0(1-\alpha)$ and $\rho_{AB} = \alpha\rho_0$. The equation can be exactly solved for α once the cavity function y_{AB} and K_0 are known.

The cavity function $y_{AB}(L)$ can be expanded in terms of molecular density ρ_{AB} at the constant total number density ρ_0

$$K/K_0 = y_{AB}(L) = y_{AB}(L)|_{\rho_{AB}=0} + (\frac{\partial y_{AB}(L)}{\partial \rho_{AB}}|_{\rho_{AB}=0})\rho_{AB} + \cdots \tag{2.5}$$

The zeroth-order approximation or the SIS is

$$K/K_0 = y_{AB}(L) = y_{AB}(L)|_{\rho_{AB}=0} = y_{AB}^{ref}(L, \rho_0, \rho_0). \tag{2.6}$$

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where ref denotes the reference system which contains only fully dissociated nonassociating particles ($\alpha=0$) and $y_{AB}^{ref}(L, \rho_A, \rho_B)$ is a function of L, the distance between particle A and B, and number densities of particles A and B.

It has been shown[1] that the SIS is nearly exact even at the full association limit if the bonding length L is equal to or greater than the hard-core diameter σ_{AB} of associating particles. However, when the bonding length L approaches 0, it was found that the pressure obtained from the SIS is exact only through the first order in number density ρ_0.[8]

Rasaiah and Zhu have also proposed a new approximation[5]

$$y_{AB}(L) = 1 + [y_{AB}^{ref}(L, \rho_0, \rho_0) - 1]/(1 - \alpha)^2 \qquad (2.7)$$

However, this approximation approaches the erroneous limit of infinity as α goes to 1. As we shall see in the next section, this approximation is far worse than the SIS.

In order to obtain a new approximation which can provide an accurate description for a bonding length less than the hard-core diameter, we first consider the limit of $L \rightarrow 0$. As $L \rightarrow 0$, the small-size particle becomes completely inside the hard core of the large-size particle. Then, molecular AB can be accurately described as atom B (assuming the hard-core diameter of atom B, σ_B, is larger or equal to the diameter of atom A, σ_A). In other words, the three-component mixture becomes a two component mixture with particle A of density $\rho_0(1 - \alpha)$ and particle B of density $\rho_B + \rho_{AB} = \rho_0$. Therefore,

$$y_{AB}(L) \rightarrow y_{AB}^{ref}(L, \rho_0(1 - \alpha), \rho_0), \qquad L \rightarrow 0 \qquad (2.8)$$

Eq. (2.8) is exact for hard-sphere particles. For the hard-sphere with an attractive tail, equation (2.8) is also exact if the tail is confined to be zero for $r > \sigma_B$. It is obvious

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from eq.(2.8) that the cavity function becomes strongly association-degree dependent as $L \to 0$ while the SIS is association-degree independent.

Since we know that the SIS is accurate if $L \geq \sigma_{AB}$, it is natural for us to interpolate between eq.(2.6) and eq.(2.8). Two simple forms of interpolation are, for $S_{AB} \leq L \leq \sigma_{AB}$,

$$y_{AB}(L) = y_{AB}^{ref}(L, \rho_0(1-\alpha), \rho_0)(1 - \frac{L - S_{AB}}{\sigma_A}) + y_{AB}^{ref}(L, \rho_0, \rho_0)(\frac{L - S_{AB}}{\sigma_A}) \tag{2.9}$$

and

$$y_{AB}(L) = [y_{AB}^{ref}(L, \rho_0(1-\alpha), \rho_0)]^{1-(L-S_{AB})/\sigma_A} [y_{AB}^{ref}(L, \rho_0, \rho_0)]^{(L-S_{AB})/\sigma_A} \tag{2.10}$$

where σ_{AB} is the closed contact distance between particle A and B and $S_{AB} = (\sigma_B - \sigma_A)/2$. It is obvious that both equations satisfy the exact limiting condition when $L \to S_{AB}$ and become the SIS when $L = \sigma_{AB}$. They are also exact when the association is turned off ($\alpha = 0$). We call the first form the additive interpolation scheme (AIS) and the second the multiplicative interpolation scheme (MIS).

