Criticality of Charged Systems: I. the Restricted Primitive Model.

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ABSTRACT

A new method, which improves upon the mean spherical approximation (MSA), is developed by including the ionic-pairing contribution using a recent theory of association. The association constant of the new approximation is obtained through the second ionic virial coefficient. In the simplest version of our theory, which we call the pairing MSA 1 (PMSA1), we neglect the activity coefficient of the fully associated ionic-pairs, which are regarded as a separate dipolar species, and obtain the critical point (ρ_c^*, T_c^*) at (0.025, 0.075). In the second PMSA (or PMSA2), we include the activity coefficient of these dipolar particles at the MSA level. The new critical point is located at (0.023, 0.073). In the third PMSA (or PMSA3), we further include the effect of the presence of the dipolar-particle cores. The final critical point is located at (0.0245, 0.0745). These critical points are considerably closer than the MSA result (0.014, 0.079) to the most recent Monte Carlo estimates of ρ_c^* from 0.025 to 0.04 and T_c^* from 0.053 to somewhat over 0.057. Both PMSA2 and PMSA3 appear to improve the critical values of pressure and the degree of association significantly over PMSA1. All expressions for the thermodynamic properties in the PMSA1, PMSA2, and PMSA3 are of simple analytic form. The equation of state in the PMSA3 reduces to the very accurate Carnahan-Starling equation of state for hard spheres if the charges are turned off, and it reduces to an accurate equation of state for a mixture of hard spheres and hard dumbbells if the charges of the associated pairs are turned off. A comparison is made between our theory and that of a recent approach of

Fisher and Levin, which is in good agreement with the simulation results if the hard-core contribution to the thermodynamics is neglected, but which falls out of agreement when an accurate core contribution is included. A discussion of the importance of an accurate core term in the treatment of the restrictive primitive model is given. Finally, the most likely reasons that the T_c^* predicted by the PMSA is somewhat too high are briefly noted.

I. INTRODUCTION

Recent assessments of the critical point (ρ_c^*, T_c^*) of the restricted primitive model (RPM) obtained by the Monte-Carlo computer simulation[1] suggest that the reduced density, ρ_c^*, is between 0.025 and 0.04 and the reduced critical temperature, T_c^*, is between 0.053 and something over 0.057. Here, $\rho^* = 2\rho_0\sigma^3$ and $T^* = k_B T\epsilon\sigma/(ze)^2$ with σ, the ionic diameter, ϵ, the solvent dielectric constant, z, the ionic charge number, e, the electronic charge, T, the temperature, $2\rho_0$, the total number density, and k_B, the Boltzmann constant. Various theoretical methods were used to obtain the critical point of the RPM.[2] One type of method, in which we are particularly interested here, is based on the mean spherical approximation (MSA).[3] The MSA provides simple analytical solutions and correctly treats the hard-core condition. However, the MSA is a linearized approximation which does not take into account ionic association. Various methods of improving it have been suggested.[2,4] One of the methods, due to Ebeling and Grigo[5] is to explicitly include the ionic pairing contribution via the second ionic virial coefficient[6] and the mass-action law, using an elegant extension of the Bjerrum theory[7] of ionic association.

In this paper, we will use instead an ionic association theory we have developed recently[8] to include the ionic pairing effect into the MSA. The resulting approximation, which we shall refer as the pairing MSA (PMSA), considers only the contribution from the unlike ionic pairs at contact. This contribution is further normalized by ensuring that the equation of state gives the correct second ionic virial coefficient.[6] This normalization gives an association constant which is identical to the one suggested by Ebeling[9] and used by Ebeling and Grigo.[5] Although the PMSA has more terms than the Ebeling and Grigo approximation (EGA)[5], the PMSA's expressions for thermodynamic properties are much simpler. This is because the degree of association in the PMSA has a simple analytical form while the degree of association in the EGA satisfies a nonlinear algebraic equation, which requires a numerical solution. In Section II, the general theory is presented in

the case of RPM. In the simplest version of our theory, which we call the PMSA1, all thermodynamic properties are obtained by approximating the dipole activity coefficient as 1. In Section III, the electrostatic part of equation of state is expanded in term of reduced inverse-Debye length x. It is shown that our PMSA1 equation of state, which is exact through order x^4, also gives a near-exact result in order x^5 at low temperature. In Section IV, a thermodynamic cycle is reintroduced in order to obtain an expression for the dipole activity coefficient. The approximation incorporating this result is PMSA2. In Section V, the PMSA3 is defined by further including the effect of the hard-dumbbell cores of associated pairs of ions. Results are discussed in Section VI where our treatment is compared with a recent treatment of the RPM by Fisher and Levin.[10] Concluding remarks are summarized in Section VII.

II. THE THEORY

Consider the restricted primitive model (RPM) in which cations and anions are modeled as charged hard spheres with same hard-core diameter σ and opposite charge numbers (z, -z). The MSA result for the RPM is well known.[3] Our goal is to find ionic association corrections to the MSA. The first question is how to define an effective association length between two unlike ions that is characteristic of the distance between two ionic centers of the ions that are to be regarded as associated. It is clearly of order σ. Many different ways of introducing such an association length have been proposed[5,10-12] since the Bjerrum theory[7] of ionic associations first appeared. In this paper, we shall simply identify it with σ in order to utilize the expressions appropriate to a simple model of association in which a single effective length is introduced.[8] As we shall see below, by adjusting the ideal association constant, we effectively take into account of a distribution of association lengths that extend somewhat beyond σ.

In a previous paper of ours[8], the chemical association constant was found to be directly proportional to the cavity function. In the zeroth-order approximation[8] the cav-

ity function of the associating particles in the presence of both free and bound particles is approximated by the cavity functions of a reference system consisting entirely of free particles. For uncharged particles, this approximation was considered earlier by Chandler and Pratt,[13] and it also follows from the Wertheim's first-order thermodynamic perturbation theory[14] as well as our own simple interpolation scheme (SIS),[15] which we developed for both charged and uncharged particles.[8] This approximation will be called the reference cavity approximation (RCA) throughout this paper. In refs. 8 and 15 the RCA was developed only for the case of chemical association which was assumed to be the result of a short-ranged interaction that is present whether or not an additional Coulombic interaction is also present. In the simple models considered in refs. 8 and 15 the associating interaction was modelled by a contact potential that acts only when the particles are a distance L $(=\sigma)$ apart and we shall refer to the resulting association as contact association. These models were used as a convenient limiting approximation to a more general class of models in which the associating potential is assumed to act over a range $L^- \le r \le L^+$ and the association degree and association constant assessed by an integral over that same range.[16] Using the RCA in this context,[8] the pressure contribution from association of ions into ionic pairs at contact, with $L = \sigma$, satisfies the following equation:

$$\beta(P - P^{ref}) = -\alpha\rho_0[1 + \rho_0\frac{d\ln y_{+-}^{ref}(\sigma)}{d\rho_0}] \qquad (2.1)$$

where α is the degree of association, ρ_0 is total number density of cations or anions (including both associated and unassociated), $y_{+-}^{ref}(r)$ is the cavity function between cations and anions of a fully dissociated reference system where r is the distance between ion centers and σ is the ionic diameter. The reference cavity function can be calculated from a thermodynamic approach[8]

$$y_{+-}^{ref}(\sigma) = \frac{\gamma_+\gamma_-}{\gamma_{M+-}(\sigma)} \qquad (2.2)$$

where γ_+ and γ_- are the activity coefficients at the complete disassociation reference

5

limit for cations and anions, respectively, and $\gamma_{M+-}(\sigma)$ is the activity coefficient for an ionic pair at contact in the *infinite dilution* limit (i.e. an ionic pair in the unassociated reference ion system).

The association degree α satisfies the law of mass action, which becomes, in the RCA,

$$K = \frac{\alpha}{\rho_0(1-\alpha)^2} = K_0 y_{+-}^{ref}(\sigma) \tag{2.3}$$

where K is the association constant and K_0 is its ideal limit. Although eqs.(2.1)-(2.3) are in the RCA, it is known that the RCA gives very accurate result for the case of contact association.[8,14,15]

Here we want to apply (2.1)-(2.3) to ionic association, which occurs even in the absence of any chemical bonding. In particular, we wish to apply (2.1)-(2.3) to ionic association in the RPM. To do so, we must reinterpret the superscript "ref" as referring not to a reference system but to a reference state, in which the effects of ionic screening are accurately described but the effects of ionic association are ignored. Put in more precise mathematical terms, this is the state described by the MSA, which correctly incorporates the linear response to charge that gives rise to screening but neglects the non-linear response that gives rise to ionic association. The nonlinear associating term is of significant strength only for a relatively short range of r beyond $r = \sigma$, so we shall continue to use the functional form of the contact association equation (2.1)-(2.3) as a convenient approximation, with $L = \sigma$.

