A comprehensive approach to critical phenomena and phase transitions in binary mixtures [1]

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Abstract

The hierarchical reference theory of fluids (HRT) combines a first-principles description of the system from the knowledge of the microscopic interaction with some of the basic concepts of the renormalization group. The application of HRT to binary mixtures has provided a theoretical justification of the critical behavior predicted by the phenomenological approach. Moreover, the reason for the strong crossovers that make it difficult to detect experimentally the asymptotic critical regime has been attributed to the competition between two different fixed points. On the basis of this analysis, the most favorable conditions that lead to an enhancement of the asymptotic region are identified: mixtures close to a change in the topology of the phase diagram are good candidates for the direct experimental observation of features like the renormalization of the critical exponents or the weak divergence of the isothermal compressibility. This theory gives information not only on critical phenomena but it is able to treat the full phase diagram in the fluid region and the static correlation functions at long as well as at short distances. Some predictions for the phase diagram and the structure factors of an argon-xenon mixture are shown.

KEY WORDS: argon-xenon mixture; binary mixtures; critical behavior; fixed points; liquid state theory; renormalization group.

Compared to the degree of accuracy achieved for simple fluids, the theoretical description of binary mixtures still appears to be somewhat rough. Actually, the study of the thermodynamics of mixtures largely rests upon van der Waals-like mean field theories which, although able to give an overall picture of the different kinds of phase diagram and topologies of the critical lines [1], are nevertheless quantitatively inadequate. Moreover, such approaches cannot satisfactorily deal with the universal features of the critical behavior; this issue has instead been addressed in the context of a phenomenological theory [2], which assumes that the universality class of critical phenomena in mixtures is Ising-like as in one component fluids, but the "thermal" and the "magnetic" scaling fields are analytic functions of the temperature and of the chemical potential of the components. This *ansatz* rigorously holds in some decorated lattice models of mixtures [3], and is believed to be true for real mixtures as well. On the other hand, some of its predictions have not been clearly proved experimentally, especially when it comes to subtle features like the so-called renormalization of the critical exponents by the quantity $1/(1-\alpha)$, α being the critical exponent of the specific heat at constant volume of the pure fluid. In fact, the experimental results [4] on criticality in mixtures appear to be affected by strong crossovers, which make it difficult to detect the true asymptotic behavior of the observables.

In order to achieve a better understanding of critical phenomena and phase transitions in binary mixtures it is therefore necessary to develop a theory able to go beyond both the mean field approximation and the phenomenological approach. The hierarchical reference theory (HRT) [5, 6] is a natural candidate to accomplish this goal, since it provides a systematic way to include fluctuations of longer and longer wavelengths on top of mean field theory reproducing the basic structure and results of the renormalization group approach. At the same time, being a microscopic theory based on the interparticle potential, it allows the quantitative evaluation of the thermodynamic and structural properties of the system. It has already been shown

that in the case of a one-component fluid HRT indeed yields a unified treatment over the whole phase plane: in fact, its accuracy in the dense regime is comparable with that of the most successful conventional theories, but on the other hand the critical behavior and the phase diagram are described in a much more realistic way [7]. Here we consider a binary mixture of two different species 1 and 2, each made up of spherical particles subject to a two-body interaction. The pair potential $v_{ij}(r)$ is then a function both of the mutual position r and of the species of the particles, which are specified by the couple of two-valued indexes i, j. Following a procedure of common use in liquid state theories [8], it is assumed that $v_{ij}(r)$ consists in the sum of a short-ranged, repulsive contribution $v_{ij}^{\mathrm{R}}(r)$ accounting for the excluded volume effect, and a longer-ranged, attractive part $w_{ij}(r)$. We refer to the system interacting via the sole potential $v_{ij}^{\mathrm{R}}(r)$ as the *reference* system; its properties are considered as known, for instance by mapping it into a mixture of hard spheres. In the present description the phase separation depends entirely on the attractive interaction $w_{ij}(r)$; it is not our purpose to deal with the entropic-driven phase transitions that may appear in a mixture of particles with purely repulsive interaction.

