Eur. Phys. J. B **53**, 61–65 (2006)
DOI: 10.1140/epjb/e2006-00344-1

THE EUROPEAN PHYSICAL JOURNAL B

Liquid-liquid critical point: an analytical approach

A. Daanoun[a]

Laboratoire de Physique Appliquée, Faculté des Sciences et Techniques de Tanger, B.P. 416 Tanger, Maroc

Received 25 October 2005 / Received in final form 30 May 2006

Abstract. Theoretical simulations and experimental studies have showed that many systems (like liquid metals) can exhibit two phase transitions: gas-liquid and liquid-liquid. Consequently the fluid phase of these systems presents two critical points, namely the usual gas-liquid (G-L) critical point and the liquid-liquid critical point that results from a phase transition between two liquids of different densities: a low density liquid (LDL) and a high density liquid (HDL). The van der Waals theory for simple fluids [Phys. Rev. E **50**, 2913 (1994)] is based on taking a system with purely repulsive forces as a reference, is able to describe two stable first-order phase transitions between fluids of different densities. The particles in our system interact via a total pair potential, which splits into a repulsive V_R and a density-dependent attractive V_A part.

PACS. 64.70.Ja Liquid-liquid transitions – 64.60.Kw Multicritical points – 64.60.-i General studies of phase transitions

1 Introduction

Simple fluids [1] are systems of identical particles whose interactions can be described by a spherical symmetric pair potential. They have been the object of considerable research. One aspect of this research is to understand the liquid-liquid transition that some pure substances can exhibit. Recent experimental studies of phosphorus [2] show a first-order phase transition between two stable liquids of different densities: a low density liquid (*LDL*) and a high density liquid (*HDL*). This transition has been shown also, through numerical simulations and theoretical approaches [3–11]. A recent study [12] predicts the possible existence of multiple liquid-liquid critical points.

In a previous study [13] we showed the existence of a first-order isostructural solid-solid transition from a dense to a more expanded solid phase. This phase transition terminates in a solid-solid critical point, wherein we put forward that two liquids of different densities might be able to coexist. This coexistence would end in a liquid-liquid critical point.

2 Potential and formalism

In the present work, the van der Waals theory for simple fluids [13] is used to verify the worthiness of the scenario described above. In order to reproduce two loops in the fluid phase, we assume that the particles in our system interact via a total pair potential, which split into a simple hard-sphere (*HS*) repulsion $V_R = V_{HS}$ and a density-dependent attraction V_A,

$$V(r) = V_{HS}(r) + V_A(r, \rho). \tag{1}$$

Tejero and Baus [14] have used the van der Waals theory with the following density-dependent pair potential whose range exhibits a nonmonotonic density variation

$$V_A(r,\rho) = \begin{cases} \infty & r < \sigma \\ -\varepsilon \left(\dfrac{\sigma}{r}\right)^{n(\rho)} & r \geq \sigma \end{cases} \tag{2}$$

where ε is the amplitude of the potential and σ the hard-sphere (HS) diameter. The potential index $n(\rho)$ is deduced from the equations that determine the critical point of the fluid phase. It is given by

$$n(\rho) = 3 + \frac{n(0) - 3}{1 - \frac{10}{3} v_0 \rho + \frac{25}{6} (v_0 \rho)^2} \tag{3}$$

where v_0 is the hard-sphere volume and $n(0)$ (*a potential parameter*) is the zero-density value which give the potential index $n(\rho)$. Tejero and Baus [14] showed that the density dependence can lead to a liquid-liquid transition. Monte Carlo calculations also confirm this result in a fluid model with density-dependent interactions [15].

We note that from the mathematical definition of the critical point [14], one can deduce that the critical density and temperature don't depend on the $n(0)$ value. So the specific functional form of the potential proposed by reference [14] presents a certain limit. We will be able to remove this limit with the potential adopted in this

---

[a] e-mail: `a_daanoun@yahoo.fr`

study. It is completely different from the one used in [14]. Indeed, the strength of the attraction is taken to depend on the density $V_A(r,\rho) = \varepsilon(\varepsilon_1,\rho)f(r)$. The variation of ε_1 in $\varepsilon(\varepsilon_1,\rho)$, reveals a double criticality in the fluid phase. This functional form allows the study of the behaviour of the density, temperature and pressure of the low-density critical point and high-density critical point by varying the potential parameter ε_1 when n is fixed, and also by varying n when ε_1 is fixed.