The MSA results for the RPM can be decoupled into two parts: the hard-sphere part and the electrostatic part. Since the hard-sphere part is known accurately, we shall first consider improving the electrostatic part only. Therefore, we write [c.f. eqs.(2.1)-(2.3)]

$$\beta P = 2\rho_0 + \beta P^{HS} + \beta [P^{MSA}]^{ele} - \alpha_0 \rho_0 \{1 + \rho_0 \frac{d\ln[y_{+-}^{ref}(\sigma)]^{ele}}{d\rho_0}\} \tag{2.4}$$

$$[y_{+-}^{ref}(\sigma)]^{ele} = \frac{\gamma_+^{ele}\gamma_-^{ele}}{\gamma_{M+-}^{ele}} \tag{2.5}$$

6

$$\frac{\alpha_0}{\rho_0(1-\alpha_0)^2} = K_0[y_{+-}^{ref}(\sigma)]^{ele} \tag{2.6}$$

In (2.4) and (2.6) we have switched from the symbol α to α_0 to be in keeping with the α_1 and α_2 we shall introduce later. From the MSA, we have[3]

$$\ln\gamma_\pm^{ele} = -\frac{z^2\lambda}{\sigma}[\frac{1+x-\sqrt{1+2x}}{x}] \tag{2.7}$$

where

$$x = \kappa\sigma, \quad \kappa^2 = 8\pi\lambda\rho_0 z^2, \quad \lambda = \frac{\beta e^2}{\epsilon} \tag{2.8}$$

Initially we also assume the activity coefficient of an ionic pair is 1.

$$\gamma_{M_{+-}}(\sigma) = 1 \tag{2.9}$$

It has been shown that this approximation is accurate only at low densities.[17]

After substituting eqs. (2.5)-(2.9) into eq.(2.4), we have

$$\beta P - 2\rho_0 - \beta(P^{HS} + [P^{MSA}]^{ele}) = -\alpha_0\rho_0[1 - (\frac{1}{8\pi\rho_0\sigma^3})\frac{x(1+x-\sqrt{1+2x})}{\sqrt{1+2x}}] \tag{2.10}$$

with

$$\alpha_0 = \frac{1 + 2\rho_0 K_0 y_0 - \sqrt{1 + 4\rho_0 K_0 y_0}}{2\rho_0 K_0 y_0} \tag{2.11}$$

where y_0, obtained from (2.2), (2.7) and (2.9), is

$$\ln y_0 = -\frac{2z^2\lambda}{\sigma}[\frac{1+x-\sqrt{1+2x}}{x}] \tag{2.12}$$

It is obvious that eq.(2.10) has only one unknown parameter K_0. If one chooses the ideal association constant K_0 in such a way that eq.(2.10) gives an exact second ionic virial coefficient,[6] we have

$$K_0 = 8\pi\sigma^3 \sum_{m=2}^{\infty} \frac{b^{2m}}{[(2m)!(2m-3)]} \tag{2.13}$$

where the $b = z^2\lambda/\sigma$ is the Bjerrum length.

This association constant turns out to be the same constant chosen by Ebeling.[9] In fact, if we neglect the second association term in eq.(2.4) we have

$$\beta P - 2\rho_0 - \beta(P^{HS} + P^{MSA}) = -\alpha_0 \rho_0 \qquad (2.14)$$

which is the Ebeling-Grigo (EG) equation of state[5] for the RPM, except that we are using a different y_0 to evaluate the degree of association, α_0, and P^{MSA} describes a reference state in which the density is taken to be the total ionic density and not the free ionic density used by EG. In the EGA,[5] the assumption is made that $\gamma_{M+-} = 1$ and that only γ_+ and γ_- vary with the degree of association. Here, we have instead let y_0 be independent of the degree of association. This procedure has already been proved to be a very accurate one in the context of chemical association.[8,14-15] We have also found recently that $\gamma_\pm$ varying with the degree of association α_0 is suitable for the case of ions associating into hard spheres (two ions of opposite sign overlapping each other with a zero dipole moment).[17] Compared to the EG equation of state,[5] our equation (2.10) is much simpler because the degree of association has a simple analytical form [eq. (2.11)] instead of satisfying a complicated nonlinear algebraic equation. As we shall see, it is also more accurate.

The hard-sphere pressure can be obtained from the Carnahan-Starling (CS) equation of state,[18] which is known to be of high accuracy,

$$\beta P^{HS} = 2\rho_0 \frac{2\eta(2-\eta)}{(1-\eta)^3} \qquad (2.15)$$

where the packing faction $\eta = \pi \rho_0 \sigma^3 / 3$. The MSA gives[3]

$$\beta[P^{MSA}]^{ele} = -\frac{(\sqrt{1+2x}-1)^3}{24\pi\sigma^3} \qquad (2.16)$$

Our final equation for pressure in the PMSA1 is

$$\beta P = 2\rho_0 \frac{(1+\eta+\eta^2-\eta^3)}{(1-\eta)^3} - \frac{(\sqrt{1+2x}-1)^3}{24\pi\sigma^3} - \alpha_0\rho_0[1 - (\frac{1}{8\pi\rho_0\sigma^3})\frac{x(1+x-\sqrt{1+2x})}{\sqrt{1+2x}}] \qquad (2.17)$$

8

where x is defined in eq. (2.8). Eq.(2.17) with (2.11), (2.12), and (2.13) provides a simple analytic equation of state for the RPM. In the PMSA1, the Helmholtz free energy also has a simple form[8]

$$\beta(A - A^{id})/N = \beta A^{HS}/N + \beta[A^{MSA}]^{ele}/N + \frac{\alpha_0}{2} + \ln(1 - \alpha_0) \qquad (2.18)$$

where α_0 is calculated from eqs. (2.11), (2.12) and (2.13). It is well known that (e.g. refs. 3, 18)

$$\beta A^{id}/N = \beta A^{\circ} - 1 + \ln\rho_0 \qquad (2.19)$$

$$\beta A^{HS}/N = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \qquad (2.20)$$

$$\beta[A^{MSA}]^{ele}/N = -\frac{3x^2 + 6x + 2 - 2(1 + 2x)^{3/2}}{24\pi\rho_0\sigma^3} \qquad (2.21)$$

The activity coefficients for cations and anions can be obtained from

$$\ln\gamma_+ = \ln\gamma_- = \frac{\beta\Delta A}{N} + \frac{\beta\Delta P}{2\rho_0} \qquad (2.22)$$

or

$$\ln\gamma_+ = \ln\gamma_- = \ln\gamma^{HS} + \ln\gamma_{\pm}^{MSA} + \ln(1 - \alpha_0) + \frac{\alpha_0}{16\pi\rho_0\sigma^3}\frac{x(1 + x - \sqrt{1 + 2x})}{\sqrt{1 + 2x}} \qquad (2.23)$$

where $\gamma_{\pm}^{MSA}$ satisfies eq.(2.7). With the CS equation of state[18] as input, the expression of activity coefficients for hard spheres is

$$\ln\gamma^{HS} = \frac{(3\eta^3 - 9\eta^2 + 8\eta)}{(1 - \eta)^3} \qquad (2.24)$$

The final equation for the chemical potential in the PMSA1 is

$$\beta\mu_{\pm} = \beta\mu_{\pm}^{\circ} + \ln\rho_0 + \frac{3\eta^3 - 9\eta^2 + 8\eta}{(1 - \eta)^3} - b[\frac{1 + x - \sqrt{1 + 2x}}{x}] + \ln(1 - \alpha_0)$$

$$+ \frac{\alpha_0}{16\pi\rho_0\sigma^3}\frac{x(1 + x - \sqrt{1 + 2x})}{\sqrt{1 + 2x}} \qquad (2.25)$$

This formally completes the derivation of the PMSA1. In next Section, we will analyze the asymptotic behaviour of the PMSA1 at low reduced inverse-Debye length.

III. REDUCED INVERSE-DEBYE LENGTH EXPANSION

Expressing ρ_0 in terms of x by eq.(2.8) and expanding the right-hand-side of eq. (2.17) in powers of the reduced Debye-length x, we have the excess pressure due to ionic charges in the PMSA1

$$\beta P^{ex}\sigma^3 = -\frac{x^3}{24\pi} + \frac{1}{16\pi}[1 - 2(T^*)^2 S_1]x^4 + \frac{1}{32\pi}(-3 + 6T^* S_1)x^5 + \cdots \qquad (3.1)$$

where T^* is the reduced temperature defined as $1/b$ and

$$S_1 = \frac{K_0}{8\pi\sigma^3} = \sum_{m=2}^{\infty} \frac{b^{2m}}{[(2m)!(2m-3)]} \qquad (3.2)$$

The exact expansion for the excess pressure for the RPM is[19]

$$\beta P^{ex}\sigma^3 = -\frac{x^3}{24\pi} + \frac{1}{16\pi}[1 - 2(T^*)^2 S_1]x^4 + \frac{1}{32\pi}\{-3 + 6T^* S_2 - S_3\}x^5 + \cdots \qquad (3.3)$$

with

$$S_2 = \sum_{m=2}^{\infty} \frac{b^{2m+1}}{[(2m+1)!(2m-2)]} \qquad (3.4)$$

$$S_3 = \frac{1}{(T^*)^2}[-\frac{2}{3} + \gamma + \ln(4x)] \qquad (3.5)$$

where γ is the Euler constant (~ 0.577215665). The two equations (3.1) and (3.3) have identical terms through order x^4 as expected. At order x^5, the first term in the PMSA1, which is contributed by the MSA, is also identical to the first term in the exact series. The second term, $6T^* S_1$, in the PMSA1 is surprisingly similar to the exact second term, $6T^* S_2$. This illustrates that the PMSA1 gives very good estimates for higher order terms with the known low-order terms. The third term, S_3, in the exact expansion is missing in the PMSA1. This term has a characteristic ionic term $\ln x$. Numerical evaluation indicates that $-3 + 6T^* S_1$ and $-3 + 6T^* S_2 - S_3$ are almost identical to each other at low temperature.