The basic idea of HRT is to build up the attractive interaction by gradually introducing in the system its Fourier components of increasing wavelength. Physically, this procedure corresponds to the gradual inclusion of fluctuations starting from large lengthscales. If we define Q as the lowest wavevector at which fluctuations are taken into account, the exact evolution equation governing the change in the free energy $\mathcal{A}_Q$ due to fluctuations on a scale $k \in (Q - dQ, Q)$ reads [9]:

$$\frac{\partial}{\partial Q}\left(\frac{\beta \mathcal{A}_Q}{V}\right) = \frac{1}{4\pi^2} \log\det\left[\mathbf{1} + \beta \mathcal{C}_Q^{-1}(Q)\widetilde{w}(Q)\right] , \tag{1}$$

where the $Q \to \infty$ limit corresponds to mean field theory while at $Q = 0$ fluctuations over all lengthscales have been included. Here β is the inverse temperature, V is the volume, and both $\mathcal{C}_Q(k)$ and $\widetilde{w}(k)$ are 2×2 symmetric matrices representing the Fourier transforms of the direct correlation function and of the attractive part of the

potential respectively.

Clearly, Eq. (1) is not closed: in fact, it is the first equation of an infinite hierarchy involving the correlation functions of higher and higher order. However, as it has already been shown for a one-component fluid [7], a successful approximation scheme is already obtained if one does not go any further than Eq. (1), and supplements it with a suitable approximate equation relating the direct correlation function $\mathcal{C}_Q(k)$ to the free energy $\mathcal{A}_Q$. Our basic assumption, and actually the only approximation in the theory, is the well-known Ornstein Zernike *ansatz*, i.e. the requirement that $\mathcal{C}_Q(k)$ has always the same range as the potential, so that it is an analytic function of k even at the critical point:

$$\mathcal{C}^Q_{ij}(k) = c^{\mathrm{R}}_{ij}(k) - \beta\lambda_{ij}\widetilde{w}_{ij}(k)\,, \tag{2}$$

Here, $c^{\mathrm{R}}_{ij}(k)$ is the direct correlation function of the reference system in Fourier space and λ_{ij} is a function of the thermodynamic state such that the (exact) compressibility sum rule is satisfied:

$$\mathcal{C}^Q_{ij}(k=0) = \frac{\partial^2}{\partial\rho_i\partial\rho_j}\left(-\frac{\beta\mathcal{A}_Q}{V}\right)\,, \tag{3}$$

where ρ_i is the number density of the species i. Eq. (1) becomes then a closed partial differential equation for $\mathcal{A}_Q$ which must be solved numerically. However, in the long wavelength limit (i.e. for $Q \to 0$) and close to a critical point, this equation simplifies allowing for analytic investigation. In fact, by suitably rescaling the densities and the free energy, Eq. (1) can then be cast in a universal form, which naturally yields a RG description of criticality in terms of flows of the rescaled free energy and fixed-points solutions. The fixed point scenario that emerges from this study is much richer than for the one-component fluid, and entails a number of interesting consequences [9]: first of all, it can be shown that in mixtures the fluctuations do not behave isotropically in the ρ_1, ρ_2 plane. Instead, a strong fluctuating field ψ and a weakly fluctuating one φ appear. The direction of the strong fluctuation specifies how the densities ρ_1, ρ_2 of the components, or equivalently the total density $\rho = \rho_1 + \rho_2$ and the

concentration $x = \rho_2/(\rho_1 + \rho_2)$, are weighted in the order parameter of the transition. Specifically, one has $\psi = \delta\rho\cos\theta + \rho\delta x\sin\theta$, where the angle θ is related to measurable thermodynamic quantities like the partial molar volumes on the critical lines [10] or the differences in molar volume and concentration of the coexisting phases close to a critical point [11]. To first order in a dimensionality expansion in the parameter $\epsilon = 4 - d$ (d being the dimension of the system), the RG flow can be studied by expanding the rescaled free energy H in powers of the fields ψ, φ and by writing down the ordinary differential equations for the evolution of the expansion coefficients resulting from Eq. (1). In the even subspace with respect to the field ψ, to which all the fixed points belong, the minimal expression for H accounting for all the relevant operators is:

$$H(\psi, \varphi) = r\psi^2 + g^2\varphi^2 + u\psi^4 + w\psi^2\varphi\,. \tag{4}$$

