Phase Separation of Ionic Fluids: An Extended Ebeling-Grigo Approach[*]

Showguei Yeh

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, NY 11794-3400

Yaoqi Zhou

Department of Chemical Engineering
North Carolina State University
Raleigh, NC 27695-7905

George Stell

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, NY 11794-3400

ABSTRACT

The Ebeling-Grigo (EG) improvement of the mean spherical approximation (MSA) via the Bjerrum theory of ionic association in the restricted primitive model (RPM) is reviewed and extended. We find that in terms of reduced density and temperature, the critical point (ρ_c^*, T_c^*) of the EG approximation (EGA) is located at (0.026, 0.0789), rather than the (0.018, 0.0837) quoted by EG. The corrected result is closer to the most recent simulation estimates of the RPM critical point. A further improvement is obtained by incorporating the activity coefficient of the associated ionic pair to yield a dipole-ion contribution. The new approximation, EGA+DI, has a critical point at (0.027, 0.0716), which is in still better agreement with the simulation estimates.

I. INTRODUCTION

The mean-spherical approximation (MSA) has been widely used in ionic systems because it provides simple analytical solutions and correctly treats the hard-core condition.[1] 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[4] is to explicitly include the ionic pairing contribution via the second ionic virial coefficient[5] and the mass-action law, using an elegant extension of the Bjerrum (BJ) theory[6] of ionic association.

In an earlier paper,[7] we improved the MSA via a new approach, similar to the approach of Ebeling and Grigo[4] but using the reference cavity theory of ionic association instead. In the simplest version of our theory,[7] which we call the pairing MSA 1 (PMSA1), we neglect the activity coefficient of the fully associated ion pairs, which are regarded as a separate dipolar species, and obtain the critical point (ρ_c^*, T_c^*) at (0.025, 0.0748). 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. In a 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, 0.0733). In a third PMSA (or PMSA3), we further include the effect of the presence of the dipolar-particle cores. The final critical point is located at (0.025, 0.0745). These critical points are considerably closer than the MSA result[3,9] (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.[10]

Conceptually our PMSA1 is on much the same level of approximation as the Ebeling-Grigo approximation (EGA),[4a] which also neglects the activity coefficient of the fully associated ionic-pairs except that the EG theory uses the BJ theory of ionic association. However, somewhat surprisingly the critical point value (0.018, 0.0837) EG give is not only in consid-

erably worse agreement with simulation than the PMSA1 critical point,[7] but their critical temperature is in even worse agreement than the MSA's critical temperature (0.079)[9]. In order to understand this difference, we have recalculated the critical point using their approximation. We find that the critical point of the EGA is in fact located at (0.026, 0.0789). The critical point is thus not far from the PMSA1 result (0.025, 0.0748), which is what one would anticipate on conceptual grounds. (A similar reassessment of EG theory has also been made independently by Guissani and Guillot.[11]) We have gone on to improve the EGA by incorporating the activity coefficient of associated ionic pairs at the MSA level to obtain a dipole-ion contribution in much the same spirit as that of Fisher and Levin in their Debye-Hückle level theory.[12] The new approximation, EGA+DI, further improves the agreement with simulations. The critical point of the EGA+DI is located at (0.027, 0.0716). In Section II, the EGA is reviewed and the new approximation (EGA+DI) is developed. In Section III, the results are compared with simulation results and other approximations.

II. THE THEORY

A. The Ebeling-Grigo Approximation (EGA)

Consider the restricted primitive model (RPM), which is a classical system of N charged hard spheres, N/2 cations and N/2 anions with same hard-core diameter σ and opposite charge numbers (z, -z). In the EGA, the pressure (P) and Helmholtz free energy (A) consist of three parts: ideal (ID), hard-core (HC), and electrostatic (EL), calculated by applying the MSA to the nonassociated ions, where the degree of association is determined via a law of mass action. In this case, the pressure and the free energy can be written as

$$\beta P = \beta(P^{ID} + P^{HC} + P^{EL}) \tag{2.1}$$

$$\beta A/N = \beta[A^{ID} + A^{HC} + A^{EL}]/N \tag{2.2}$$

where $\beta = 1/k_B T$.