Another way[7] to attain these same limits when $L \to S_{AB}$ and $L \to \sigma_{AB}$ is to change ρ_A^{ref} so that

$$\rho_A^{ref} \to \rho_0, \qquad L \to \sigma_{AB} \tag{2.11}$$

$$\rho_A^{ref} \to \rho_0(1-\alpha), \qquad L \to S_{AB} \tag{2.12}$$

Let the packing fraction of atom A in the reference system be invariant so that

$$\eta_A^{ref} = \eta_{AB} + \eta_A - \eta_B \tag{2.13}$$

Then, we have

$$\rho_A^{ref} = (1-\alpha)\rho_0 + \alpha\rho_0(\frac{V_{AB} - V_B}{V_A}) \tag{2.14}$$

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where V_{AB}, V_A and V_B are the volumes, of dumbbell AB, and atom A and B, respectively, so

$$\frac{(V_{AB} - V_B)}{V_A} = \frac{(L - S_{AB})^2(3\sigma_{AB}^2 - 2LS_{AB} - L^2)}{2L\sigma_A^3} \tag{2.15}$$

Eq.(2.14) extends the KHD approximation[7] to the unequal-size case. It is obvious that eq.(2.14) satisfies eq.(2.11) and eq.(2.12). As a result, the KHD approximation can be expressed as

$$y_{AB}(L) = y_{AB}^{ref}(L, \rho_A^{ref}, \rho_0) \tag{2.16}$$

Amos and Jackson[6] used σ_A and σ_B as parameters to approximate the cavity function for $L < \sigma_{AB}$ by the cavity function for $L = \sigma'_{AB}$ where σ'_A and σ'_B are obtained by letting a nonsphericity parameter be a constant. However, this approximation is limited to the fully associative case and will therefore not be discussed here further. (We observe, moreover, that this approximation does not satisfy the exact limiting condition of eq.(2.8) so that attempts to extend it to partial association may not be worthwhile.)

Once the cavity function is known, the excess Helmholtz free energy (over the unassociated reference system) can be obtained from[1]

$$\beta A^{ex}/N = \frac{\alpha}{2} + \ln(1 - \alpha) + \frac{1}{2}\int_0^\alpha \alpha \frac{d\ln y_{AB}(L)}{d\alpha} d\alpha \tag{2.17}$$

Eq.(2.17) was obtained by us in earlier work by considering the system as as a two-component mixture. However, through the cavity function,[1] any approximation procedure developed in two-component language can be expressed in the three-component language we use here.

We recall that the cavity function can be calculated from either integral-equation methods (which yield distribution functions as well as thermodynamics) or chemical potentials (which involve a purely thermodynamic route). We shall use the latter route here.

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An exact equation for the cavity function at $r = L$ obtained via the thermodynamic route is[1]

$$\ln y_{AB}(L) = \beta[\mu_A^{ex} + \mu_B^{ex} - \mu_{M_{AB}}^{ex}(L)] \tag{2.18}$$

or

$$y_{AB}(L) = \frac{\gamma_A \gamma_B}{\gamma_{M_{AB}}} \tag{2.19}$$

where $\beta = 1/k_B T$ with the temperature T and Boltzmann constant k_B. μ_i^{ex} and γ_i are the excess chemical potential and the activity coefficient for particle i (i=A, B, M_{AB}).

III. RESULTS FOR STICKY-POINT HARD-SPHERE ASSOCIATION INTO FUSED-SPHERE DIMERS

For association of shielded sticky-point or shielded-sticky shell particles into fused-sphere dimers, very accurate activity coefficients can be obtained from the Boublík equation of state[9] from which $y_{AB}(L)$ can be calculated using eq.(2.19). As a result, K can be attained from eq. (2.4) more-or-less exactly. This "exact" result is compared with the SIS [eq. (2.6)], the Rasaiah-Zhu approximation [(eq. (2.7)], our new approximations [Eq.(2.9) and Eq.(2.10)], and the KHD approximation [eq.(2.16)] in Figure 1 and Figure 2. Since our approximations are expected to be best at $L \leq S_{AB}$ and $L = \sigma_{AB}$, the comparison is made for a system with $L = \sigma/2$ with $\sigma_A = \sigma_B = \sigma_{AB} = \sigma$ in order to provide a stringent test. It turns out that both the AIS and the MIS significantly improve the accuracy of the association constant K and association degree α. It is interesting that the MIS is somewhat better than the AIS in predicting both K and α. It turns out that the MIS is even better than the KHD approximation [eq. (2.16)], which is already satisfactory, so that we restrict our attention in the remaining work here to the MIS. It should be mentioned

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here that the cavity function we have used for the reference hard-sphere system has been obtained from the Boublík equation of state.[9]

IV. IONIC ASSOCIATION: A SIMPLE THEORY OF WEAK ELECTROLYTES

Just as a fluid of charged hard spheres serves as a primitive model of a strong electrolyte, a charged hard-sphere model to which an associating shielded sticky-point (SSP) interaction is added can be used as a primitive model of a weak electrolyte. For $L \leq \sigma/2$, $\sigma = \sigma_A + \sigma_B$, the charged shielded sticky-shell model has thermodynamic behavior identical to the charged SSP model, as discussed in [4], and can also be used as a weak-electrolyte model, as mentioned in [10]. Our MIS of Section II can be readily extended to the charged case as follows. We represent y_{AB} as the product of a term that describes the nonelectrostatic (uncharged) system y_{AB}^{NE} times an electrostatic term $y_{AB}^{ELE}(L)$ that embodies the effect of turning on the charges of the system.