At the most stable fixed point all the coefficients in Eq. (4) are non-vanishing, so that strong and weak fluctuations are coupled through a universal coefficient w^*. We refer to this as the *two-components* (TC) *fixed point* H^*_{TC}. However, other fixed points are found: in particular, an unstable *one-component* (OC) *fixed point* H^*_{OC} exists, whose structure is again that of Eq. (4), but does not contain the field-mixing term in $\psi^2\varphi$. Although both H^*_{TC} and H^*_{OC} give rise to a critical behavior in the Ising universality class, the presence of the field mixing in the stable fixed point H^*_{TC} induces several important features: in fact, close to H^*_{TC} the compressibility diverges both along the strong and the weak direction of fluctuation, and the critical exponents are renormalized with respect to the Ising ones, in agreement with the predictions of the phenomenological theory. On the other hand, the behavior observed experimentally is more adequately described by the unstable fixed point H^*_{OC}, which gives a non-divergent compressibility and unrenormalized exponents along the strong direction of fluctuation. Unless the effective parameter w is exactly zero at the critical point, H^*_{TC} will eventually prevail in the asymptotic regime. However, even if w is different from

zero, the reduced temperature $t = (T - T_c)/T_c$ below which the system experiences the attraction of H^*_{TC} is usually quite small and extremely sensitive to the actual value of the mixing parameter w: in fact the reduced crossover temperature $t_\times$ can be estimated as $t_\times \sim (w/w^*)^{2/\alpha}$, where the specific heat exponent α is equal to $\simeq 0.12$. For the asymptotic critical behavior to become experimentally detectable, it is then crucial to determine which conditions allow for an increase of the parameter w/w^*. By unfolding the rescaling that links the physical free energy to the rescaled form (4), this quantity can be expressed in terms of a purely thermodynamic contribution $w_{\rm th}$ and a "fluctuation" contribution $w_{\rm fl}$ which contains the range of the interactions [12]. We have investigated the magnitude of this mixing parameter in mixtures of rare gases, which can be reliably modeled in terms of Lennard-Jones potentials. For a given interaction, the thermodynamic contribution accounts for the most important features of w/w^*. Along the high-density part of the critical lines, where the transition is mainly of the mixing-demixing type, this appears to be everywhere small, and the resulting crossover temperature is definitely beyond the reach of the experiments. On the other hand, in the low-density region of the phase diagram the mixing ratio is considerably enhanced *whenever a critical line gets close to a stability limit*. This condition can be obviously met at a critical endpoint, where the stability limit is exactly reached, but it can be satisfied also close to a change of topology of the phase diagram between the so-called class II and class III [1], since on the boundary between these classes one would have two critical lines intersecting in a point of marginal stability. Such a change of topology can be approached for instance in some mixtures of CO_2 or CHF_3 with hydrocarbons as the length of the hydrocarbon increases ([1, 13]). Among the binary mixtures of noble gases, the most favorable situation in this respect is found for the argon-xenon system [14] which we have analyzed in some detail. Unfortunately we are not aware of a precise determination of the critical properties in this mixture and therefore we cannot compare our results

with experimental data.