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The ideal part after association is

$$\beta P^{ID} = 2\rho_0 - \alpha\rho_0 \tag{2.3}$$

$$\beta A^{ID}/N = \beta A^\circ/N - (1-\alpha)\{1 - \ln[(1-\alpha)\rho^*]\} - (\alpha/2)\{1 - \ln[(\alpha\rho^*)(2\sigma^3/K_0)]\} \tag{2.4}$$

where α is the degree of association which satisfies the law of mass action:

$$\frac{\alpha}{\rho_0(1-\alpha)^2} = K_0 \frac{\gamma_+\gamma_-}{\gamma_{M_{+-}}} \tag{2.5}$$

Here γ_+ and γ_- are the activity coefficients of free (unassociated) cations and anions, respectively, and $\gamma_{M_{+-}}$ is the activity coefficient for associated ionic pairs, ρ_0 is total number density of cations or anions including those constituting the associated pairs, and K_0 is the ideal association constant. The EGA evaluates $\gamma_\pm$, the mean activity coefficient of free ions, in the MSA and approximates the $\gamma_{M_{+-}}$ as 1.

$$\gamma_\pm^{EGA} = \gamma_\pm^{EL} \tag{2.6A}$$

$$\gamma_{M_{+-}}^{EGA} = 1 \tag{2.6B}$$

As a result, the degree of association, α_0, in the EGA can be obtained from

$$\frac{\alpha_0}{\rho_0(1-\alpha_0)^2} = K_0 \left[\gamma_\pm^{EL}\right]^2 \tag{2.7}$$

The EGA hard-core part is obtained from the Carnahan and Starling[14] equation, which is known to be very accurate for the pressure and free energy of hard spheres.

$$\beta P^{HC} = 2\rho_0 \frac{2\eta(2-\eta)}{(1-\eta)^3} \tag{2.8}$$

$$\beta A^{HC}/N = \frac{\eta(4-3\eta)}{(1-\eta)^2} \tag{2.9}$$

where the packing fraction $\eta = \pi\rho_0\sigma^3/3$. The hard-core part is assumed to be independent of the degree of association.

From the MSA we have[1]

$$\ln\gamma_\pm^{EL} = -\frac{z^2\lambda}{\sigma}[\frac{1+x-\sqrt{1+2x}}{x}] \tag{2.10}$$

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where

$$x = \kappa\sigma, \quad \kappa^2 = \frac{4\pi\beta\rho_i(ze)^2}{\epsilon} \tag{2.11}$$

and ρ_i is the number density of free cations and anions. The MSA also gives[1]

$$\beta[P^{EL}] = -\frac{(\sqrt{1+2x}-1)^3}{24\pi\sigma^3} \tag{2.12}$$

$$\beta[A^{EL}]/N = -\frac{3x^2 + 6x + 2 - 2(1+2x)^{3/2}}{24\pi\rho_0\sigma^3} \tag{2.13}$$

The final equation for pressure of the EGA is

$$\beta P = 2\rho_0 \frac{(1+\eta+\eta^2-\eta^3)}{(1-\eta)^3} - \frac{(\sqrt{1+2x}-1)^3}{24\pi\sigma^3} - \alpha_0\rho_0 \tag{2.14}$$

where α_0, the degree of association of EGA, is calculated from eq.(2.7) and the ideal association constant K_0 in eq.(2.7) is chosen so that eq.(2.14) gives an exact second ionic virial coefficient,[13]

$$K_0 = 8\pi\sigma^3 \sum_{m=2}^{\infty} \frac{b^{2m}}{[(2m)!(2m-3)]} \tag{2.15}$$

where $b = \beta(ze)^2/(\epsilon\sigma)$ is the Bjerrum length.