$$y_{AB}(L) = y_{AB}^{NE}(L)y_{AB}^{ELE}(L) \tag{4.1}$$

$$y_{AB}^{ELE}(L) = [\gamma_A^{ELE}(\rho_0(1-\alpha), \rho_0(1-\alpha))\gamma_B^{ELE}(\rho_0(1-\alpha), \rho_0(1-\alpha))]^{1-(L-S_{AB})/\sigma_A}$$

$$\times [\gamma_A^{ELE}(\rho_0, \rho_0)\gamma_B^{ELE}(\rho_0, \rho_0)]^{(L-S_{AB})/\sigma_A} \tag{4.2}$$

where eq.(2.19) was used and the electrostatic part of the activity coefficient for the molecular AB has been approximated as 1. This approximation is based on the idea that when a positive ion and negative ion are associated such that the smaller one is completely within the larger, the electrostatic effect of the remaining dipole is negligible.

Analytical expressions for activity coefficients of free ions, γ_A^{ELE} and γ_B^{ELE} can be obtained from the Mean Spherical Approximation (MSA)[11] or an improved MSA-based result such as MSA + B$_2$.[12] For simplicity, we use only the equal-size equations of the MSA below:

$$\ln\gamma_A^{ELE} = \ln\gamma_B^{ELE} = -\frac{z^2\lambda}{\sigma}\left[\frac{1 + \kappa\sigma - \sqrt{1 + 2\kappa\sigma}}{\kappa\sigma}\right] \tag{4.3}$$

where $z = |z_A| = |z_B|$ is the absolute value of charge number of particle A or B, $\lambda = \beta e^2/\epsilon$ with the electron charge e and solvent dielectric constant ϵ, $\sigma = \sigma_A = \sigma_B$ is the charged hard-sphere diameter, and $\kappa^2 = 8\pi\lambda\rho_i z^2$, where κ is the inverse Debye screening length and ρ_i is the number density of cations or anions.

Fig.3 shows $y_{AB}(\sigma)$ calculated from HNC approximation[13] in comparison with $y_{AB}(\sigma)$ calculated from eqs.(4.1-4.3). It indicates that the cavity function from the MSA is quite accurate for low concentration. From Fig.3, one also sees that the approximation that the molecular activity coefficient is 1 for $L = \sigma$ is very accurate up to concentrations of 0.1M. Since the effect of the electrostatic contribution to our result becomes smaller as the bonding length L decreases, the approximation of neglecting the molecular activity coefficient is even more accurate as L decreases. At the highest concentrations the MSA tends to underestimate the cavity function.

It is noted that the electrostatic part of cavity function is dependent on the bonding length only through the exponents, as a result of our neglecting the activity of the AB molecule.

The conventional way of calculating the reduced association constant can be expressed as follows:

$$K/K_0 = \frac{\gamma_A\gamma_B}{\gamma_{AB}} \tag{4.4}$$

Neglecting the molecular activity, we have

$$K/K_0 = \gamma_A(\rho_0(1-\alpha), \rho_0(1-\alpha))\gamma_B(\rho_0(1-\alpha), \rho_0(1-\alpha)) \tag{4.5}$$

Eq.(4.5) can also be decoupled into a nonelectrostatic part and an electrostatic part.

$$K/K_0 = \gamma_A^{NE}(\rho_0(1-\alpha), \rho_0(1-\alpha))\gamma_B^{NE}(\rho_0(1-\alpha), \rho_0(1-\alpha))$$

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$$\times \gamma_{A}^{ELE}(\rho_0(1-\alpha), \rho_0(1-\alpha))\gamma_{B}^{ELE}(\rho_0(1-\alpha), \rho_0(1-\alpha)) \qquad (4.6)$$

It is obvious that eq.(4.6) is independent of the bonding length L. As L approaches 0, our approximation (4.2) becomes equivalent to the electrostatic part of eq.(4.6). Therefore, we conclude that the conventional way of calculating the reduced association constant may only be suitable for the case of the bonding length $L/\sigma \ll 1$.

Fig. 4 compares the reduced association constant at different bonding length L. It shows that the association constant increases fastest with concentration for smaller L and higher concentration. This is mainly due the packing effects. At high concentration, the reaction is shifted towards the side saving the most space.

Fig. 5 shows a comparison of the association constant obtained from experimental data of monochloroacetic acids[14] with that of our theory[15]. The theoretical result in which the experimental K_0 of monochloroacetic acid is used as input is seen to be in reasonable agreement with the experimental data. One expects that the agreement may be improved if unequal diameters are used for hydrogen and monochloroacetate, respectively, and we are pursuing this application of our MIS. The figure also shows the effect of changing K_0 on the reduced association-constant curve.