The effective interaction when fitted to some experiments such as colloidal systems and liquid metals, is found to depend on density and/or temperature. For these systems, the thermodynamic properties can be affected by this dependence [16].

We consider a simple fluid composed of N spherical particles enclosed in a volume V at an equilibrium temperature T and interacting via the pair potential $V(r)$ described above, in which the function $\varepsilon(\varepsilon_1,\rho)$ takes the form of an exponential. The function $f(r)$ is an inverse-power potential. Obviously, many choices of $f(r)$ are possible. So the interaction $V(r)$ can be written as follows

$$V_A\left(r,\rho\right) = \begin{cases} \infty & r < \sigma \\ -\varepsilon_0 \exp\left(-\varepsilon_1 \dfrac{\rho}{\rho_0}\right) \dfrac{1}{\left({}^{r}\!/_{\sigma}\right)^n} & r \geq \sigma \end{cases} \tag{4}$$

where r is the center-to-center distance and σ is the HS diameter. While ρ is the number density and $\rho_0 = 0.495/v_0(v_0$ is the hard-sphere volume). ρ_0 represent the maximum density for which the fluid phase can exist [13,17].

In addition, within the van der Waals theory, the reduced free energy per particle $f$of the system can be written as the superposition of a repulsive (HS) and attractive (A) contribution (see [13,17] for details).

$$f = f_{HS} + f_A \tag{5}$$

where f_{HS} is the free energy of the HS system. The equation of state for the HS given f_{HS} is a simple free-volume approximation. So that $[1-(\rho/\rho_0)]V$ is the free volume accessible to the HS in a fluid of volume V and $(\rho/\rho_0)V$ is the excluded volume. Hence

$$f_{HS} = t\left[\ln\left(\rho\Lambda^3\right) - 1\right] - t\ln\left(1 - \frac{\rho}{\rho_0}\right) \tag{6}$$

where t is the reduced temperature and Λ the thermal de Broglie wavelength.

f_A is the cohesion energy due to attractions. According to [13,17], f_A can be written as

$$f_A = -\frac{2\pi}{\varepsilon_0}\rho\sigma^3 \exp\left(-\varepsilon_1\frac{\rho}{\rho_0}\right)\int_1^\infty dx x^2 f(x) \tag{7}$$

where $x = r/\sigma$. This allows us to write the free energy f of the fluid as follows

$$f = t\left[\ln\left(\rho\Lambda^3\right) - 1\right] - t\ln\left(1 - \frac{\rho}{\rho_0}\right) - \frac{2\pi}{\varepsilon_0}\rho\sigma^3 \exp\left(-\varepsilon_1\frac{\rho}{\rho_0}\right)\int_1^\infty dx x^2 f(x). \tag{8}$$

From the expression of the free energy f, we deduced the reduced pressure p and the reduced chemical potential μ.

$$p = \eta^2\frac{\partial f}{\partial\eta} \tag{9a}$$

$$\mu = \frac{\partial\left(\eta f\right)}{\partial\eta} \tag{9b}$$

where $\eta = \rho v_0$ is the packing fraction.

The critical point is characterized by the fact that both derivatives of the pressure vanish

$$\frac{\partial p}{\partial\eta} = 0, \quad \frac{\partial^2 p}{\partial\eta^2} = 0. \tag{10}$$

The complete fluid-fluid coexistence curve can be obtained by solving the condition for two coexisting phases. Namely, the pressures and the chemical potentials of the two phases must be the same:

$$\begin{aligned} p(\eta_1,t) &= p(\eta_2,t) \\ \mu(\eta_1,t) &= \mu(\eta_2,t) \end{aligned} \tag{11}$$

where η_1 denotes the value of η for the low-density fluid phase, and η_2 that of high-density fluid phase.

The parameter controlling the decay rate ε_1 is a "*regulating parameter*". For the clearness we will henceforth work with the inverse of ε_1. It will be noted $\gamma = (1/\varepsilon_1)$.