The projection of the critical line in the density-concentration plane is shown in Fig. 1. Both the mean field approximation (dotted line) and the results of the numerical integration of Eq. (1) are drawn. The critical temperature, not shown in the figure, drops monotonically by increasing Argon concentration. The arrows identify the direction of the order parameter in the density-concentration plane: the previously introduced mixing angle θ coincides with the angle between the direction of the arrow and the density axis. The mean field critical line joins the two critical points of the pure species and can be therefore interpreted as the locus of liquid-vapor critical points. A clear effect which emerges from the comparison between mean field and HRT results is the enhancement of the hump in the critical line in the region of small Xenon concentration, i.e. where the order parameter has an appreciable component also along the concentration axis. This feature can be interpreted as the tendency towards a change in topology in the phase diagram of this mixture leading to an enhancement of concentration fluctuations along the liquid vapor critical curve. Therefore we expect that in this region of the phase diagram the mixture gets close to the marginal stability limit leading to strong field mixing and experimentally detectable Fisher renormalization of critical exponents. In fact a mean field estimate of the reduced crossover temperature shows a sharp enhancement in this region attaining values of the order of $t_\times \sim 10^{-3}$ [12].

In order to perform the present computations we used a set of Lennard-Jones parameters [14] obtained from measures on transport properties. These values do not accurately reproduce the critical points of the pure species which are in fact overestimated by more than 10%. Moreover the numerical integration of the partial differential equation (1) has been performed on a rather coarse mesh in the density-concentration plane which does not allow the precise determination of the critical parameters. Due to these limitations, on the basis of the present results we cannot

rule out the possibility that for such a mixture the fluctuations might even induce a change in the topology of the critical lines with respect to the mean field prediction. This is an interesting issue, which will be investigated in the future, by means of a more efficient algorithm for the numerical solution of Eq. (1).

An isothermal section of the pressure-concentration plane is shown in Fig. 2a where we marked by squares the states within the coexistence region. Interestingly, the numerical solution satisfies the thermodynamic stability constraint which requires the collapse of these points on the same curve when plotted in the pressure-chemical potential plane (Fig. 2b).

Finally, the density-density, concentration-concentration and density-concentration structure factors are shown in Fig. 3 for a state (marked by an asterisk in Fig. 1) close to a point along the critical line. We used the standard notation introduced by Bathia and Thornton [15]:

$$S_{NN}(k) = c_1 S_{11}(k) + c_2 S_{22}(k) + 2\sqrt{c_1 c_2} S_{12}(k) \tag{5}$$

$$S_{cc}(k) = c_1 c_2 \left[c_2 S_{11}(k) + c_1 S_{22}(k) - 2\sqrt{c_1 c_2} S_{12}(k)\right] \tag{6}$$

$$S_{Nc}(k) = c_1 c_2 \left[S_{11}(k) - S_{22}(k) + \frac{(c_2 - c_1)}{\sqrt{c_1 c_2}} S_{12}(k)\right] \tag{7}$$

where $c_i = \rho_i/\rho$ and

$$S_{ij}(k) = \delta_{ij} + \sqrt{\rho_i \rho_j} \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} \left[g_{ij}(r) - 1\right] , \tag{8}$$

where the radial distribution function $g_{ij}(r)$ measures correlations between species i and j. Fig. 3 shows that density fluctuations are rather similar to the case of one component fluids near the critical point: $S_{NN}(k)$ is large at small k because of the presence of strong density fluctuations near phase separation and at the same time, it reveals the presence of short range structure through the oscillations at larger wavevector. On the other hand, $S_{cc}(k)$ is remarkably structureless but show an enhancement at small k which signals the increase of concentration fluctuations.

The example we have briefly discussed shows the possibility to obtain phase diagrams and transition lines in mixtures of simple fluids where density and concentration fluctuations are properly taken into account. In particular we focused our attention on the observable effects of field mixing near phase transitions. The unexpected growth of concentration fluctuations along a liquid-vapor critical line is the consequence of a non negligible component of the order parameter along the concentration axis. According to our model calculations, such an effect should be particularly visible in an Argon-Xenon mixture at low Xenon concentration and should be experimentally detectable both by accurate PVT measures and by scattering experiments. Near the critical point, a marked crossover towards the renormalized values of the critical exponents is also expected due to the proximity to the stability limit in this region of the phase diagram. Likely, the same effects might be more easily observed in mixtures of hydrocarbons or of polar molecules but the model we have studied cannot be directly applied to such systems.