B. An Improvement over the Ebeling-Grigo Approximation

One natural way to improve the EGA is to take into account the ion-pair (dipole) activity coefficient.[7,12] In this case, the free energy can be rewritten as

$$\beta A/N = \beta[A^{ID} + A^{HC} + A^{EL} + A^{DI}]/N \tag{2.16}$$

where the dipole contribution is approximately obtained from

$$\beta A^{DI}/N = \frac{\rho_d}{2\rho_0}\ln\gamma_{M_{+-}} \tag{2.17}$$

with ρ_d the number density of ion pairs and $\gamma_{M_{+-}}$ the ion-pair activity coefficient at the infinite dilute limit of the pair. Here we shall use an accurate expression for the dipolar-dumbbell activity coefficient $\gamma_{M_{+-}}$ obtained in a previous paper [7] of ours

$$\ln\gamma_{M_{+-}} = \frac{z^2\lambda}{\sigma}\left[\frac{(2x+2)\sqrt{1+2x}-x^2-4x-2}{x^2}\right] \tag{2.18}$$

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where x is defined in eq.(2.11).

Eq.(2.17) provides a new contribution to the activity coefficients of free ions:

$$\ln\gamma_\pm^{DI} = \left[\frac{\partial(\beta A^{DI})/V}{\partial\rho_i}\right]_{\rho_d} \tag{2.19}$$

and also the new contribution to the total pressure as

$$\beta P^{DI} = \left[\frac{\partial(-\beta A^{DI})}{\partial V}\right]_T \tag{2.20}$$

As a result, the equation of state for our new approximation, EGA+DI, is

$$\beta P = 2\rho_0\frac{(1+\eta+\eta^2-\eta^3)}{(1-\eta)^3} - \frac{(\sqrt{1+2x}-1)^3}{24\pi\sigma^3} + \beta P^{DI} - \alpha_1\rho_0 \tag{2.21}$$

with the degree of association, α_1, given by

$$\frac{\alpha_1}{\rho_0(1-\alpha_1)^2} = K_0\frac{(\gamma_\pm^{EL})^2(\gamma_\pm^{DI})^2}{\gamma_{M_{+-}}} \tag{2.22}$$

where the ideal association constant K_0 is the same as in the EGA [eq.(2.15)], and $\gamma_\pm^{EL}$, $\gamma_\pm^{DI}$ and $\gamma_{M_{+-}}$ are obtained from eqs. (2.10), (2.19), and (2.18), respectively. Here we shall continue to assume that the hard-core part is independent of the degree of ionic association.

III. RESULTS AND DISCUSSION

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

$$P^* = \frac{\epsilon\sigma^4}{(ze)^2}P \equiv \phi\rho^*T^* \tag{3.1}$$

with T^*, the reduced temperature $(= 1/b)$, ρ^*, the reduced density $(= 2\rho_0\sigma^3)$, and ϕ, the osmotic coefficient $[= \beta P/(2\rho_0)]$.

Nonlinear algebraic equations of α_0 and α_1 and the derivatives in the EGA+DI approximation have been evaluated numerically by us using IMSL routines. When the association term in EGA is turned off, i.e. $\alpha_0=0$, we recover the simple MSA results as expected.[1] However, we are unable to reproduce the pressure and the critical point of the EGA obtained

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in ref. 4a. In Table I, we compare our EGA result for osmotic coefficients with the results obtained in the original EG paper[4a]; our values of the degree of association agree with theirs. The agreement between the HNC results[15] and our EGA results is not as good as the agreement between the HNC and original EGA results. We also find that the critical point of EGA is located at (0.026, 0.0789) instead of (0.018, 0.0837).[4a] This new critical point is close to the PMSA1 result (0.025, 0.0748), as one would expect on conceptual grounds. A similar re-evaluation of the EG result was also made independently by Guissani and Guillot.[11] In Table II, the critical points in the EGA and EGA+DI are compared with some of earlier theories and most recent computer simulations. The critical point of EGA+DI is located at (0.027, 0.0716), which is in somewhat better agreement with the most recent Monte Carlo estimates than the PMSAs.[7]

