

The influence of the closest approach to the wall distance on phase behavior of ionic fluids in slit-like pores: a density functional approach for the restricted primitive model

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We apply density functional theory to investigate changes in the phase behavior of ionic fluid in narrow slit-like pores, caused by the difference in the distances of the closest approach to pore walls of two species, D_s . This difference causes that the point of zero surface charge of the walls does not coincide with the zero value of the electrostatic potential at the wall. Our calculations demonstrate that an increase of D_s increases slightly the value of the critical temperature and lowers the density of the coexisting liquid-like phase.

1. INTRODUCTION

The so-called restricted primitive model (RPM) has been widely used to represent physical and structural properties of electrolytes. This model comprises charged hard spheres of valency Z_i , all of the same diameters d . Bulk (uniform) RPM systems have usually been studied by means of Ornstein-Zernike equation with various closures [1-9]. The simplest closure, which also yields quite reasonable results for the structure, is the mean spherical approximation (MSA) [6-8]. The equation of state obtained from MSA energy route predicts the first-order gas-liquid phase transition. However, the critical temperature and density evaluated from this equation are rather distinct from those obtained from computer simulations [10]. Moreover, neither the MSA virial nor the MSA compressibility equations of state predict the existence of the phase transition.

The latter drawback of the MSA theory can be removed if one considers the generalized mean-spherical approximation [11,12].

At an early stage of the development of theories of nonuniform RPM's the singlet integral equations for the density profile [13,14] were employed. These studies aimed at the description of ions adsorption at planar charged walls and in pores of different geometry. Latter, the second-order integral equations, which allow for instantaneous evaluation of one- and two-particle correlation functions, were also used [15,16]. However, the approaches based on different versions of density functional theory (DFT) have recently provided the most successful method of description of nonuniform RPM's [17-29].

Any DFT determines thermodynamic properties of an inhomogeneous fluid from the Helmholtz free energy, F , and from its functional dependence on the local densities of different particles, $\{\rho_i(\mathbf{r})\}$. The free energy functional is commonly decomposed into the sum of three contributions, namely the ideal, F_{id} , the hard-sphere, F_{hs} and the electrostatic, F_{el} , terms. Various versions of the DFT discussed in literature differ by the formulation of expressions for the F_{hs} and F_{el} terms. However, despite of a great number of publications, only few papers dealt with the problem of phase transitions in nonuniform ionic fluids [28,30-32]. The works of Groh et al. [28], Telo da Gama et al. [30] and Weiss and Schröer [31] were devoted to the description of the gas-liquid interface for the RPM. In particular, the density-functional approximation of Groh et al. [28] was based on the incorporation into the grand potential functional the contribution due to electrostatic interactions with pair correlation functions of the homogeneous fluid as obtained from the bulk MSA theory, and thus it followed the MSA energy route. However, Weiss and Schröer [31], as well as Telo da Gama et al. [30] and Weiss and Schröer applied the square-gradient.

Recently, we have proposed [32-34] a new version of the DFT for RPM of nonuniform electrolytes that is able to predict surface-mediated phase transitions. The theory was applied to evaluate phase diagrams for ionic solutions confined in slit like pores [32], to explain puzzling temperature dependence of the double layer capacitance [33] and to describe nonuniform associating ionic fluids [34].

Experimental results indicate that the point of the zero surface charge (PZC) does not usually coincide with the point of zero value of the electrostatic potential at the surface, $V = \Psi(z=0)$. One of the simplest models of electric double layer, which predicts this type of behavior, is a RPM with different closest approach distances to the wall, $d_{s,i}$, for different ionic species i . The difference in $d_{s,i}$ for $i=1$ and 2 suffices to shift the PZC toward nonzero values of V . The aim of this work is to determine how the difference in $d_{s,i}$ influences the phase behavior of ionic fluids confined to slit-like pores. The theory we apply here has

been described in details in our previous works and thus we present only its basic points.