Acknowledgments

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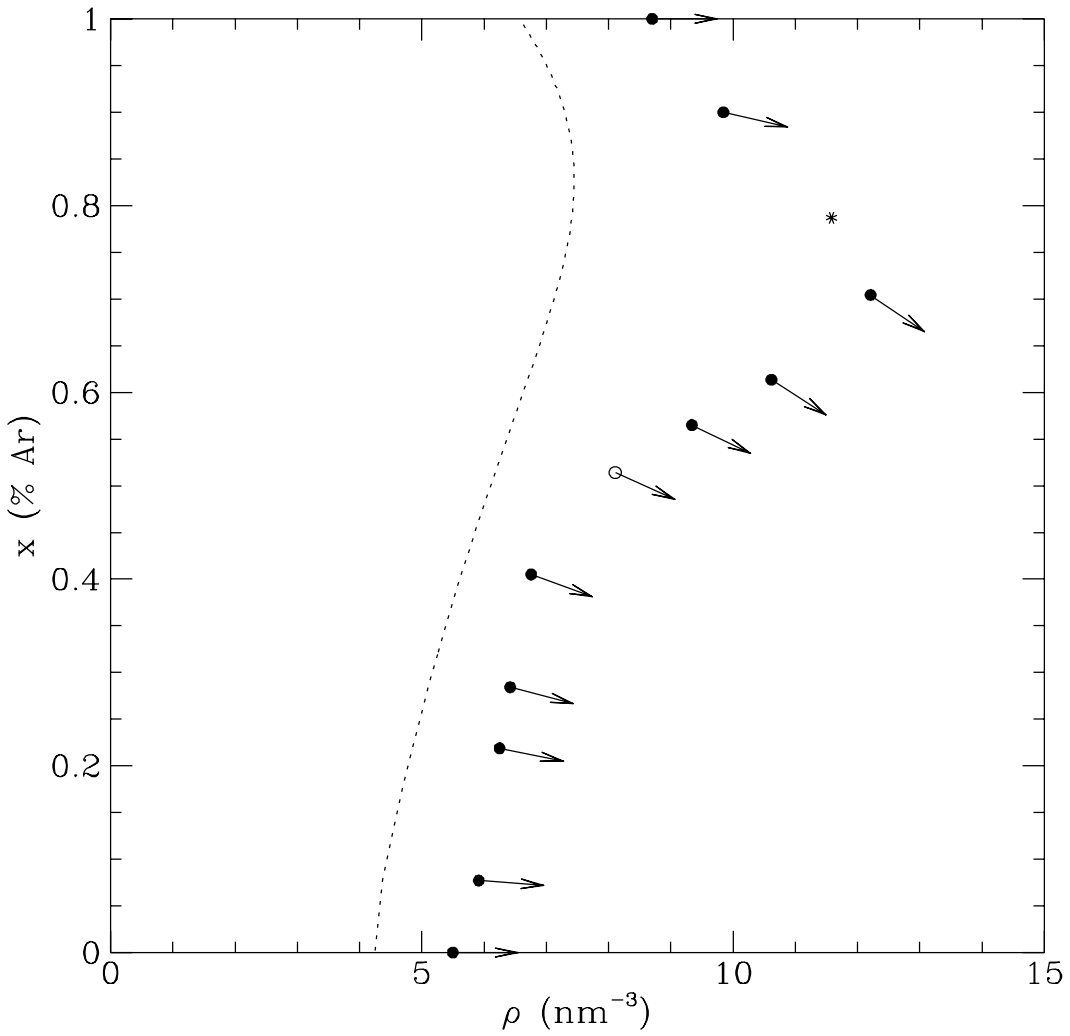
FIGURE CAPTIONS