IV. DIPOLE ACTIVITY COEFFICIENT

An immediate conceptual improvement over the PMSA1 comes from introducing the effect of the molecular activity coefficient of an ionic pair (dipole species) in an ionic solution at the infinite dilution of the pair. We consider a thermodynamic cycle introduced earlier.[8,20] In Fig.1, ΔF_2 and ΔF_4 are the reversible work needed to bring two ions (i, j) from infinity away to distance r apart in a vacuum and in a solution, respectively, ΔF_1 is the free energy change when moving the fixed pair of ions from the vacuum to solution, and ΔF_3 is the sum of two single ion solvation free energies. In our case here, the solution is an ionic solution. As has been shown,[8,20] these four free energy terms can be rewritten as

$$\Delta F_1 = k_B T \ln \gamma_{M_{ij}}|_{\rho_{ij}=0} \tag{4.1}$$

$$\Delta F_2 = u_{ij}(r) \tag{4.2}$$

$$\Delta F_3 = k_B T [\ln \gamma_i|_{\rho_i=0} + \ln \gamma_j|_{\rho_j=0}] \tag{4.3}$$

$$\Delta F_4 = \bar{u}_{12}(r) = -k_B T \ln g_{ij}(r) \tag{4.4}$$

where $\gamma_{M_{ij}}|_{\rho_{ij}=0}$ is the activity coefficient of the molecular species (ij pairs) at infinite dilution, $u_{ij}(r)$, $\bar{u}_{ij}(r)$, $g_{ij}(r)$ are the pair potential, the potential of mean force, and the pair correlation function between species i and j, respectively. It is obvious that ΔF_1 is the term of our main interest. From the thermodynamic cycle (Fig.1), we have[8,20]

$$\Delta F_1 = \Delta F_4 + \Delta F_3 - \Delta F_2 \tag{4.5}$$

If one applies the hypernetted chain approximation (HNC) to obtain $g_{ij}(r)$ for the infinite dilute species in eq.(4.4), one finds[8,20]

$$\Delta F_4 = -k_B T \ln g_{ij}^{HNC}(r) = -k_B T h_{ij}^{MSA}(r) \tag{4.6}$$

where $h_{ij}^{MSA}(r)$ is the pair correlation function in the MSA for the infinite dilute species. Now, let the particle species i and j be identical to the cations + and anions − in the

ionic solution. The electrostatic part of eq. (4.5) becomes

$$\ln\gamma_{M+-}^{ele}(r) = -[h_{+-}^{MSA}(r)]^{ele} + 2\ln[\gamma_{\pm}^{MSA}]^{ele} - \beta u_{ij}^{ele}(r) \qquad (4.7)$$

where the ionic solution has been treated by the MSA. Substituting eq.(4.7) into (2.5) we have, at $r = \sigma$,

$$\ln[y_{+-}^{ref}(\sigma)]^{ele} = [\beta u_{+-}(\sigma) + h_{+-}^{MSA}(\sigma)]^{ele} \qquad (4.8)$$

Eq.(4.8) can be rewritten as

$$[g_{+-}(\sigma)]^{ele} = e^{[h_{+-}^{MSA}(\sigma)]^{ele}} \qquad (4.9)$$

This is because the cavity function is defined as $e^{\beta u(r)}g(r)$. Eq.(4.9) also follows from a well-known approximation – the EXP (for exponential) approximation[21] – when the latter is applied to the RPM. It is known that the EXP-approximation result gives considerably better structural information for the RPM than the MSA.[21] It appears that this thermodynamic cycle derivation gives further theoretical justification for the EXP-approximation result. We observe that the EXP-approximation expression (4.9) is at the same level of accuracy as the activity coefficient obtained through the energy route.

Eq.(4.8) provides a simple analytic method to calculate $y^{ref}(\sigma)$ which includes the effect of molecular activity coefficient. Although there are slightly more accurate analytical methods (such as $T\Gamma2A^{4c}$) to evaluate the contact value of pair correlation function for ions, we do not intend to use them here, because they do not yield as simple a picture with regard to correcting the MSA in terms of the thermodynamic cycle and cavity function. Moreover, the quantitative changes that would result from using a slightly more accurate contact value of pair correlation function are expected to be small, since the next dominant contribution should come from the n-mer formations $(n > 2)$.

From the analytical result of the MSA,[3] we have [cf.(4.8)]

$$\ln y_1 = \ln[y^{ref}(\sigma_{+-})]^{ele} = -\frac{2z^2\lambda}{\sigma}[\frac{x^2/2 - x - 1 + \sqrt{1 + 2x}}{x^2}] \qquad (4.10)$$

Here, we have used the symbol y_1 to distinguish this quantity from the previous cavity function y_0. Via eq. (2.5) and eq. (2.7), eq. (4.10) equivalently implies a molecular activity coefficient given by:

$$\ln\gamma_{M+-} = \frac{z^2\lambda}{\sigma}[\frac{(2x+2)\sqrt{1+2x} - x^2 - 4x - 2}{x^2}] = -\frac{z^2\lambda x^2}{4\sigma} + O(x^3) \qquad (4.11)$$

Fisher and Levin[10] used a dipolar hard-sphere to approximate an ionic pair in order to obtain the molecular activity coefficient. Their eq. (8) for f_{id}, obtained from a Debye-Hückel level theory, yields in our notation

$$\ln\gamma_{dhs}^{FL} = [\frac{\partial(-\beta f_{id}^{FL})}{\partial\rho_d}]_{\rho_i} = -\frac{z^2\lambda\sigma_i^2}{\sigma_{id}^3}\frac{3[\ln(1+x_{id}+\frac{1}{3}x_{id}^2) - x_{id}+\frac{1}{6}x_{id}^2]}{x_{id}^2} = -\frac{z^2\lambda x^2}{12\sigma_{id}} + O(x^3)$$
$$(4.12)$$

where $x_{id} = \kappa\sigma_{id}$, σ_{id} is the closest contact distance between ion and dipole $[(\sigma_i+\sigma_d)/2]$, dhs denotes dipolar hard sphere and we also used σ_i $(= \sigma)$ in order to clearly distinguish the ionic diameter, σ_i, from the dipole diameter, σ_d, and from σ_{id}. In eq. (4.12) the density used in computing κ is the free-ion density. It is interesting to compare eq.(4.12) with the MSA solvation free energy of a dipolar hard-sphere in ionic solution[22] of density ρ_0

$$\ln\gamma_{dhs}^{MSA} = -\frac{2z^2\lambda}{\sigma_i}[\frac{x^2}{6\nu[1+x+\sqrt{1+2x}] + 3(1+\sqrt{1+2x})(2+\nu^2 x) + x^2\nu^3}]$$
$$= -\frac{z^2\lambda x^2}{12\sigma_{id}} + O(x^3) \qquad (4.13)$$

where ν is the diameter ratio between the dipole and ion $(= \sigma_d/\sigma_i)$. In obtaining the above equation for a dipolar hard-sphere, we have assumed that the dipolar moment of the dipolar hard-sphere is same as the dipolar dumbbell $(= ze\sigma_i$, two ions at contact). We see that eq. (4.12) and eq. (4.13) agree to $O(x^2)$, but we believe (4.13) is a more accurate expression than (4.12) for x not small.

In Fig.2, a comparison between various molecular activity coefficients is made. Although eq.(4.11), eq.(4.12) and eq.(4.13) appear quite different from each other analytically, they do predict similar trend of molecular activity coefficients. In particular,

the result of dipolar hard-spheres in MSA result agrees well with the dipolar hard-sphere DH result at low concentration. However, both underestimate the effect of the molecular activity of dipolar hard-dumbbells.

Once the reference cavity function is known, we can obtain all other thermodynamic quantities. The new equations, which we shall identify as the PMSA2, are obtained by using derivations similar to those given in Section II, and we find

$$\alpha_1 = \frac{1 + 2\rho_0 K_0 y_1 - \sqrt{1 + 4\rho_0 K_0 y_1}}{2\rho_0 K_0 y_1} \tag{4.14}$$

$$\beta P = 2\rho_0 \frac{(1 + \eta + \eta^2 - \eta^3)}{(1 - \eta)^3} - \frac{(\sqrt{1 + 2x} - 1)^3}{24\pi\sigma^3}$$
$$- \alpha_1 \rho_0 [1 - (\frac{1}{8\pi\rho_0\sigma^3}) \frac{(x + 2)\sqrt{1 + 2x} - 3x - 2}{\sqrt{1 + 2x}}] \tag{4.15}$$

$$\beta(A - A^{id})/N = \beta A^{HS}/N + \beta[A^{MSA}]^{ele}/N + \frac{\alpha_1}{2} + \ln(1 - \alpha_1) \tag{4.16}$$

$$\beta\mu_{\pm} = \beta\mu_{\pm}^{o} + \ln\rho_0 + \frac{3\eta^3 - 9\eta^2 + 8\eta}{(1 - \eta)^3} - b[\frac{1 + x - \sqrt{1 + 2x}}{x}] + \ln(1 - \alpha_1)$$
$$+ \frac{\alpha_1}{16\pi\rho_0\sigma^3}[\frac{(x + 2)\sqrt{1 + 2x} - 3x - 2}{\sqrt{1 + 2x}}] \tag{4.17}$$

where y_1 is evaluated from eq.(4.10) and K_0 is evaluated from eq.(2.13).

V. THE EFFECT OF HARD DUMBBELL CORES OF ASSOCIATED IONIC PAIRS

In the gas phase, ions are thought to be highly associated.[1c,11] Thus, to a first approximation, the ionic system can be expected to behave more or less like a dipolar hard-dumbbell system. In order to have an accurate equation state near the complete association limit, one must build in an accurate equation of state for the hard-sphere, hard-dumbbell mixture. This can be easily accomplished by including the hard-sphere part of the reference cavity function:[8]

$$y_2 = y^{CS}(\sigma)y_1 \tag{5.1}$$

14

where $y^{CS}(\sigma)$ is the contact value for cavity function under the Carnahan-Starling equation of state.

$$y^{CS}(\sigma) = \frac{(2 - \eta)}{2(1 - \eta)^3} \tag{5.2}$$

As a result, our equations in the PMSA3 are

$$\alpha_2 = \frac{1 + 2\rho_0 K_0 y_2 - \sqrt{1 + 4\rho_0 K_0 y_2}}{2\rho_0 K_0 y_2} \tag{5.3}$$

$$\beta P = 2\rho_0 \frac{(1 + \eta + \eta^2 - \eta^3)}{(1 - \eta)^3} - \frac{(\sqrt{1 + 2x} - 1)^3}{24\pi\sigma^3}$$

$$-\alpha_2\rho_0[\frac{1 + \eta - \eta^2/2}{(1 - \eta)(1 - \eta/2)} - (\frac{1}{8\pi\rho_0\sigma^3})\frac{(x + 2)\sqrt{1 + 2x} - 3x - 2}{\sqrt{1 + 2x}}] \tag{5.4}$$

$$\beta(A - A^{id})/N = \beta A^{HS}/N + \beta[A^{MSA}]^{ele}/N + \frac{\alpha_2}{2} + \ln(1 - \alpha_2) \tag{5.5}$$

$$\beta\mu_{\pm} = \beta\mu_{\pm}^{\circ} + \ln\rho_0 + \frac{3\eta^3 - 9\eta^2 + 8\eta}{(1 - \eta)^3} - b[\frac{1 + x - \sqrt{1 + 2x}}{x}] + \ln(1 - \alpha_2)$$

$$-\frac{\alpha_2}{2}\frac{\eta(5 - 2\eta)}{(2 - \eta)(1 - \eta)} + \frac{\alpha_2}{16\pi\rho_0\sigma^3}[\frac{(x + 2)\sqrt{1 + 2x} - 3x - 2}{\sqrt{1 + 2x}}] \tag{5.6}$$

where y_2 is evaluated from eq.(5.1) and K_0 is evaluated from eq.(2.13).