2. THEORY

We consider a RPM fluid confined in a slit-like pore of the width h . The interaction between the ions is the sum of hard-sphere (the hard-sphere diameter is d) and ion-ion Coulombic interactions. Moreover, the dielectric constant, ε , is assumed to be uniform throughout the entire system. The interaction between the ions of species i and the wall is given by,

$$u_i(z) = v_i(z) + w_i(z) \quad (1)$$

where $v_i(z)$ and $w_i(z)$ are the non-electrostatic and the electrostatic contributions to the external potential, respectively. The non-electrostatic potential is

$$v_i(z) = \begin{cases} \infty, & (-h + d_{s,i})/2 < z < (h - d_{s,i})/2, \\ 0, & \text{otherwise} \end{cases}, \quad (2)$$

whereas the electrostatic interaction between an ion and a single surface is given by,

$$w_i'(z') = (4\pi\sigma Z_i e / \varepsilon) z', \quad (3)$$

where z' is the distance from the wall and σ is the wall charge density and the dielectric constant, ε , is uniform throughout the entire system. Of course, $w_i(z) = w_i'(-h/2 + z) + w_i'(h/2 - z)$.

The electrostatic potential $\Psi(z)$ is determined by the Poisson equation,

$$\nabla^2 \Psi(z) = -\frac{4\pi e}{\varepsilon} \sum_{i=1,2} Z_i \rho_i(z). \quad (4)$$

The method of integration of the Poisson equation has been described in our earlier work [32]. We only note here that the integration is carried out assuming the boundary condition $\Psi(z=h/2) = \Psi(z=-h/2) = V$, i.e. fixing the value of the electrostatic potential at each wall of the pore. A coupling between the density profiles and the charge density at each wall of the pore, σ , is given by,

$$\sigma/e = -\frac{1}{2} \sum_{i=1,2} Z_i \int \rho_i(z) dz. \quad (5)$$

In a DFT the grand potential of an inhomogeneous fluid is written in the form [29],

$$\Omega = F[\{\rho_i\}] + \frac{1}{2} \sum_{i=1,2} eZ_i \int \rho_i(z) \Psi(z) d\mathbf{r} + \sum_{i=1,2} \int \rho_i(z) [u_i(z) - \mu_i] d\mathbf{r}, \quad (6)$$

where $F[\{\rho_i\}] = F_{id}[\{\rho_i\}] + F_{hs}[\{\rho_i\}] + F_{el}[\{\rho_i\}]$ and where μ_i is the chemical potential of species i . The ideal term is known exactly, $F_{id}[\{\rho_i\}] = \sum_{i=1,2} \int d\mathbf{r} [\rho_i(z) \ln \rho_i(z) - \rho_i(z)]$. For the hard-sphere term, however, we apply the expression resulting from a recent version [35] of the Fundamental Measure Theory [19], as described in details in [29].

In Ref. [32] we have proposed the following representation of the electrostatic free energy functional

$$F_{el}[\{\rho_i\}] = \int d\mathbf{r} f_{el}[\{\bar{\rho}_i(z)\}], \quad (7)$$

where $\bar{\rho}_i(z)$ denote suitably defined inhomogeneous average densities of a reference fluid. One of the simplest possible choices of $f_{el}[\{\bar{\rho}_i(z)\}]$ is to apply the expression resulting from the MSA equation of state evaluated via the energy route [5,7], namely

$$f_{el}[\{\rho_i\}]/kT = -\frac{e^2}{\epsilon kT} [Z_1^2 \rho_1 + Z_2^2 \rho_2] \frac{\Gamma}{1+\Gamma} + \frac{\Gamma^3}{3\pi} \quad (8)$$

where $\Gamma = (\sqrt{1+2\kappa d} - 1)/2d$, and where κ denotes the inverse Debye screening length, $\kappa^2 = (4\pi e^2/\epsilon kT) [Z_1^2 \rho_1 + Z_2^2 \rho_2]$.

At this point some comments are necessary. It is known that bulk MSA theory is thermodynamically inconsistent, i.e. virial, compressibility and energy routes yield different expressions for the excess free energy. However, in spite of yielding reasonable results for the structure and thermodynamics in a general sense, neither virial nor compressibility equations permit to obtain the gas-liquid transition for the restricted primitive model, in contradiction to energy equation and to computer simulation data. Therefore, only the expression for the free

energy obtained from the energy route can be used for the study of phase transitions. Of course, Eq. (8) is an approximation only. Its approximate character is also connected with the fact that the inverse length κ (which is formally obtained within the linearized Poisson equation) is a valid expression for large interparticle separations.