3 Results

3.1 Effect of γ on the phase transitions

For $\gamma = 0$ one find a system of HS exhibiting an order-disorder transition without any critical point [17]. From a critical value γ_c (this value will be determined below), the phase diagram contains just the usual critical point (G-L). This point will increase towards the upper limit

$$C_n^l\left(\eta_c^{l,n}, t_c^{l,n}, p_c^{l,n}\right) = \left(0.1650, 1.76/(n-3), 0.1089/(n-3)\right). \tag{12}$$

This limit corresponds to a γ approaching infinity. So the construction of the phase diagram will be done for γ values between the interval zero and γ_c, where there is an evidence of a double criticality. We choose γ and n so that the free energy of the fluid is smaller than the free energy of the solid. For a solid phase the free energy per particle f_S can be reproduced from [17]. In order to construct an accurate fluid phase diagram, we calculate the critical points $C_{i,n}\left(\eta_{c_i}^n, t_{c_i}^n, p_{c_i}^n\right)$, where $1 \leq i \leq 2$: $C_{1,n}$ is the low-density critical point and $C_{2,n}$ is the high-density critical point, characterized by the three quantities $\eta_{c_i}^n$, $t_{c_i}^n$ and $p_{c_i}^n$. Then we perform Maxwell's double tangent construction on each loop $\{l_i\}$ developed by the free energy. We find two coexisting curves in the fluid phase $F_{i,n}^1 - F_{i,n}^2$ ending in the critical point $C_{i,n}$. This result corresponds

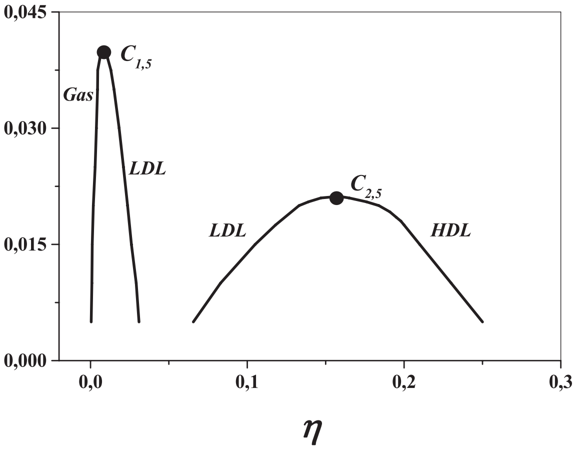

Fig. 1. Phase diagram with two critical points $C_{1,5}$ and $C_{2,5}$ of a system interacting with a density dependent potential with $\gamma = 0.067$ and $n = 5$ in the temperature-density plane, where $\eta = \rho v_0$ is the packing fraction. The dots represent critical points.

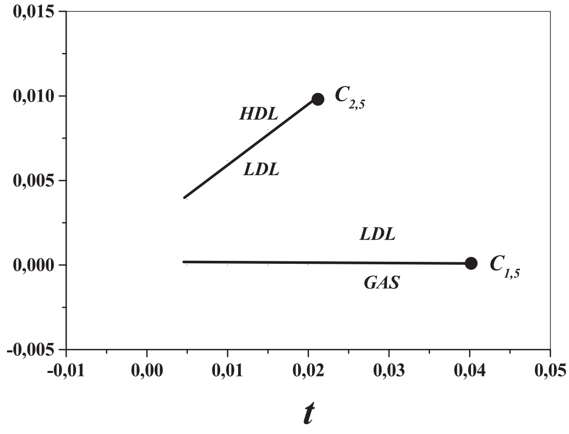

Fig. 2. Phase diagram with two critical points $C_{1,5}$ and $C_{2,5}$ of the same system but in the pressure-temperature plane. Solid lines represent phase transition lines, dots represent critical points.

to the gas-liquid $F^1_{1,n} - F^2_{1,n}$ and LDL-HDL $F^1_{2,n} - F^2_{2,n}$ transitions.