The rationale for these equations is that when x is set equal to zero in (5.4), it becomes an equation that is nearly exact [8,15] for a hard-sphere, hard-dumbbell mixture in which $2\rho_0$ is total density, η is total volume fraction, and α_2 is the ratio of dumbbell density to total density.

VI. RESULTS AND DISCUSSIONS

To investigate the critical phenomena, it will be easier to deal with the reduced parameters. The reduced pressure is defined as

$$P^* = \frac{\epsilon\sigma^4}{(ze)^2}P \equiv \phi\rho^*T^* \tag{6.1}$$

with T^* the reduced temperature ($= 1/b$), ρ^* the reduced density ($= 2\rho_0\sigma^3$), and ϕ the osmotic coefficient [$= \beta P/(2\rho_0)$]. The reduced inverse-Debye length can also be expressed

15

in terms of the reduced temperature and density through

$$x^2 = \frac{4\pi\rho^*}{T^*}.$$ (6.2)

The critical density and critical temperature can be obtained by solving following two equations:

$$(\frac{\partial P^*}{\partial \rho^*})_{T^*} = 0$$ (6.3)

$$(\frac{\partial^2 P^*}{\partial [\rho^*]^2})_{T^*} = 0$$ (6.4)

The equations are solved by using IMSL routines for nonlinear algebraic equations. When the association terms in PMSA are turned off, we recover the lowest-order gamma-ordered (LOGA) results given in Stell, Wu and Larsen,[4a] which are identical to the MSA results[24] when the hard-sphere contributions to the MSA and LOGA are evaluated in the same approximation.[24] Our critical points in the PMSA1, PMSA2 and PMSA3 are compared with some of earlier theories and most recent computer simulations in Table I. Our theory is in an excellent agreement with recent simulation results for the RPM critical density while our critical temperature is about 40% higher than those results. The difference between the results of the PMSA1 with those of Ebeling and Grigo[5] provide a comparison between the RCA approach and EG's Bjerrum-like approach. We believe the Table I value they give for their $(\rho_c^* T_c^*)$ is in error, and find instead (0.026, 0.0789), which is not far from our PMSA values.

Although the critical temperature and critical density do not change much ($< 8\%$) as one goes from the PMSA1 to PMSA2 or PMSA3, the critical pressure is decreased about 35%. We also evaluate the critical compressibility z_c ($=P_c^*/\rho_c^* T_c^*$). We find that the critical compressibility in the PMSA3 is 0.101, which is in excellent agreement with the experimental average of 0.098,[27] although the precise simulation value is as yet unavailable. The corresponding values of z_c for the PMSA1 and PMSA2 are 0.14 and 0.104, respectively. It is obvious that significant improvements are made as one goes from the PMSA1 to PMSA2 or PMSA3.

As we see from Table I and Fig.3, Fisher and Levin's result[10] of adding the DH, Bjerrum, and dipole-ion (DI) contributions is in good agreement with the computer-simulation results. We note however that this free-energy expression includes no hard-core term and hence does not reduce to a hard-sphere term correctly when the charges are turned off. The contributions of various terms in our own theory at the critical point are listed in Table II. It shows that the ideal (ID) and MSA electrostatic (MSA-ELE) parts of the pressure determine the first derivative while the hard-sphere (HS), MSA-ELE and ionic-association parts determine the second derivative. Thus, we view the hard-sphere term as a fundamental ingredient of a satisfactory theory of the RPM.

In this regard, it is worth noting the sensitivity of the RPM thermodynamics in its critical region upon not just the presence of a hard-core contribution but also upon the accuracy to which that contribution is approximated. To assess the hard-core contribution, Fisher and Levin[10] advocate adding to the free energy a free-volume term of simple logarithm form [their eq. (3)]. Using the free-volume form, Fisher and Levin[10] found that its addition to their DH + Bjerrum + DI result significantly changed the shape of the (ρ^*, T^*) coexistence curve, bringing it in somewhat poorer agreement with the simulation data over a broad range of densities above the critical density ρ_c^* as a result of its substantially more negative slope for ρ^*. Guissani and Guillot have found[28] that if one exactly follows the Fisher-Levin prescription but replaces the free-volume form by the far more accurate Mansoori-Carnahan-Starling-Leland (MCSL)[29] hard-core contribution for a binary hard-sphere mixture, the resulting coexistence curve departs much more substantially in the same direction from the simulation data. We further find that there is negligible change in this result if we replace the MCSL term by any other hard-core contribution to the free-energy that is known to have good accuracy over a broad range of fluid densities (e.g. the scaled-particle/Percus-Yevick (PY) compressibility term that is often used in liquid-state studies) or vary somewhat the way the effect of association on the core contribution is handled. In Fig.3, we compare some of the results that have

led us to this conclusion. We show there, in addition to the Fisher-Levin and Guissani-Guillot coexistence curves, two more coexistence curves that otherwise follow from the Fisher-Levin prescription but treat the hard-core contribution to the free energy in ways that deviate from that prescription. The curve that is closest to the coexistence curve computed by Guissani-Guillot and slightly below it treats the core of an associated pair of ions just as we do in the PMSA3. In other words, the core is that of a diatomic dumbbell formed from two hard spheres in contact, with each sphere having the diameter of an ion. The remaining curve shown in Fig.3 (by a dashed line) results from making no distinction between the core contribution of ions that are free and those that are part of an associated pair; the core contribution is computed using the Carnahan-Starling approximation for a system of equal-diameter hard spheres of reduced density ρ^*. (We note that the critical-point shift common to all these treatments yields (ρ_c^*, T_c^*) values that are *not* worse than the coreless FL value.)

These last two treatments of the hard-core term nicely complement one another with respect to the way they handle the effect of association on the core term—they represent the two extremes of assuming maximal core proximity between associated ion pairs and of ignoring the effect of association altogether, in both cases preserving the spherical symmetry of the individual ionic cores. It is reassuring that they yield results in relatively close agreement with each other and with the core treatment of Guissani-Guillot. In fact, as Fisher has noted to us in private communication, if one uses an exact hard-sphere B_1 in the FL eq. (3) with $B_2 = 2B_1$ as the sphere-dumbbell contribution, one obtaines a hard-core contribution that is quite adequate over the coexistence region at issue; it too yields a coexistence-curve correction close to the ones we have developed. However the very different values of B_j actually used by FL are instead based upon a crystal-packing structure appropriate to a free-volume theory tailored to do justice to a high-density regime. In light of the fact that the addition of an adequate core term to the coreless version of the Fisher-Levin approximation destroys its good agreement with the

simulation coexistence curve, we conclude that the agreement may be due to the presence of compensating errors.

We note in passing that the anomalous "banana" shape of the coexistence curve in the DH + Bjerrum approximation[10,11] becomes even narrower when one adds an accurate core contribution to it, an effect Fisher has also noted in private communication. The "banana" shape appears to be the result of the combined presence of the DH and Bjerrum approximations; it is not found when a core term is added to the simple DH result nor is it found when the MSA is combined with the Bjerrum approach as in the Ebeling-Grigo work[5]. We also note that sensitivity to the accuracy of the hard-core contribution is not confined to the DH + Bjerrum + DI starting points. As one of us has already remarked,[2d] it occurs as well when one adds a hard-core contribution to the Debye-Hückel limiting law term. (Compare in ref. 2d, the critical values in eq.(2.1) with those given a few lines above (2.5)).

Returning to our own PMSA approach, we find sensitivity to the hard core term there too. In particular, we are unable to find a critical point in our PMSA1 if the hard-sphere part is turned off. With respect to sensitivity on the ion-dumbbell term, although PMSA2 includes a contribution from the ion/dipolar-dumbbell interaction, as does the Fisher-Levin approximation, we find that the effect of the molecular activity coefficient is not as significant on our level of approximation as it is in DH-level theory of Fisher and Levin.[10]

The phase diagram of the RPM can be calculated through the constructions involving the intersection of the Gibbs free energy and pressure at each temperature.[30] The critical point obtained from this approach is in perfect agreement with the results obtained through eqs. (6.3) and (6.4), as it should be. The phase diagrams in the PMSA1, PMSA2, PMSA3 are compared with the most recent simulation[1d] in Fig.4. Although our critical temperature is higher than the simulation data, the shapes of our curves do show correct qualitative features as expected.

In Fig.5, the degree of association is plotted as a function of reduced density at various temperatures in the PMSA3. While the degree of association approaches zero at the zero-density limit, it increases to a maximum at a medium density and then decreases at a high-density region. The degree of association increases as the temperature decreases at low densities but decreases at high densities. Similar phenomena were also found in the EGA.[5] Fig.6 shows that the PMSA3 and PMSA2 give a much higher value of degree of association than the PMSA1 at the high density region. The degree of association along the coexistence curve is plotted for PMSA2 in Fig.7. In the gas phase, ions have a high degree of association. In the liquid phase, about 50% of ions are associated. This is in agreement with the results of Friedman and Larsen[11] and of Ebeling and Grigo.[5]

In Fig.8, the reduced pressure is plotted as a function of the reduced density at various temperatures. In Fig.9, the reduced chemical potentials in the PMSA1, PMSA2, and PMSA3 are compared with the MSA and computer simulation data.[1a,1d] As the figure shows, our theories provide a much better agreement with the simulation data than the MSA, in particularly, at low temperature. The PMSA2 and PMSA3 are significantly better than PMSA1 at low temperature, but slightly worse at high temperature and high density.

VII. SUMMARY

In this paper, we have shown that the combination of the MSA with our RCA theory of chemical associations[8] yields a better description of critical phenomena for the RPM than the Ebeling-Grigo approach[5] combining the MSA with an extension of the Bjerrum theory of association,[7] although both approaches build in an exact second ionic virial coefficient. The advantages of the PMSA3 are summarized as follows:

1. It is a simple analytic theory free of nonlinear equations,

2. It has built into it near-exact hard-sphere fluid and hard-dumbbell/hard-sphere

mixture pressures,

3. It treats the hard-core condition accurately,

4. It includes an exact second ionic virial coefficient,

5. It is readily extendable to asymmetrical charged hard-sphere systems and mixtures of having more than one anion and cation species.