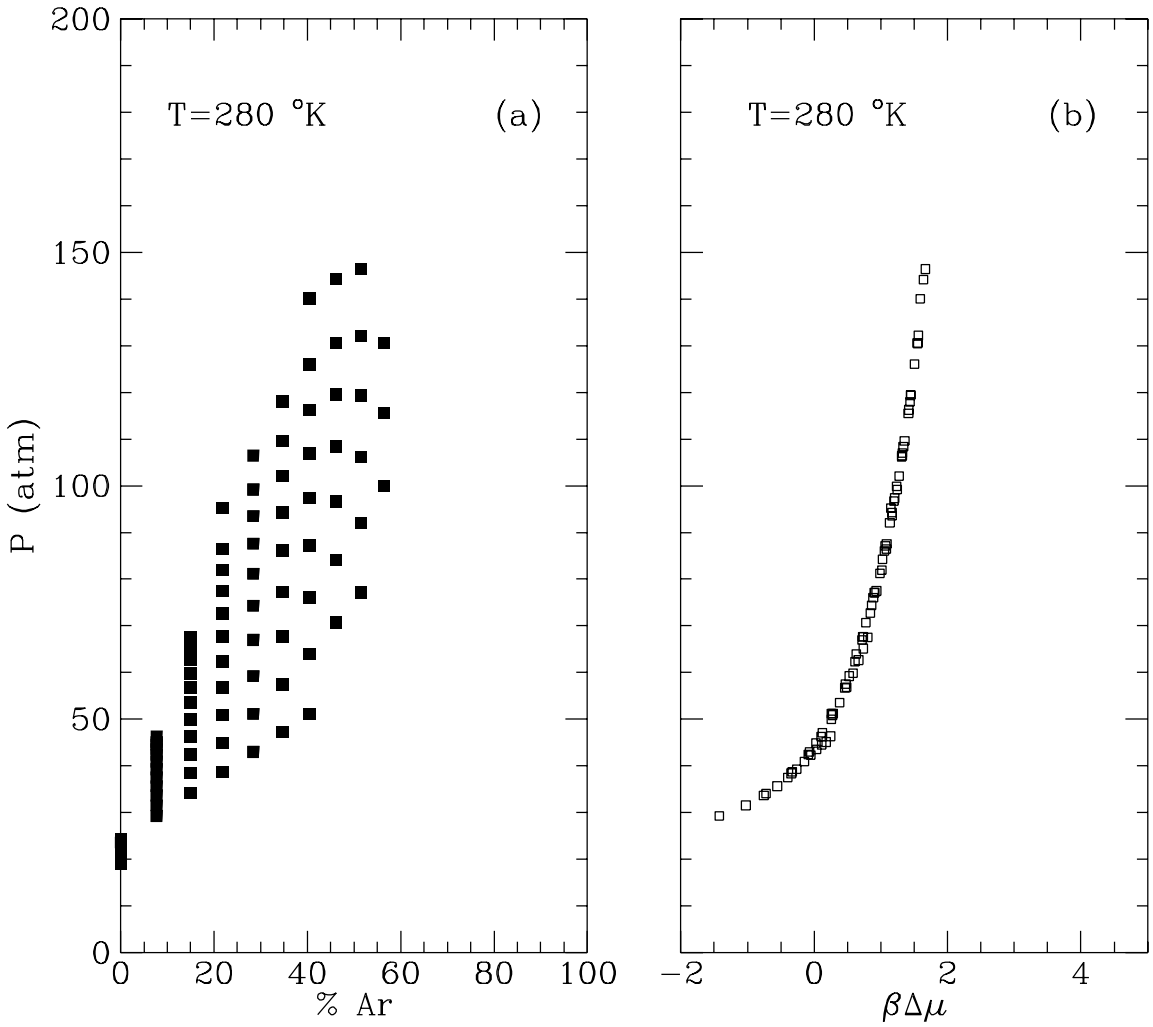
Fig. 1 Density - concentration projection of the liquid-vapor critical line in an Ar-Xe mixture. Dotted line: mean field theory. Circles: HRT results. The arrow represents the direction of the order parameter. The open circle marks the critical point of the isothermal section shown in Fig. 2. The asterisk identifies the (ρ, x) projection of the thermodynamic state which Fig. 3 refers to.