ACKNOWLEDGMENTS

REFERENCES

[1] Y. Zhou and G. Stell, *J. Chem. Phys.* **96**, 1507 (1992)

[2] D. Chandler and L. R. Pratt, *J. Chem. Phys.* **65**, 2925 (1976).

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[3] M. S. Wertheim, *J. Chem. Phys.* **85**, 2929, (1986); **87**, 7323 (1987); M. S. Wertheim, *J. Stat. Phys.* **35**, 19, 35 (1984); **42**, 459, 477 (1986).

[4] G. Stell and Y. Zhou, *J. Chem. Phys.* **91**, 3618 (1989).

[5] J. C. Rasaiah and J. Zhu, *J. Chem. Phys.* **92**, 7554 (1990).

[6] M. D. Amos and G. Jackson, *J. Chem. Phys.* **96**, 4604 (1992).

[7] Y. V. Kalyuzhnyi, M. F. Holovko, and Y. J. Duda, preprint, to be published.

[8] Y. Zhou and G. Stell, *J. Chem. Phys.* **96**, 1504 (1992)

[9] a) T. Boublík and I. Nezbeda, *Colln. Czech. Chem. Commun.* **51**, 2301 (1986). b) T. Boublík, *Mol. Phys.* **59**, 371, 775 (1986).

[10] J.C. Rasaiah and S.H. Lee, *J. Chem. Phys.* **83**, 5870 (1985); see also J.C. Rasaiah, *Int. Journ. of Thermophys.* **11**, 1 (1990).

[11] E.g. E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **56**, 3093 (1972).

[12] a) G. Stell and B. Larsen, *J. Chem. Phys.* **70**, 361 (1979). b) G. Stell and C. G. Joslin, *Biophys* **50**, 855 (1986).

[13] E.g. H. L. Friedman, *A Course in Statistical Mechanics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey 1985).

[14] T. Shedlovsky, A. S. Brown and D. A. MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

[15] In ref. [5], experimental data for monochloroacetic and trichloroacetic acid were used to obtain profiles for $y_{AB}(L)$ vs. concentration for those acids, assuming the same model but a different approximation from ours. No comparison was made in [5] between those profiles and its theoretical profiles, however.

FIGURE CAPTIONS

Fig.1 The association degree α as a function of $\rho_0\sigma^3$ obtained using the nearly exact Boublík equation of state[9] (—), the MIS [(eq.(2.10)] (- - -), the AIS [eq.(2.9)] (— —), the KHD approximation [eq.(2.16)] (— - - —), the SIS [eq.(2.6)] (— - - - —), and the Rasaiah-Zhu approximation [eq.(2.7)] (— - - - - —). Here $\sigma_A = \sigma_B = \sigma$, $K_0/\sigma^3 = 1$, and $L/\sigma = 0.5$.