The phase diagrams can be calculated through the constructions involving the intersection of the Gibbs free energy and pressure at each temperature. The coexistence curves for EGA and EGA+DI are compared with the most recent simulation and PMSA3 in Fig.1. Both EGA and EGA+DI have coexistence curves of reasonable shape and EGA+DI is in the best agreement with simulation. In Fig.2, the reduced chemical potential of EGA+DI is compared with that of MSA and of PMSA3 and computer simulation data. The reduced chemical potential of EGA+DI, $\beta\mu'$, is calculated from the equation

$$\beta\mu' = \ln(\rho_0\sigma^3) + \frac{\beta\Delta A}{N} + \frac{\beta P}{2\rho_0} - 1 \tag{3.2}$$

with

$$\frac{\beta\Delta A}{N} = \frac{\beta A}{N} - \ln(2\rho_0\sigma^3) - \frac{\beta A^\circ}{N} \tag{3.3}$$

As figure 2 shows, EGA+DI is in excellent agreement with the simulation data, in particular, in the low-temperature and low- density region. It is in slightly worse agreement in the high-temperature and high-density region.

One can contemplate further extension of the EG approach through the addition of dipole-dipole contributions as well as contributions from clusters larger than the dimers

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considered here. It is our conclusion that both of these contributions are significant and that their neglect is most likely responsible for the disagreement that remains between the results in this paper and the most recent RPM simulation results. We are currently extending our theory to include them.

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Table I. Osmotic coefficient for 2-2 electrolytes calculated in different theories

C[mol/l]	α_0[†]	EGA Ref. 4a	EGA This Work	MSA	HNC[15]
0.0625	0.3826	0.6741	0.6120	0.6303	0.6452
0.25	0.3915	0.5907	0.5740	0.5543	
0.5625	0.3687	0.5965	0.6024	0.5732	0.6028
1.0	0.3463	0.6654	0.6810	0.6520	0.6666
2.0	0.3193	0.9136	0.9342	0.9112	0.8865

† Our values of α_0 agree with those of EG.[4a]

Table II   Comparison of different theoretical results with simulations.

Theory	Ref.	T_c^*	ρ_c^*	P_c^*	α_c
MSA	9	79×10^{-3}	0.014	9.7×10^{-5}	
EGA	4a	83.7×10^{-3}	0.018	35.4×10^{-5}	
EGA	†	78.9×10^{-3}	0.026	60.0×10^{-5}	41.8%
EGA+DI	†	71.6×10^{-3}	0.027	26.5×10^{-5}	60.8%
PMSA3	7	74.5×10^{-3}	0.025	18.4×10^{-5}	56.2%
FL (DH+Bj+DI)	12	58×10^{-3}	0.025		
MC, 1994	10d	53×10^{-3}	0.025		
MC, 1994	10c	$\geq57\times10^{-3}$			
MC, 1992	10b	56×10^{-3}	0.04		

† This work

FIGURE CAPTIONS

Fig.1 The coexistence curves of the RPM in the EGA (— · —); EGA+DI (—); PMSA3 (- - -). See text for further details. The simulation data (ref. 10d) is indicated by the square symbol (□). Critical points in various approximations are indicated by dots (●).