There are two factors we have not discussed that are potential sources of error in our theory. One of them is our neglect of association into n-mer clusters (n> 2). The primary effect to be expected from such neglect is an overestimate of the fraction of free ions, and hence the free-ion density. This tends to give rise to underestimate of both ρ_c^* and α_c. While it is true that our ρ_c^* is at the low end of the simulation range and our α_c is considerably lower than some other theoretical estimates,[2] our values are not inconsistent with current simulation results or known theoretical facts. This suggests that our neglect of association into larger clusters is not a serious source of error. It further suggests that our overestimation of T_c^* (by perhaps 40% higher or so, according to current simulation estimates) cannot be primarily attributed to that neglect, although considerable uncertainty remains in this connection. On one hand, it is found in Fisher and Levin's work[10] that the contribution of n-mers ($n > 2$) to the critical point are very small (less than 1% of the dipolar part), and our own preliminary investigation based on the extended PMSA also finds that effects of trimers seem to be small. From such considerations, it would seem reasonable to believe that the effect of n-mers, all $n > 2$, would be less than the effects of dimers, which lowers the critical temperature from 0.079 (MSA) to 0.075 (PMSA). That would suggest that at most, the effects of higher n-mers would further reduce T_c^* from 0.075 to 0.070, which is still much higher than the most recent simulation value of 0.053-0.057.[1] On the other hand, other studies of the effects of ionic clustering suggest that the population of higher n-mers at the critical point may be large.[31-33] The extent of higher-order clustering revealed in the recent simulation result of Bresme et. al.[33] is particularly striking and we hope to incorporate the results of the

study into an extension of our theory.[34]

An important second factor that may well result in an overestimation of T_c is the mean-field nature of our theory, which neglects the critical fluctuations that would be found in an exact treatment. In mean-field treatments of Argon of a comparable level of sophistication as our PMSA's, this neglect also results in a critical temperature significantly higher than the true T_c but a critical density of good accuracy (as in, e.g., the Baker-Henderson perturbation theory[35]). Although the source of error due to neglecting of critical fluctuations does not seem easy to remove, we aspire to at least estimate its magnitude in further work.

In recent work by Zhang and Stell,[36,2d] it is concluded that asymmetric charged models have mean-field like critical exponents. If this is true, the extension of our PMSA to an asymmetric charged hard-sphere system, which is trivial, might yield much better agreement with simulation than in the RPM case. In this connection, recent simulation results for NaCl[37] indeed appear to be more consistent with typical mean-field behaviour that the RPM simulation results, but further results will be needed to elucidate such points.

ACKNOWLEDGMENTS

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strength. However, in computing the thermodynamics from the internal energy

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Table I   Comparison of different theoretical results with simulations.

Theory	Ref.	T_c^*	ρ_c^*	P_c^*	α_c
DH	25	63×10^{-3}	0.00497		
DH+Bj+DI(FL)	10	58×10^{-3}	0.025		
Padé	4a	74×10^{-3}	0.010	6×10^{-5}	
MSA	~~4a, 23–24~~	79×10^{-3}	0.014	9.7×10^{-5}	
HNC	26	136×10^{-3}	0.0004		
MSA+Bj(EG)	5	83.7×10^{-3}	0.018	35.4×10^{-5}	
PMSA1	†	74.8×10^{-3}	0.025	26.9×10^{-5}	22.7%
PMSA2	†	73.3×10^{-3}	0.0229	17.4×10^{-5}	56.3%
PMSA3	†	74.5×10^{-3}	0.0245	18.4×10^{-5}	56.2%
MC, 1994	1d	53×10^{-3}	0.025		
MC, 1994	1c	$\geq57\times10^{-3}$			
MC, 1992	1b	56×10^{-3}	0.04		

† This work

Table II. Contributions of various terms at the critical point in the PMSA3

	ID	HS	MSA-ELE	ASSOCIATION
$\dfrac{\partial P^*/T^*}{\partial \rho^*}$	1.00	0.11	−1.15	0.04
$\dfrac{\partial^2 P^*/T^*}{[\partial \rho^*]^2}$	0.00	4.61	−1.00	−3.61

26

FIGURE CAPTIONS

Fig.1 The thermodynamic cycle.

Fig.2 Logarithm of the reduced dipole activity coefficient, $T^*\ln\gamma_M$, as a function of reduced inverse Debye length x (the infinite dilute dipolar species in an ionic solution). The dipolar dumbbell in the MSA (—), the dipolar hard-sphere in the MSA (- - -), and the dipolar hard-sphere in the DH approximation [ref. 10] (— - —). Here the diameter ratio of dipolar hard-sphere to ion, $r = \sigma_d/\sigma_i$, is 1.324 which is the value used by Fisher and Levin [ref. 10].

Fig.3 The phase diagram of the RPM in the Fisher-Levin approximation (DH + Bjerrum + DI, — - —); the Fisher-Levin approximation plus the Fisher-Levin hard-core term(— - - —); the Guissani-Guillot result(— - - - —); the Fisher-Levin approxiamtion plus a hard-core term of PMSA3 form(—); the Fisher-Levin approximation plus a hard-core term of Carnahan-Starling form(- - -). See text for further details. The simulation data^{1d} is indicated by the square symbol (□). Critical points in various approximations are indicated by dots (•).

Fig.4 The phase diagram of the RPM in the PMSA1 (— - —), PMSA2 (- - -), PMSA3 (—) and by simulation^{1d} (○). The critical points of the PMSA's and simulation are indicated by the symbols + and •, respectively.

Fig.5 The degree of association α as a function of the logarithm of reduced density ($\ln\rho^*$) at various reduced temperatures in the PMSA3. T*=0.08 (—), 0.075 (- - -), and 0.07 (— - —).

Fig.6 The degree of association α as a function of the logarithm of reduced density ($\ln\rho^*$) in various approximations at T*=0.075. PMSA1 (— - —), PMSA2 (- - -), and PMSA3 (—).

Fig.7 The degree of association α along the coexistence curve in PMSA2. The cross sign indicates the location of the critical point.

Fig.8 The reduced pressure P^* as a function of reduced density ρ^* at various temperatures. PMSA3 (—), PMSA2 (- - -) and PMSA1 (— - —). From top to bottom, T^*=0.10, 0.075, and 0.070, respectively.
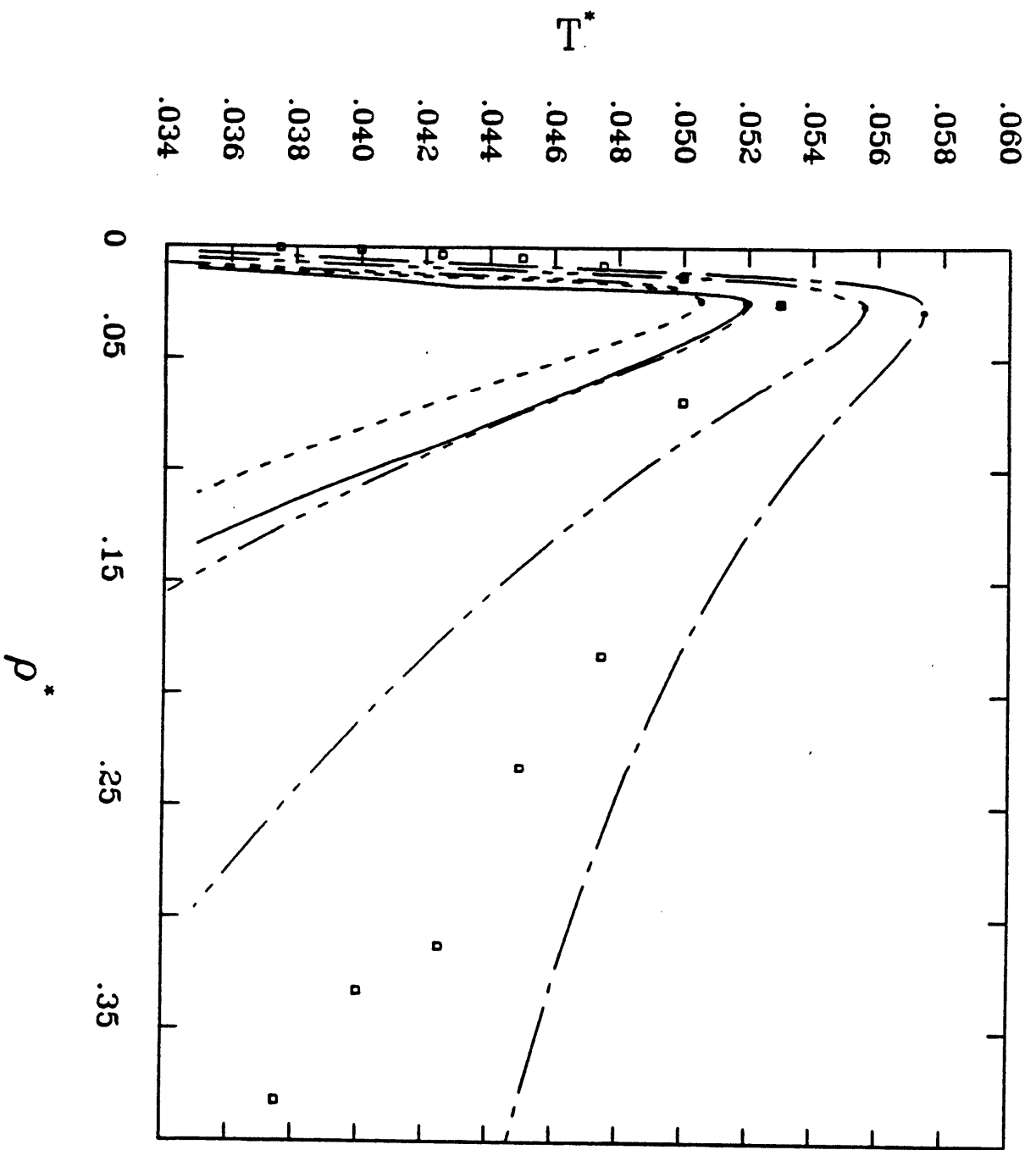
Fig.9 The reduced chemical potential, $\beta\mu' = \ln(\rho_0\sigma^3\gamma_\pm)$, as a function of the logarithm of the reduced density ($\log\rho^*$) at various temperatures. The PMSA3 (—), PMSA2 (- - -), PMSA1 (— - —) and the MSA (— - - —) results are compared with simulation data [◻ (T^*=0.147, ref. 1a); ○ (T^*=0.07 and 0.045. ref. 1d)]. From top to bottom, T^* =0.147, 0.07, and 0.045, respectively.