Fig. 2 (a): Isothermal section of the concentration - pressure plane. Full symbols show the thermodynamic states inside the coexistence region. (b): Collapse of points of panel (a) when plotted in the chemical potential - pressure plane.

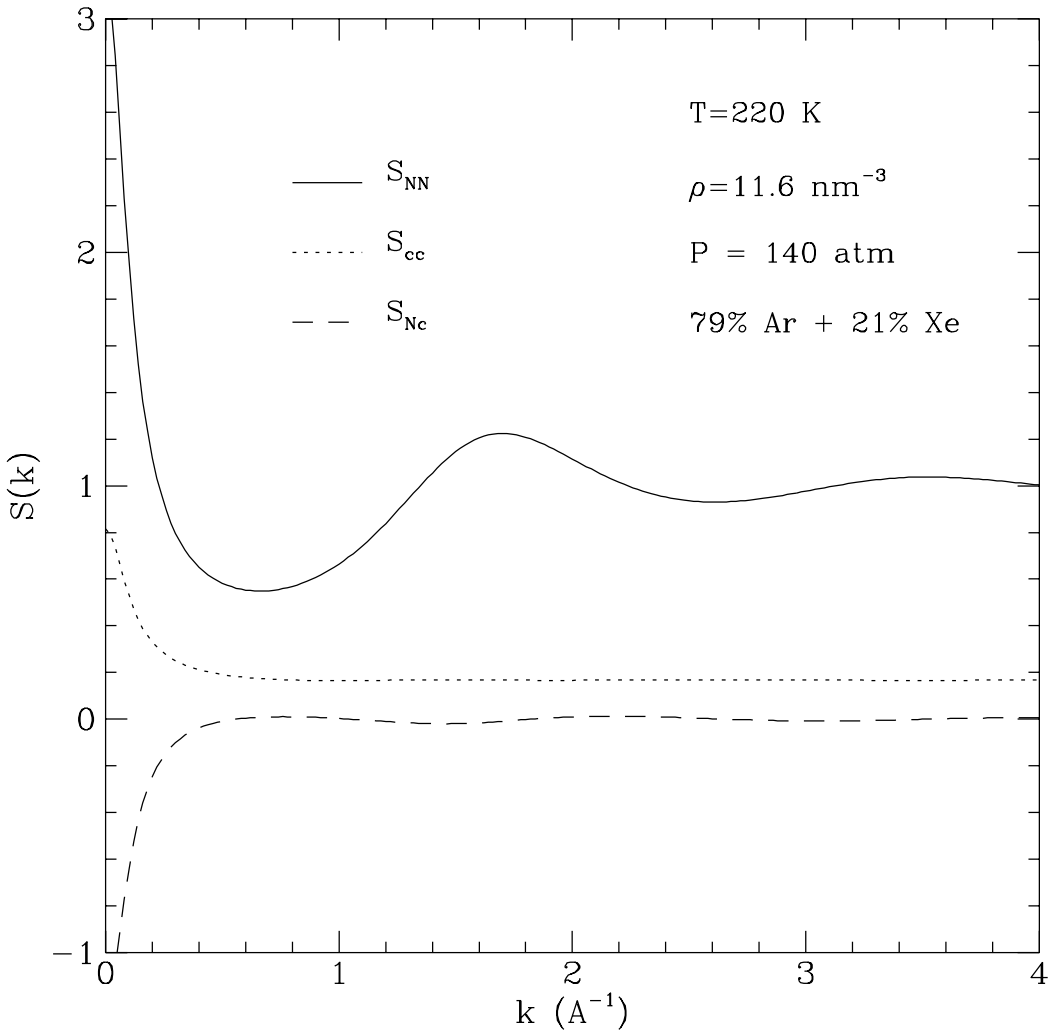
Fig. 3 Density ($S_{NN}(k)$), concentration ($S_{cc}(k)$) and cross ($S_{Nc}(k)$) structure factors for the state shown in Fig. 1.



Pini et al. Fig. 1



Pini et al. Fig. 2



Pini et al. Fig. 3