The last expressions correspond to an electroneutral fluid. Therefore, we need to introduce the reference fluid and the corresponding averaged densities $\{\bar{\rho}_i(z)\}$. This reference fluid should be defined in such a way that the averaged densities $\{\bar{\rho}_i(z)\}$ must not violate electroneutrality condition at any point \mathbf{r} , because otherwise Eq.(8) could not be applied. In order to do this we follow the approach of Gillespie et al. [29,36]. The weighted densities, $\{\tilde{\rho}_i(z)\}$, are given by

$$\tilde{\rho}_i(z) = \int \rho_i(z) W_i(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (9)$$

where the weight function $W_i(r)$ is a normalized step function

$$W_i(|\mathbf{r} - \mathbf{r}'|) = \frac{\theta(|\mathbf{r} - \mathbf{r}'| - R_f(\mathbf{r}'))}{(4\pi/3) R_f^3(\mathbf{r}')}. \quad (10)$$

The radius of the sphere, over which the averaging is performed, R_f , is not a well-defined characteristics. According to Gillespie et al. [29,36] it is approximated by the "capacitance" radius, i.e. by the ion radius plus the screening length, i.e. $R_f(\mathbf{r}) = d/2 + 1/\sqrt{2\Gamma(\{\tilde{\rho}_i(\mathbf{r})\})}$. In addition, Gillespie et al. [29,36] have required that the reference fluid must have the same ionic strength as the system with weighted densities $\tilde{\rho}_i(z)$. Consequently, in the case of a symmetric 1-1 electrolyte the averaged densities $\{\bar{\rho}_i(z)\}$ are defined as,

$$\bar{\rho}_1(z) = \bar{\rho}_2(z) = [\tilde{\rho}_1(z) + \tilde{\rho}_2(z)]/2 \quad (11)$$

Note that a general definition of the averaged densities $\{\bar{\rho}_i(z)\}$ for a multicomponent system can be found in Refs. [28,29]. Because Eqs. (8) – (12) are coupled, the evaluation of R_f requires an iteration procedure. This iteration loop should be carried out in addition to the main iteration procedure for evaluating the density profiles.

The density profile equation is obtained by minimizing the excess grand potential functional $\Delta\Omega = \Omega - \Omega_b$, where Ω_b is the grand potential of the bulk fluid at the temperature T and the chemical potentials μ_i , $i=1,2$. Thus

$$\frac{\delta\Delta\Omega}{\delta\rho_i(z)} = 0, \quad \text{for } i = 1, 2, \quad (12)$$

and the resulting equation for the density profiles has been given in Ref. [32].

In order to complete the theory, we write down the relation between the chemical potential, μ ($\mu = \mu_1 = \mu_2$) and the bulk fluid density,

$$\begin{aligned} \mu_i/kT = \ln \rho_{b,i} + \frac{[2\eta(4-3\eta) + 3\eta^2](1-\eta) + 2\eta^2(4-3\eta)}{(1-\eta)^3} - \\ \frac{e^2}{\epsilon kT} \frac{Z_i^2 \Gamma}{1+\Gamma} - \frac{e^2}{\epsilon kT} \frac{(Z_1^2 \rho_{b,1} + Z_2^2 \rho_{b,2}) * \Gamma'}{(1+\Gamma)^2} + \frac{\Gamma^2 \Gamma'}{\pi}. \end{aligned} \quad (13)$$

where the prime denotes the first-order derivatives with respect to density of one species.

The knowledge of the density profiles of ions permits to calculate the total average density of ions in the pore,

$$\langle \rho \rangle = \int_{-h/2}^{h/2} dz \sum_{i=1,2} \rho_i(z) / (h - 2d_{s,1}). \quad (14)$$

The normalization of the average density is performed over the region of the pore in which the one of the density profiles is nonzero (in the calculations we assume that $d_{s,1} < d_{s,2}$). The average density, density profiles and the surface charge are expressed as reduced quantities, and defined as follows: $\rho_i^*(z) = \rho_i(z) d^3$, $\langle \rho^* \rangle = \langle \rho \rangle d^3$ and $\sigma^* = \sigma d^2 / e$, respectively. We also apply a usual definition of the reduced temperature, $T^* = kT \epsilon d / e^2 Z^2$.