Vacuum:

ΔF_2

ΔF_1

ΔF_3

Solution:

ΔF_4
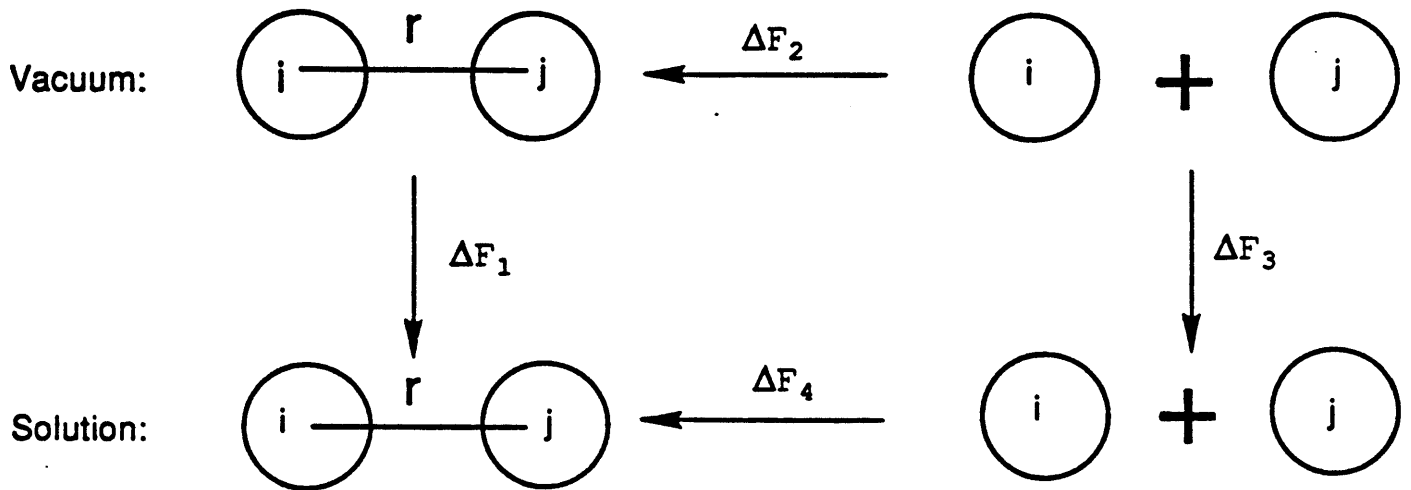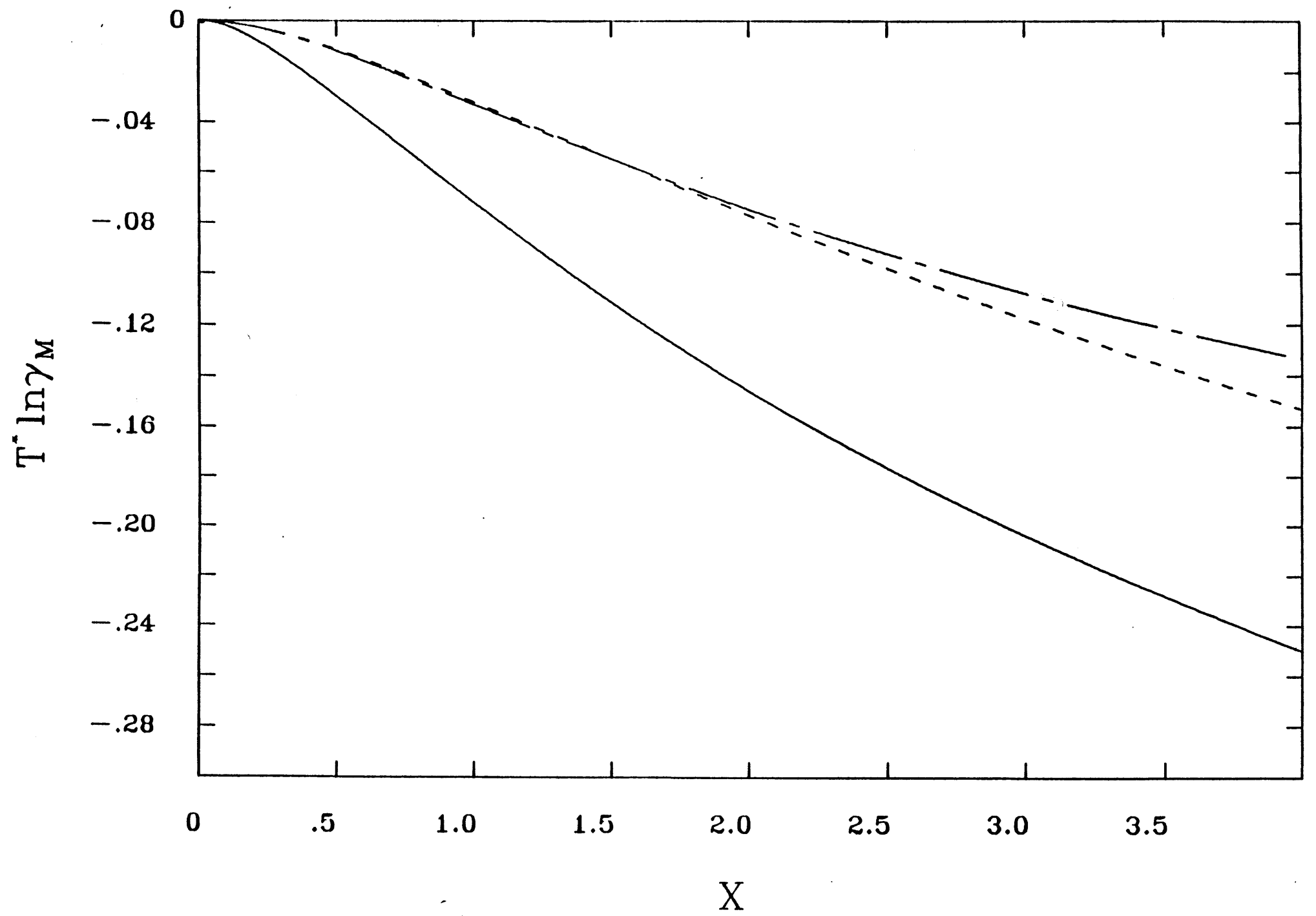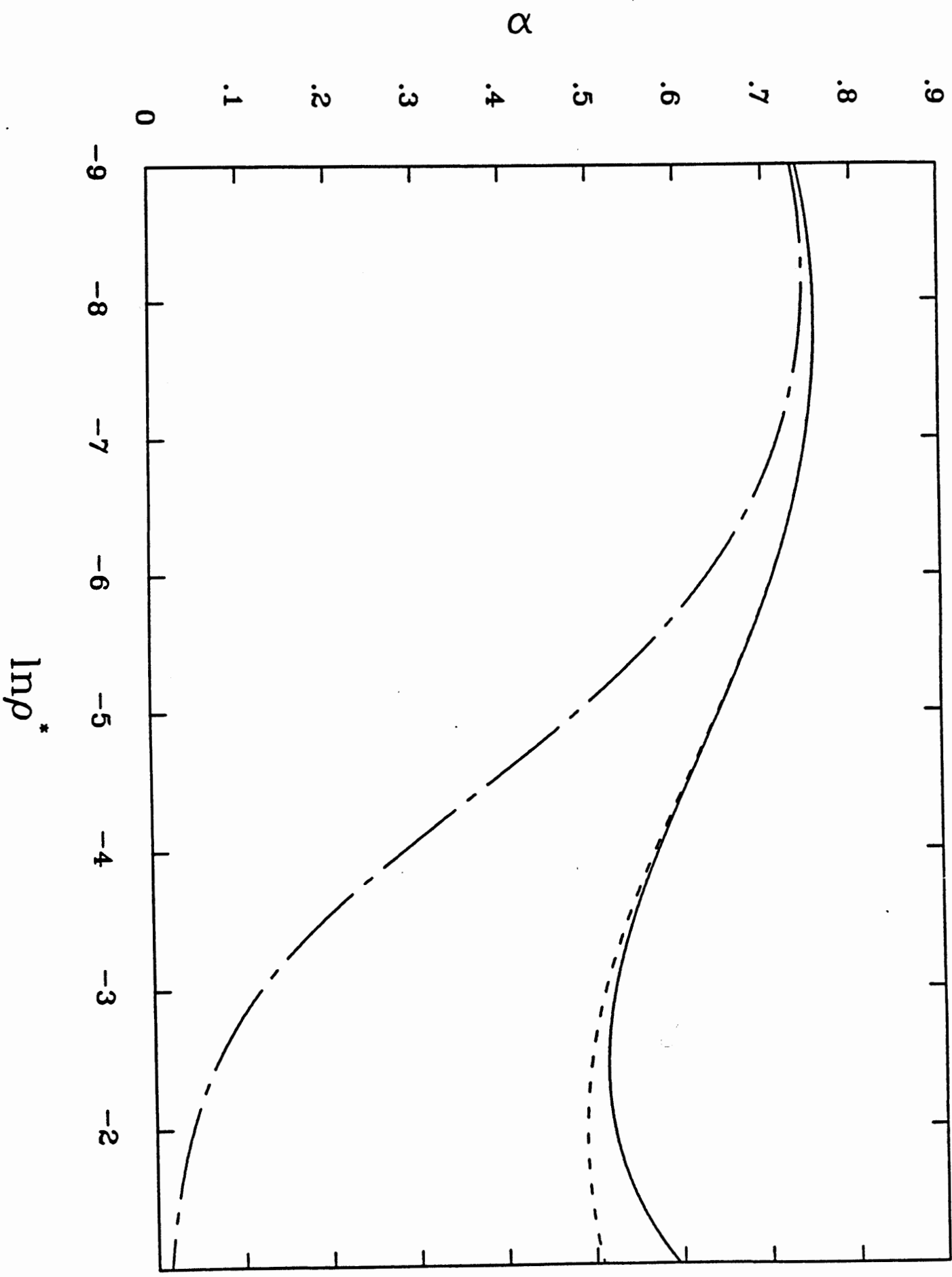