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 logarithm of the contact cavity function $\ln y_{AB}(\sigma)$ as a function of square root of total concentration (in mole/liter) $[100\sqrt{C}]$. Shown are the HNC approximation (o) and the MSA [eqs.(4.1-4.3)]. In the MSA, the nonelectrostatic part of cavity function is obtained from Boublík equation of state.[9] Here, $\epsilon = 78.54$, $z_1 = -z_2 = 1$, $\sigma_A = \sigma_B = 4$Å, $T = 25°$C.
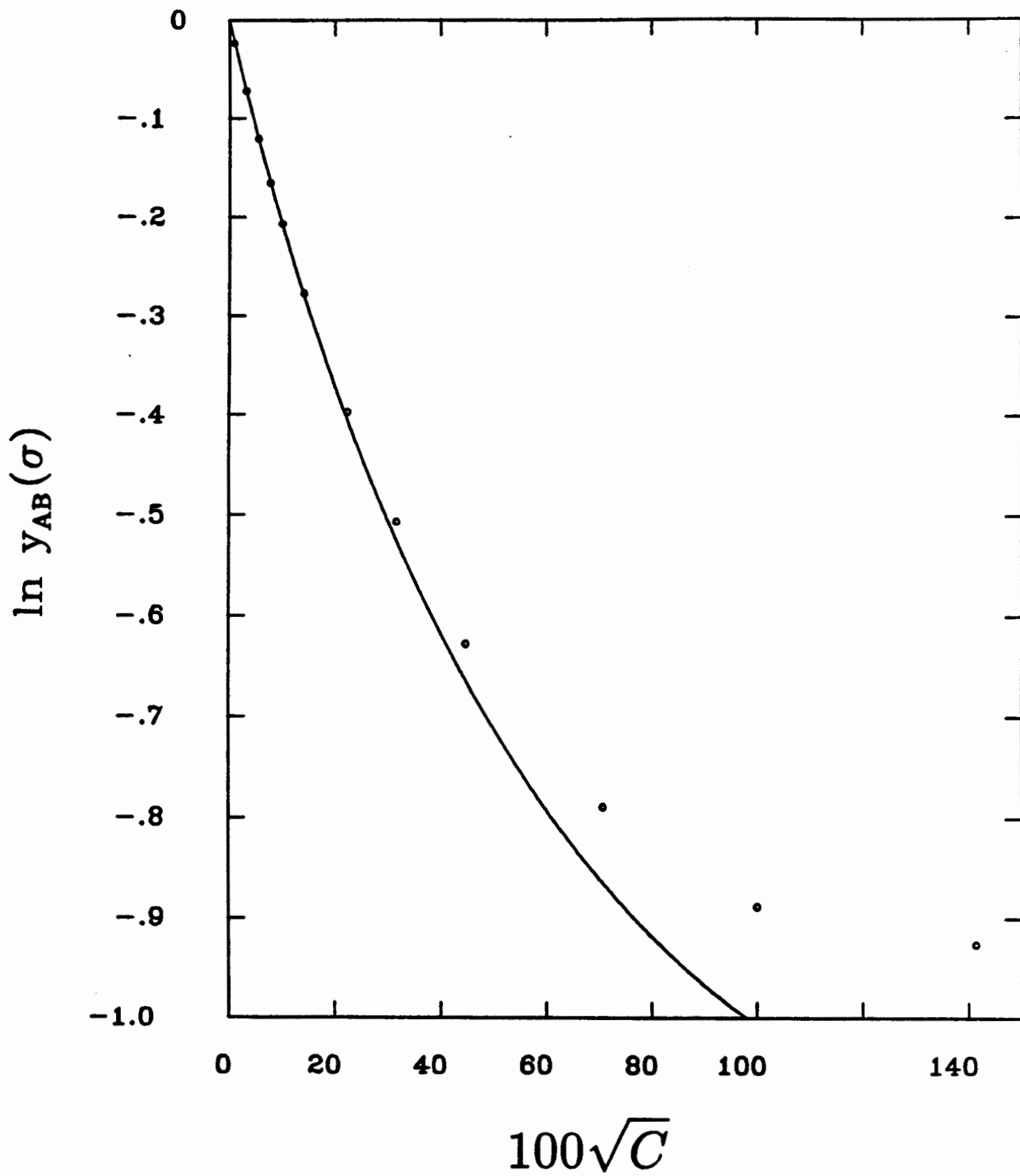
Fig.4 The logarithm of the reduced association constant $\ln(K/K_0)$ as a function of free ionic concentration, $100\sqrt{C(1-\alpha)}$, (C in mole/liter). From top to bottom, $L = 0$, $L = \sigma/2$ and $L = \sigma$ respectively. $\sigma = 8$Å. $K_0 = 1.2 \times 10^6$Å^3. All other parameters as in Fig.3.