Principal objective of the present study is to construct and analyze the phase diagrams. They have been obtained in a standard way, analyzing the dependence of the grand thermodynamic potential, $\Delta\Omega$, on the chemical potential of the species, at several temperatures and looking for the crossing points between branches corresponding to different phases. The density profile equation was solved employing an iterational procedure and all the integration were carried

out using Simpson method with the grid size of $0.02d$. For the sake of convenience the electric potential at the pore walls, V , has been chosen as a variable that specifies the system, as common in DFT calculations. Consequently, the charge density at the pore walls, σ , results from the calculations of the profiles.

3. RESULTS AND DISCUSSION

We study the phase behavior of ionic fluids in slit-like pores under the condition that the electrostatic potential at the wall is zero, $V=0$. At this stage of our research, we restrict the presentation of results to the case of confined 1-1 electrolytes only. Before reporting the results we want to stress that the present theory has been already tested against computer simulations in the case of a RPM fluid adsorbed at a single wall and a reasonable agreement was found [32,33]. For this reason we have omitted such comparisons here. Our intention is to determine how the phase behavior of the RPM is influenced by the difference in the values of $d_{s,1}$ and $d_{s,2}$. The calculations have been carried out for the pores of the width $h=6d$, $11d$ and $21d$. The value of $d_{s,1}$ was kept constant and equal to $0.5d$, whereas the values of $d_{s,2}$ were equal to d and $0.75d$. For the sake of brevity we abbreviate the investigated systems by the values of the difference $d_{s,2}-d_{s,1}$, i.e. as 0.5 and 0.25 . For the system 0.5 the distance of the closest approach of ions "2" is two times larger than for the species "1".

Figure 1 gives examples of the profiles for gas-like (parts a and c) and liquid-like (part b and d) phases in the pores of $h=6d$ and $h=11d$ at $T^*=0.055$. The profiles for coexisting gaseous and liquid-like phases were plotted with the same line styles. Under the assumption that $V=0$ the profiles of two ionic species having the same closed approach distances, $d_{s,1}=d_{s,2}$, are identical and $\sigma=0$. However, the difference between $d_{s,1}$ and $d_{s,2}$ causes that the profiles of two species become different. The difference in the profiles leads to non-zero charge at the pore walls, cf. Eq. (5). From Figure 1 we realize that the profiles, especially for dense phases, exhibit strong depletion close to the pore walls. For narrow pore this depletion extends almost to the pore center. The behavior of the profiles for two coexisting phases obtained at other temperatures was similar to that presented in Figure 1.

Phase diagrams for the systems under study are displayed in Figures 2 and 3; they have been evaluated according to the procedure described in our previous work [32]. Figure 2 shows the diagram in the density-temperature plane, whereas Figure 3 - in the temperature - chemical potential plane. In addition, we have included the bulk phase diagram (Figs 2 and 3) and the diagram for the system with $d_{s,1}=d_{s,2}=0.5d$ and $h=21d$ (Fig. 2). The inset to Figure 2 shows the magnified parts of the diagrams in the vicinity of the critical temperature.

The main effect of geometric confinement on the phase behavior of RPM is similar as in the case of confinement of a Lennard-Jones fluid in a pore with repulsive walls. Each of the liquid-vapor coexistence envelopes terminates at a critical temperature and the confinement leads to a shift of the entire phase diagram towards lower temperatures. One should also note that this shift is larger for narrower pores. The transition in confined systems occurs at a higher value of the chemical potential than in the bulk fluid. Therefore the observed phenomenon is the capillary evaporation.