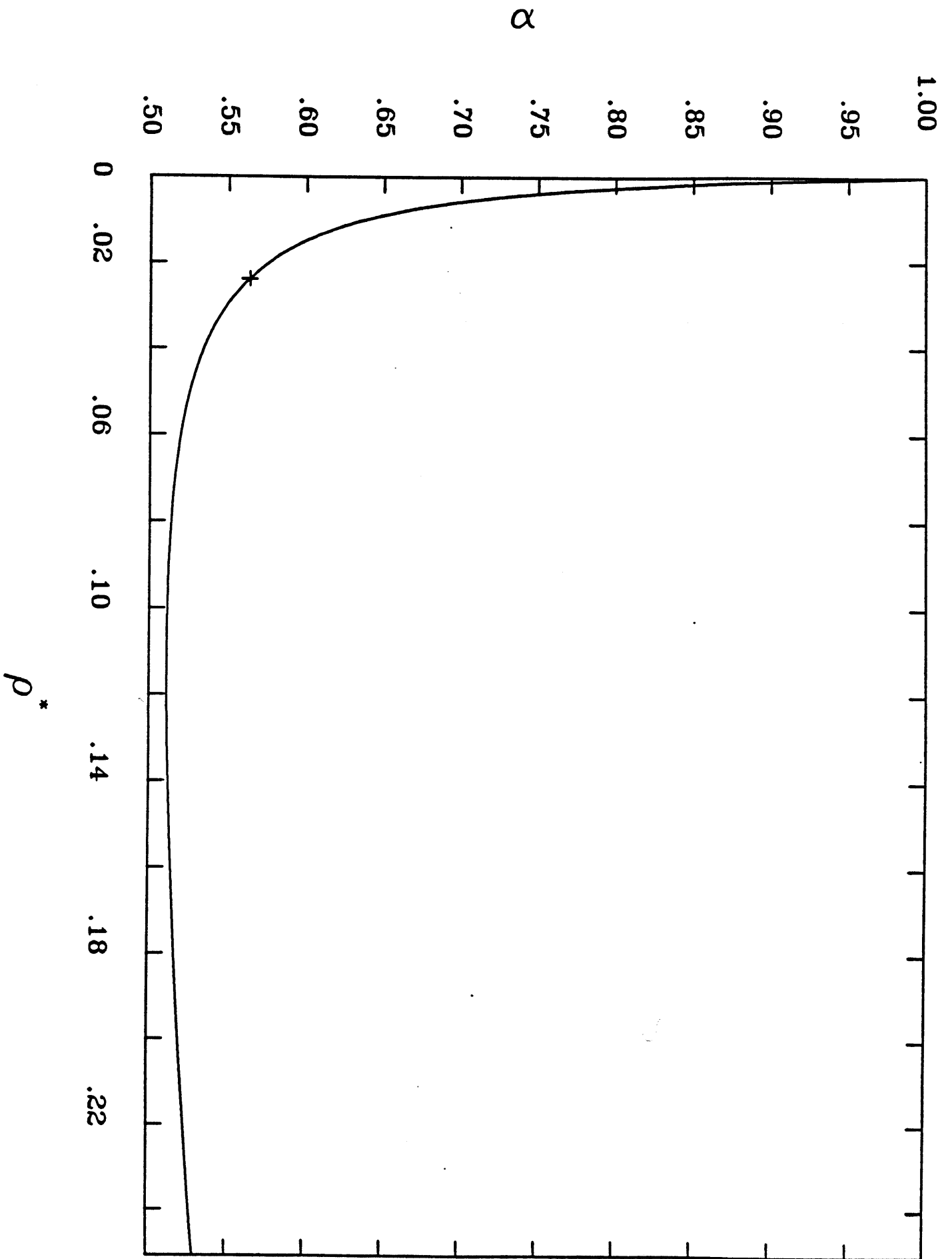
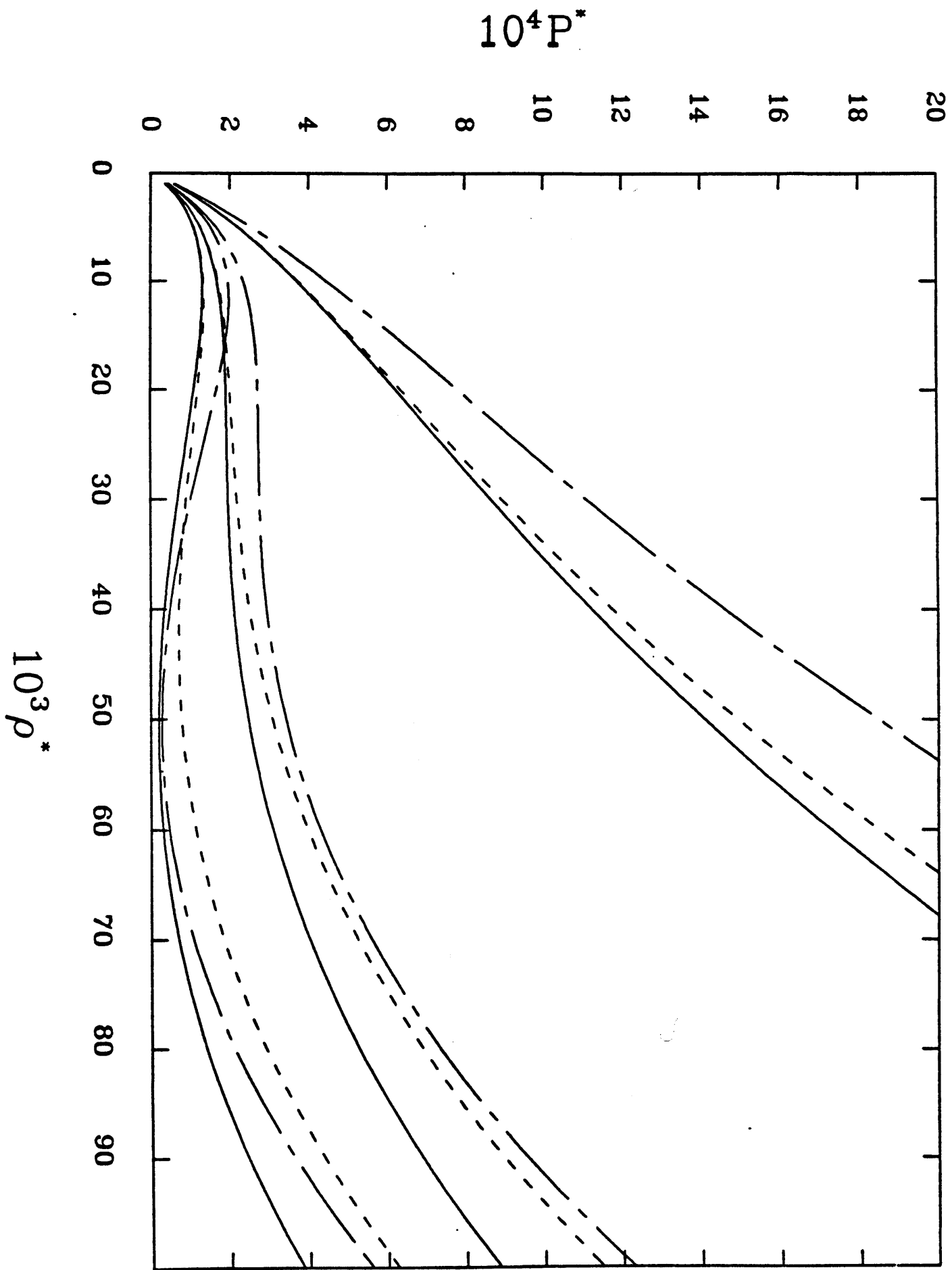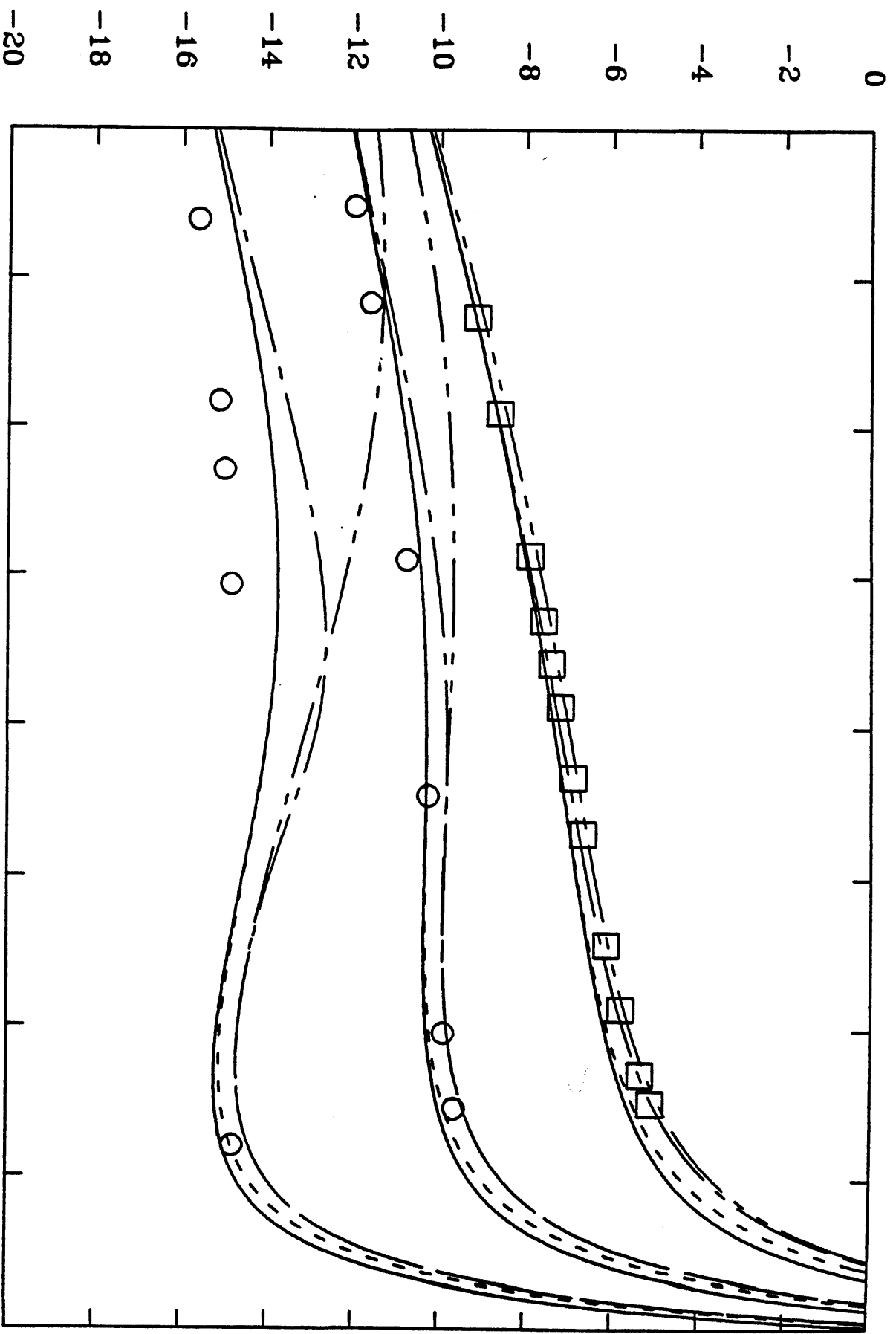Zhou, Yeh and Stell, Fig.2