Fig.2 The reduced chemical potential, $\beta\mu'$, as a function of the logarithm of the reduced density ($\log\rho^*$) at various temperatures. The EGA+DI(—), PMSA3 (- - -), and the MSA (— · · —) results are compared with simulation data [□ (T^*=0.147, ref. 10a); ○ (T^*=0.07 and 0.045. ref. 10d)]. From top to bottom, T^* =0.147, 0.07, and 0.045, respectively.
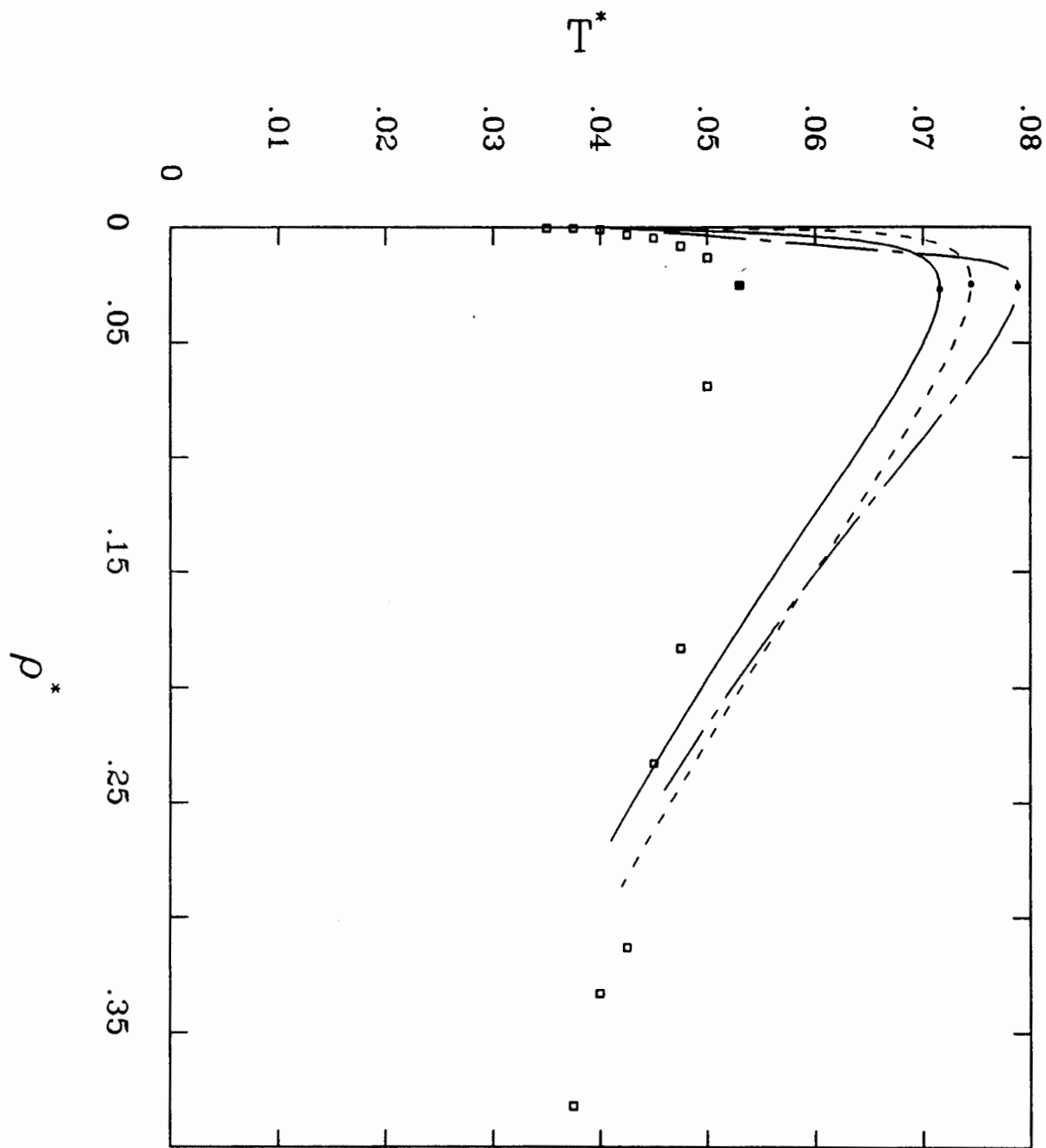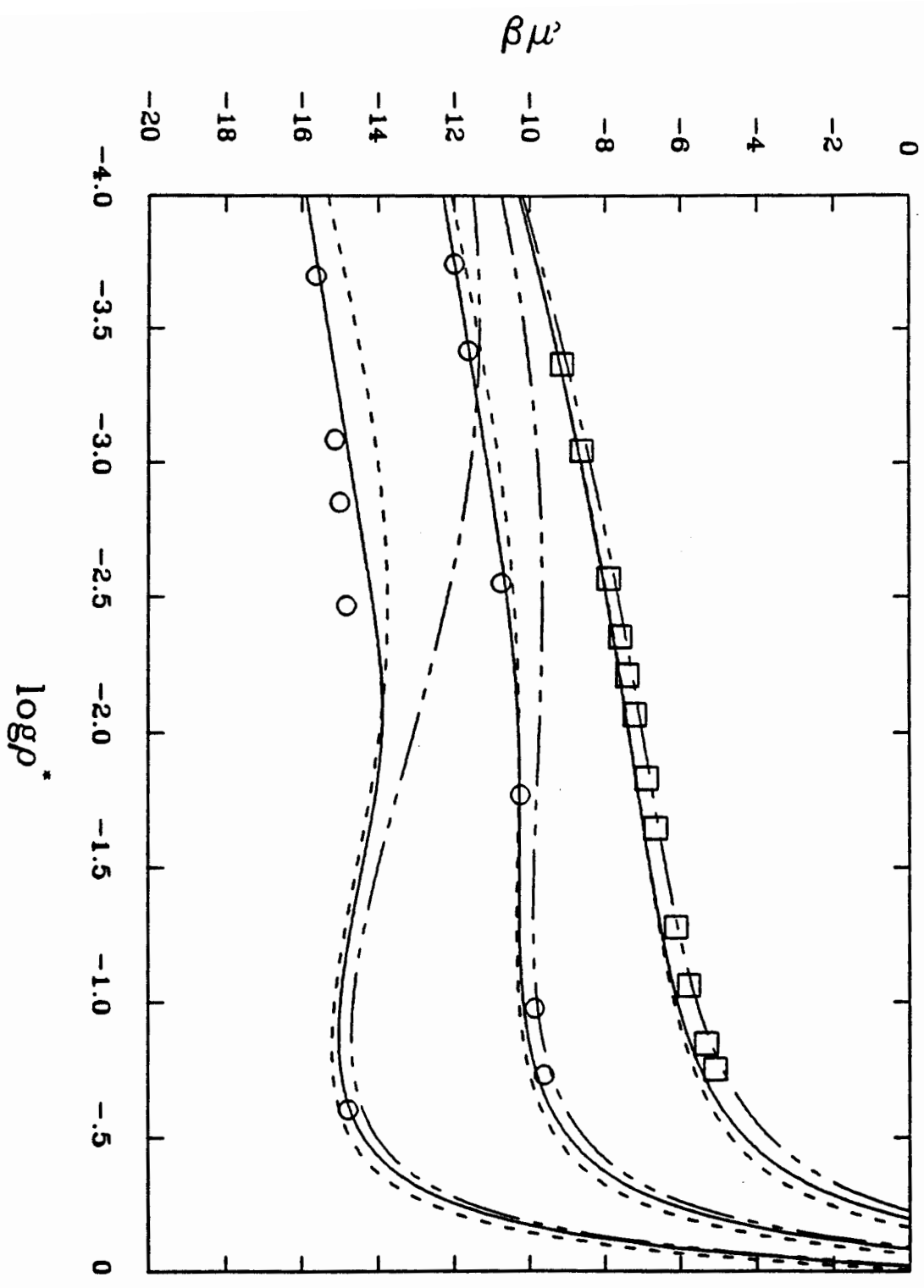
Fig. 1

Fig. 2

The figure plots $\beta\mu$ (vertical axis, ranging from 0 to -20) versus $\log\rho^*$ (horizontal axis, ranging from -4.0 to 0).