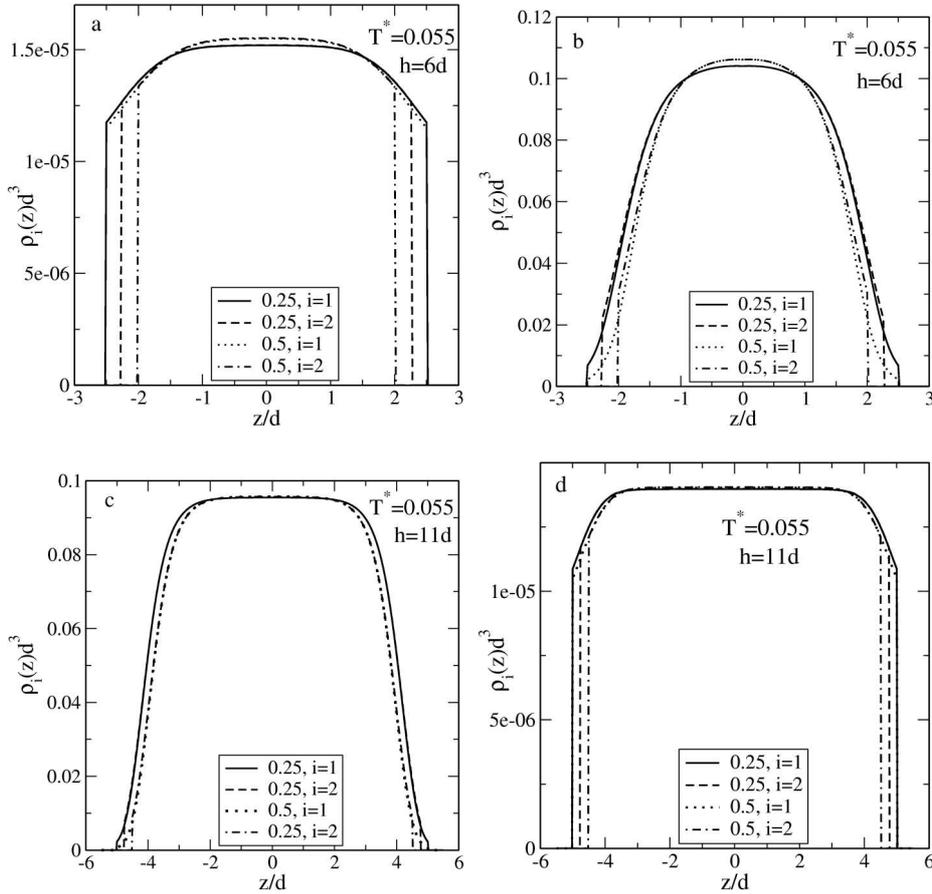


Fig. 1. Part a: A comparison of the density profiles for gas-like (parts a and c) and for liquid-like (parts b and d) coexisting phases in slit-like pores of the width $h=6d$ (parts a and b) and $h=11d$ (parts c and d) at $T^*=0.055$. The symbols 0.25 and 0.5 refer to the difference $d_{s,2}-d_{s,1}$, as explained in the text.

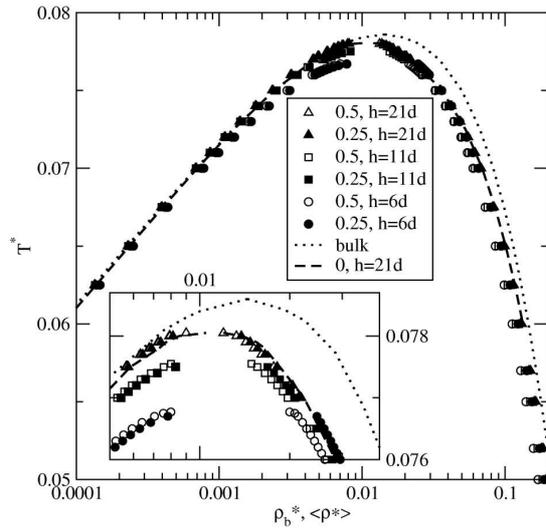


Fig. 2. The phase diagrams, in the density-temperature plane, for the RPM confined in slit-like pores and the corresponding bulk phase diagram obtained from the energy route MSA equation of state. The meaning of all symbols is explained in the figure. The inset shows the diagrams in the vicinity of the critical temperatures. The symbols 0.25 and 0.5 refer to the difference $d_{s,2}-d_{s,1}$, as explained in the text.

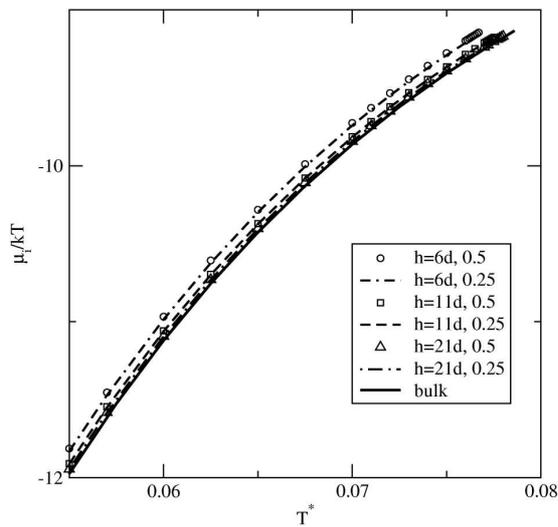


Fig. 3. The phase diagrams, in the chemical potential-temperature plane, for the RPM confined in slit-like pores and the corresponding bulk phase diagram obtained from the energy route MSA equation of state. The meaning of all symbols is explained in the figure. The symbols 0.25 and 0.5 refer to the difference $d_{s,2}-d_{s,1}$, as explained in the text.