Zhou, Yeh and Stell, Fig.3
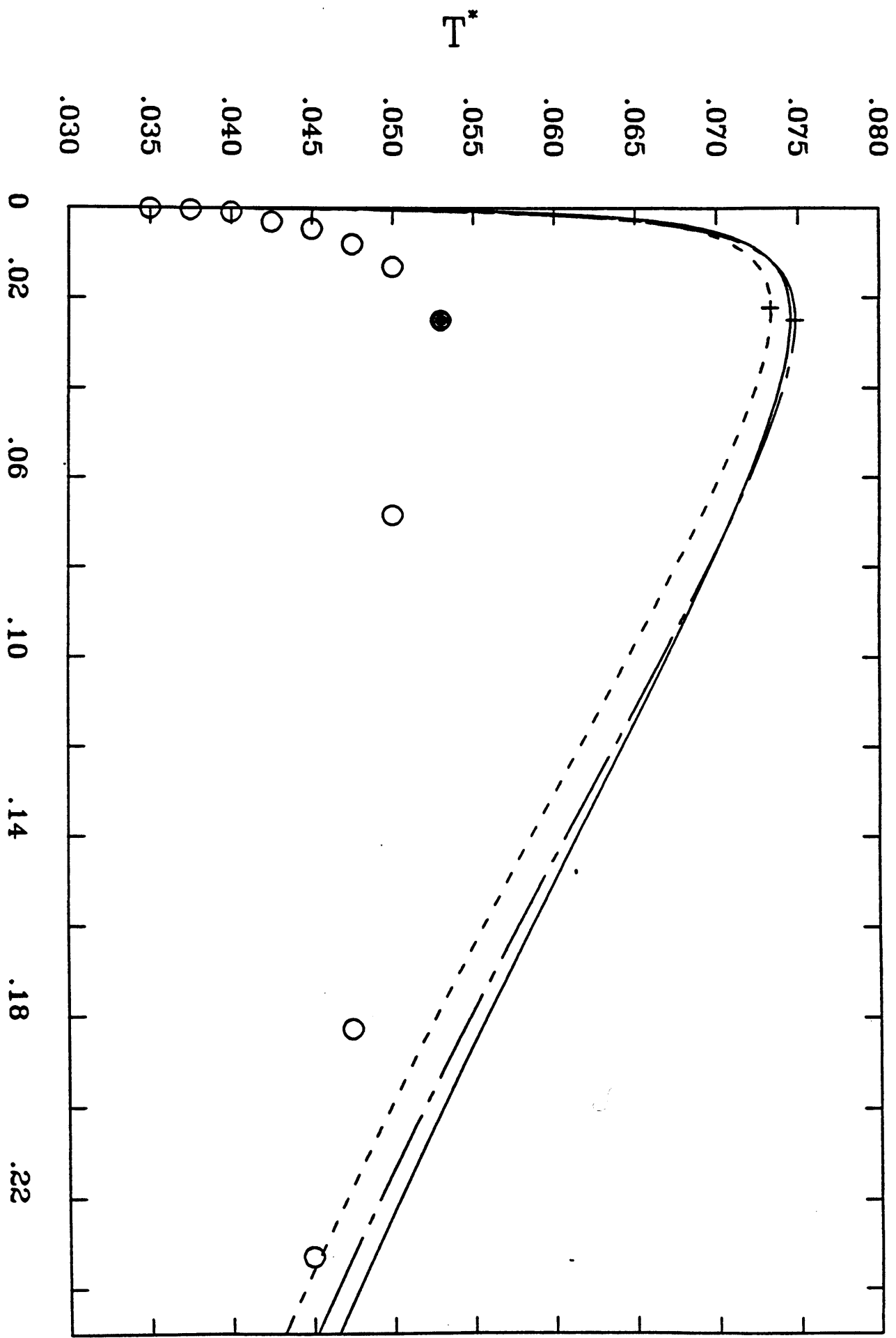
Zhou, Yeh and Stell, Fig.4
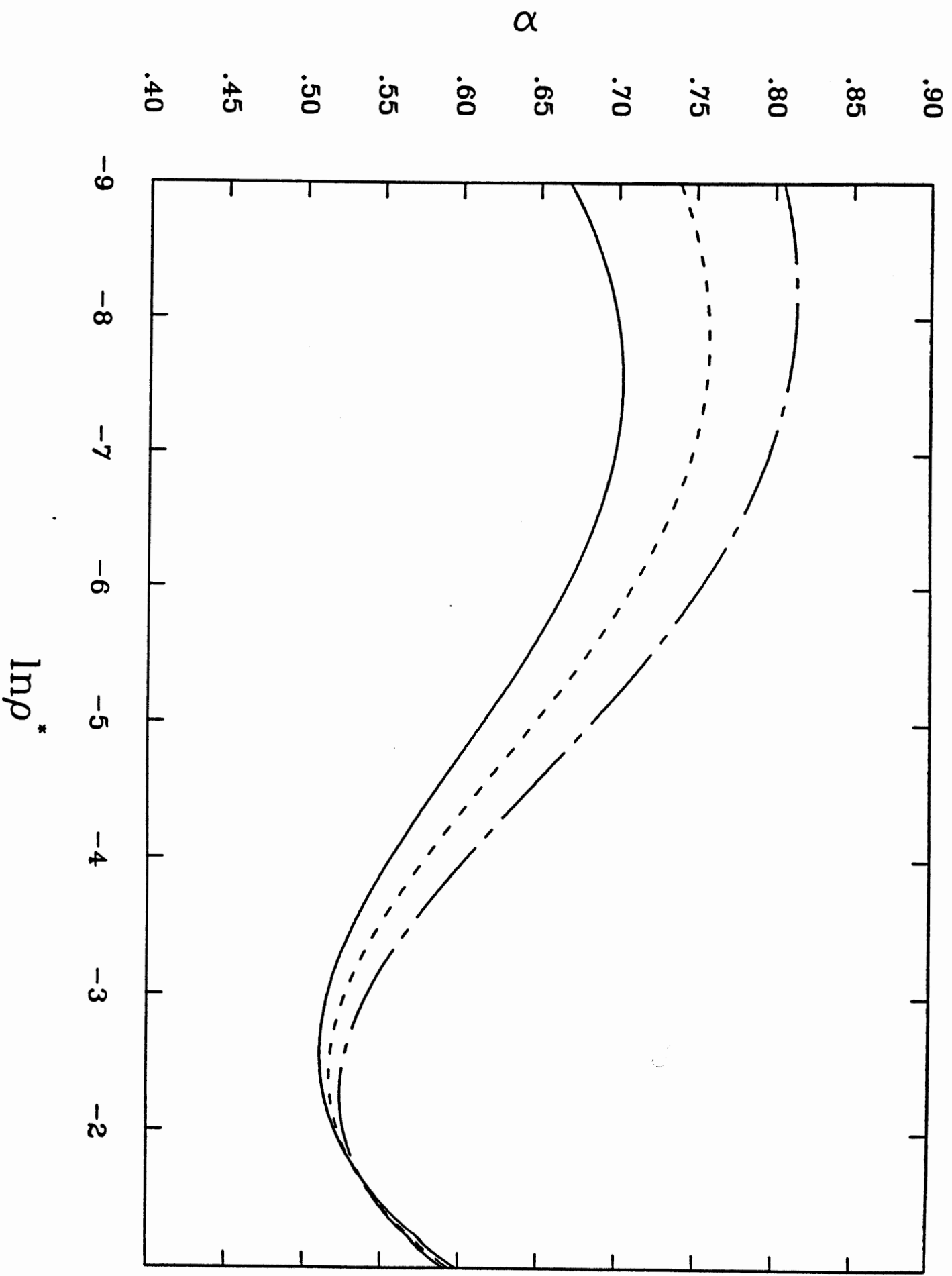
Zhou, Yeh and Stell, Fig.5

Zhou, Yeh and Stell, Fig.6

α

ρ^*

Zhou, Yeh and Stell, Fig.7

$10^4 P^*$

$10^3 \rho^*$

Zhou, Yeh and Stell, Fig. 8

Zhou, Yeh and Stell, Fig.9