Fig.5 The logarithm of the reduced association constant $\ln(K/K_0)$ as a function of free ionic concentration, $100\sqrt{C(1-\alpha)}$, (C in mole/liter). Experimental data for monochloroacetic acid (o),[13] $\sigma = 8$Å, $K_0 = 1.2 \times 10^6$Å^3 (—); $\sigma = 7$Å, $K_0 = 1.2 \times 10^6$Å^3 (- - -); $\sigma = 8$Å, $K_0 = 10^8$Å^3 (— - —). Here, $L = \sigma/2$. $K_0 = 1.2 \times 10^6$Å^3 is the experimental result for monochloroacetic acid. All other parameters as in Fig.3.
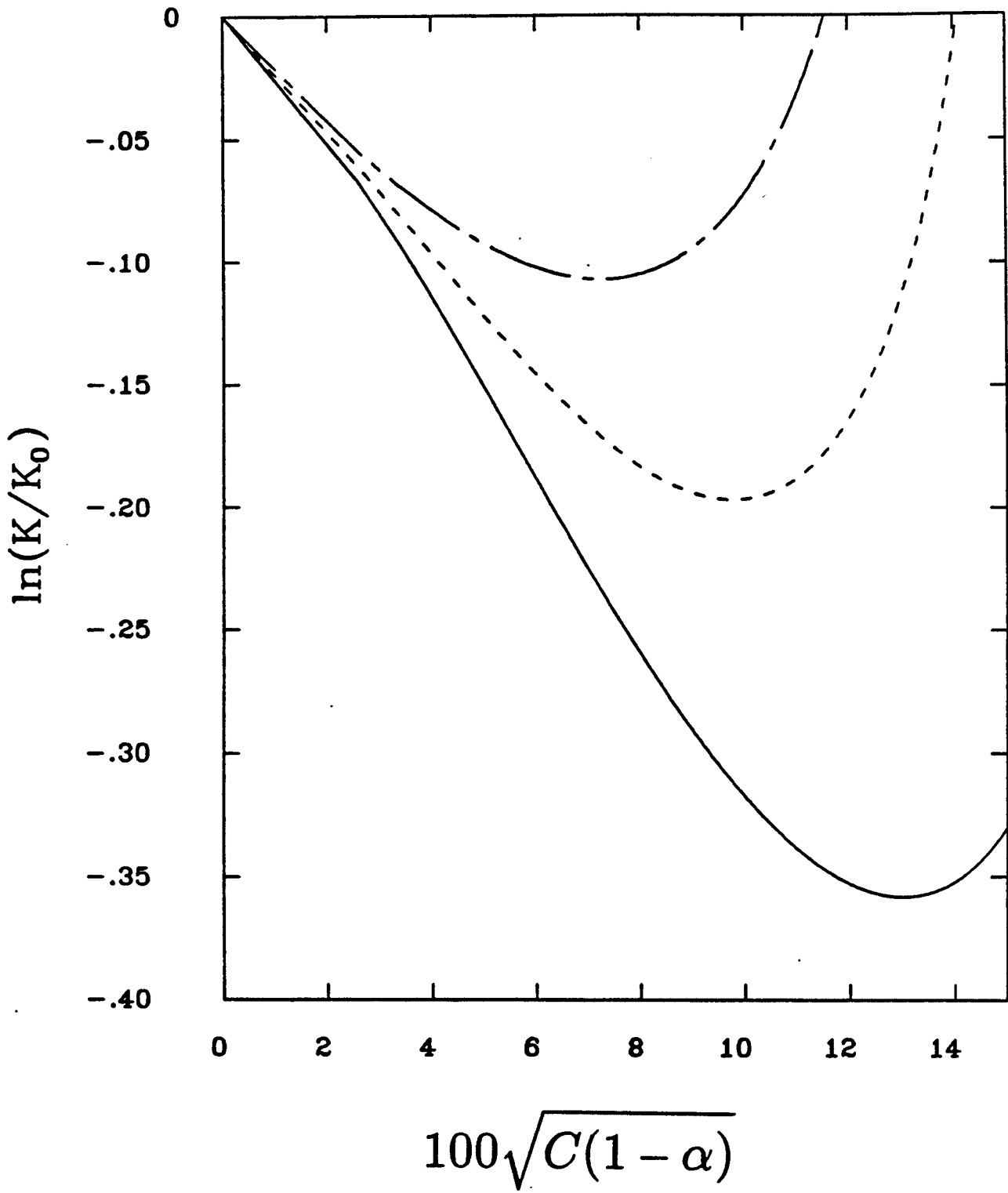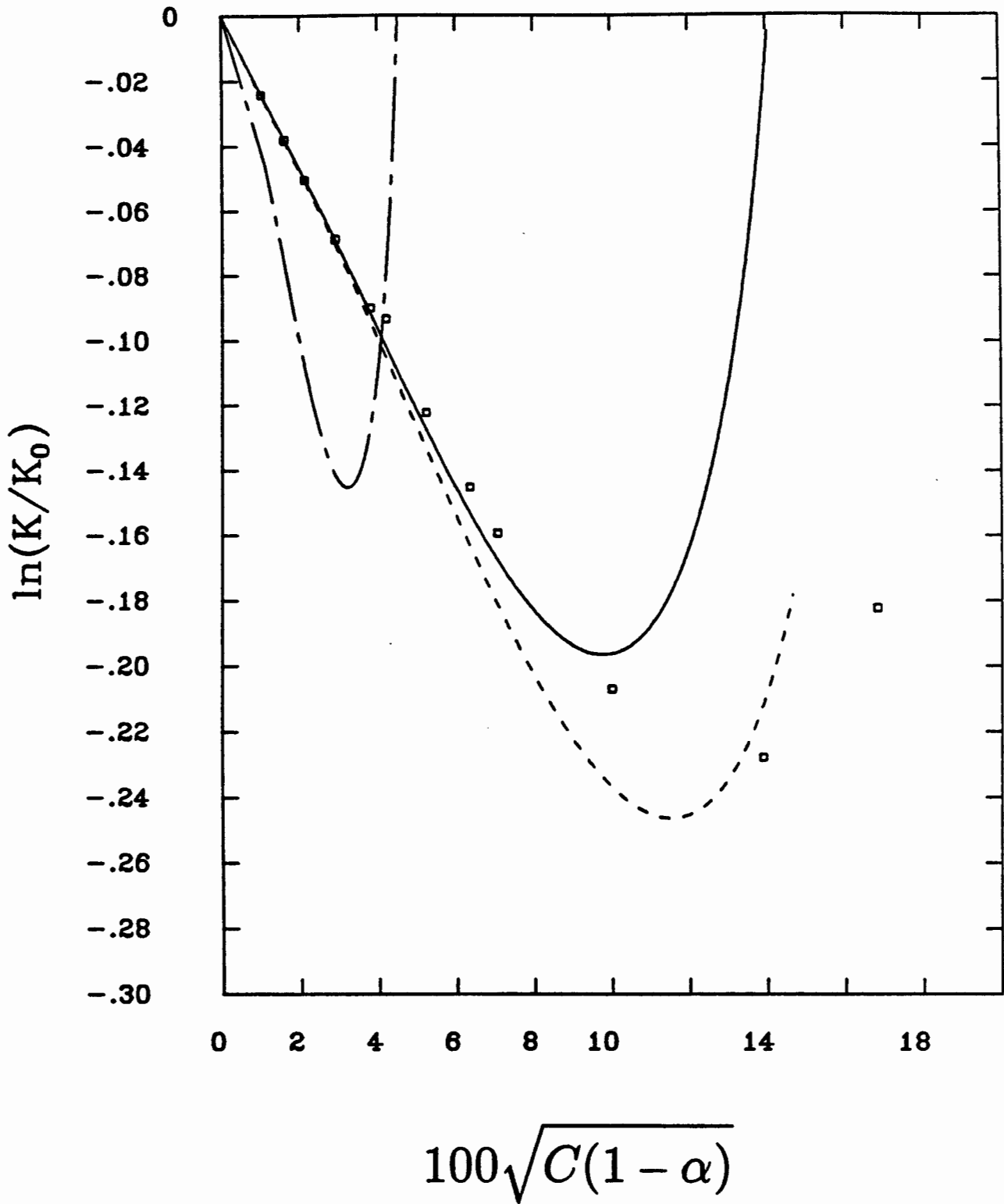