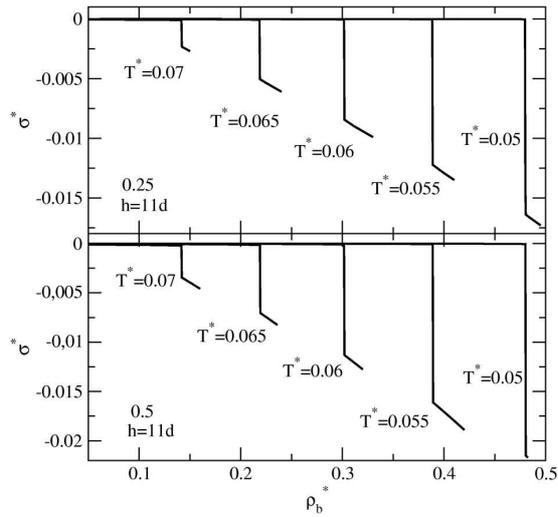


Fig. 4. Examples of the "charge adsorption isotherms" in the pore of $h=11d$. The upper panel is for the system $d_{s,2}-d_{s,1}=0.25$, while the lower panel for the system $d_{s,2}-d_{s,1}=0.5$.

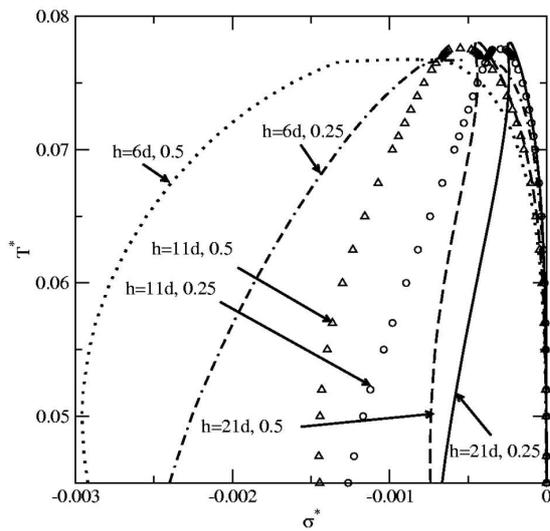


Fig. 5. Changes of the surface charge versus temperature at the phase transition point. The meaning of all symbols is explained in the figure. The symbols 0.25 and 0.5 are explained in the text.

The influence of the difference in the closest approach distances on the critical temperature is evident, though very small (see the inset to Fig. 2) - an increase of the difference $D_s=|d_{s,1}-d_{s,2}|$ leads to an increase of the critical temperature. Moreover, at lower temperatures an increase of D_s lowers the density of the liquid-like coexisting phase.

It is obvious that for the systems with non-zero value of D_s the charge at the pore walls is different for two co-existing phases. Figure 4 shows examples of the "charge adsorption isotherms". Vertical jumps in the charges are associated with the evaporation transition. Collecting similar data at different temperatures we can construct the phase diagrams in the surface charge-temperature plane. Such diagrams for the systems under study are displayed in Figure 5. The difference between the charge for two coexisting phases increases with a decrease of the pore width and with the difference in the distances of the closest approach, D_s . This effects increase as the pore width decreases. Indeed, the diagram from Figure 5 for the pore of $h=6d$ is much wider than for all remaining pores studied.

This work is a first step towards the investigation of the effects of different interactions of two ionic species with pore walls on the phase behavior of confined ionic fluids. Different ion-surface interactions are the most important factor influencing the position of the PZC. The model considered in this work is the simplest one, what allows for the modeling of the shift in the location of PZC.

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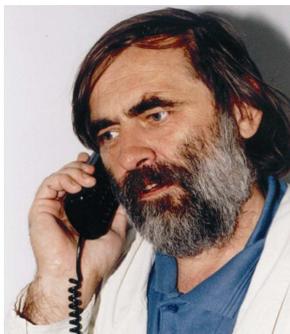
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