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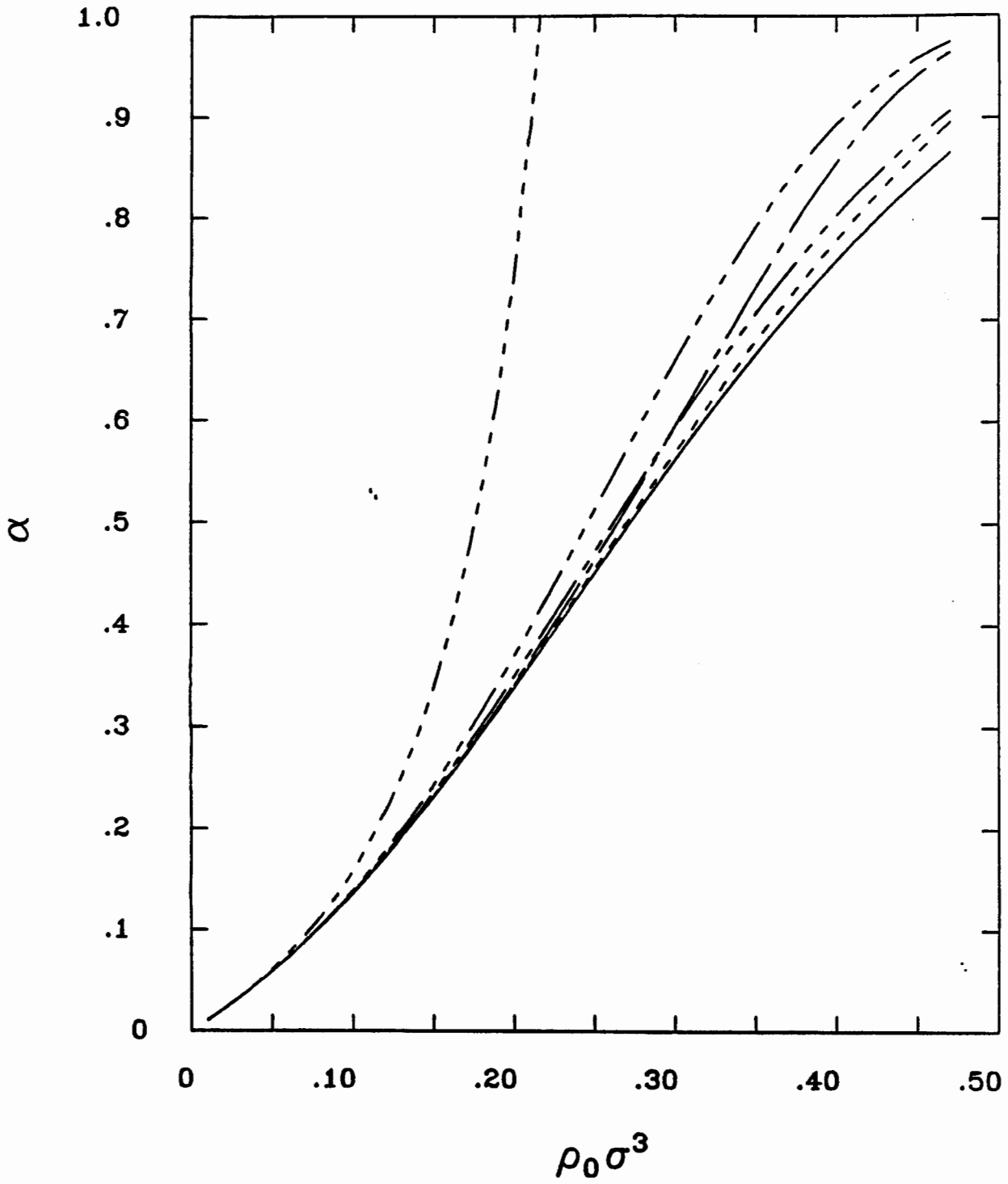
Zhoul Stell   Fig. 1
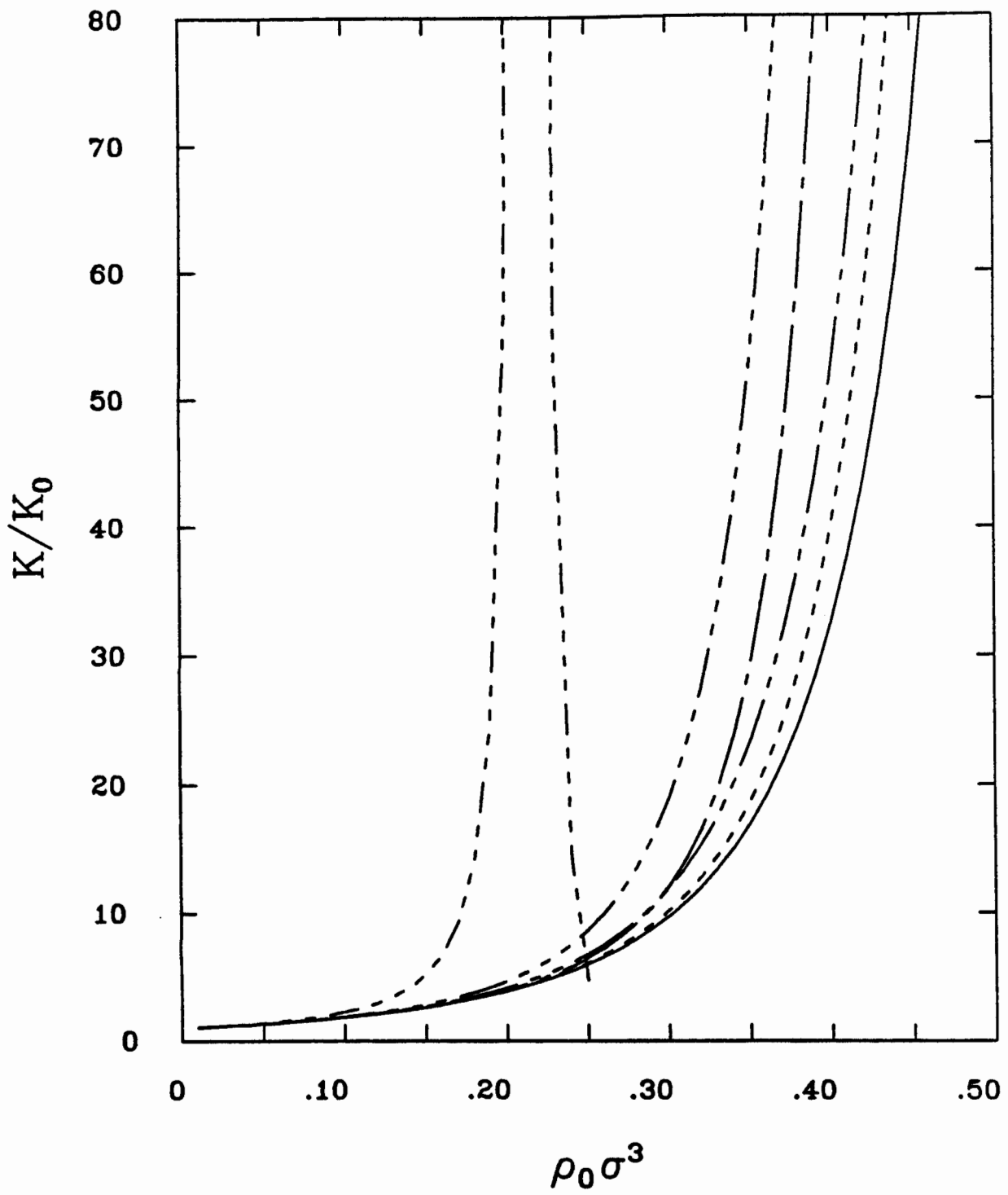
Zhou & Stell   Fig 2

Zhou & Stell   Fig. 3

Zhou & Stell Fig 4

$100\sqrt{C(1-\alpha)}$

Zhou & Stell, Fig.5