The position of the critical points depends strongly on the potential parameter γ. So by calculating equations (9a,10) and accepting only physical solutions, namely a positive critical temperature and pressure and a critical density lower than $\eta_0 = 0.495$; the condition to get a second critical point is found. It appears in the phase diagram when

$$0 < \gamma \leq \gamma_c = 0.29 \tag{13a}$$

$$n > 3. \tag{13b}$$

For $\gamma_c = 0.29$, the two limiting critical points are deduced

$$C^l_{1,n}\left(\eta^{l,n}_{c_1}, t^{l,n}_{c_1}, p^{l,n}_{c_1}\right) = (0.0313, 0.3141/(n-3), 0.0031/(n-3)) \tag{14a}$$

$$C^l_{2,n}\left(\eta^{l,n}_{c_2}, t^{l,n}_{c_2}, p^{l,n}_{c_2}\right) = (\eta_0, 0, 0.2334/(n-3)). \tag{14b}$$

Figures 1 and 2 show respectively the coexisting curves of the fluid phase in the temperature-density and pressure-temperature planes for $(\gamma, n) = (0.067, 5)$. They show that double criticality is obvious. For the same value of n, Figures 3a–3f show the behaviour of the density, temperature and pressure of the two critical points as the potential parameter γ is varied.

It is known that the fluid cannot exist beyond the density η_0, and we have shown that γ must be lower than 0.29 so that the phase diagram contains two critical points. Thus by increasing γ up to 0.29, $C_{2,5}$ the high-density critical point approaches the limiting critical point $C^l_{2,5}(\eta^{l,5}_{c_2}, t^{l,5}_{c_2}, p^{l,5}_{c_2}) = (\eta_0, 0, 0.1167)$; whereas $C_{1,5}$ the low-density critical point goes towards the other limiting critical point $C^l_{1,5}(\eta^{l,5}_{c_1}, t^{l,5}_{c_1}, p^{l,5}_{c_1}) = (0.0312, 0.1571, 0.0016)$. Beyond the critical value 0.29, $C_{2,5}$ exists only in a purely mathematical way. Indeed, the density of $C_{2,5}$ is more than η_0, whereas the temperature is negative. So the phase diagram will contain the single gas-liquid critical point, that continues to grow towards the limiting point $C^l_5(\eta^{l,5}_c, t^{l,5}_c, p^{l,5}_c) = (0.1650, 0.8800, 0.0545)$.

According to Figures 3b, 3d, 3f, we deduce that, when γ approaches zero, $C_{1,5}\left(\eta^5_{c_1}, t^5_{c_1}, p^5_{c_1}\right)$ decreases towards $(0, 0, 0)$ faster than $C_{2,5}\left(\eta^5_{c_2}, t^5_{c_2}, p^5_{c_2}\right)$. This result suggests that for a very weak attraction, the gas-liquid critical point $C_{1,5}$ would disappear and only the liquid-liquid critical point $C_{2,5}$ would subsist just before crystallization develops [18,19].

It is easy to show that, according to equations (9a,10) the critical densities $\eta^n_{c_i}$ are independent of the n values (so we can drop the superscript n on $\eta^n_{c_i}$), while the critical temperatures $t^n_{c_i}$ and pressures $p^n_{c_i}$ are inversely proportional to $n - 3$, for a given value of γ. So Figures 3a, 3b remain unchanged for any value of n. However, the points represented in Figures 3c–3f undergo a simple translation along the Y axis, without changing the shape of the plotted curves. Therefore the phase diagram of a simple fluid should undergo a strong modification only when the relative attraction strength with the density versus repulsion is strongly modified.

In references [4,5], authors showed that a phase diagram with two liquids phases requires a balance between a repulsive soft core of width w_R and an attractive well of width w_A of an isotropic potential. Clearly, the liquid-liquid transition resulting from our potential has a different physical origin. But we can see that γ has the same role as w_A, when the other parameters remain constant. We note also, that the behaviour of the low-density critical point $C_{1,n}$ is comparable with that in [5].

Fomin et al. [3], using a generalized van der Waals theory showed that the existence of liquid-liquid transition is not only determined by the interplay of the parameters of an isotropic repulsive soft-core attractive potential, but also by the structure of a reference liquid. Moreover, they showed that for a very weak attraction, the system develops only a liquid-liquid phase transition. This is similar to what we found.

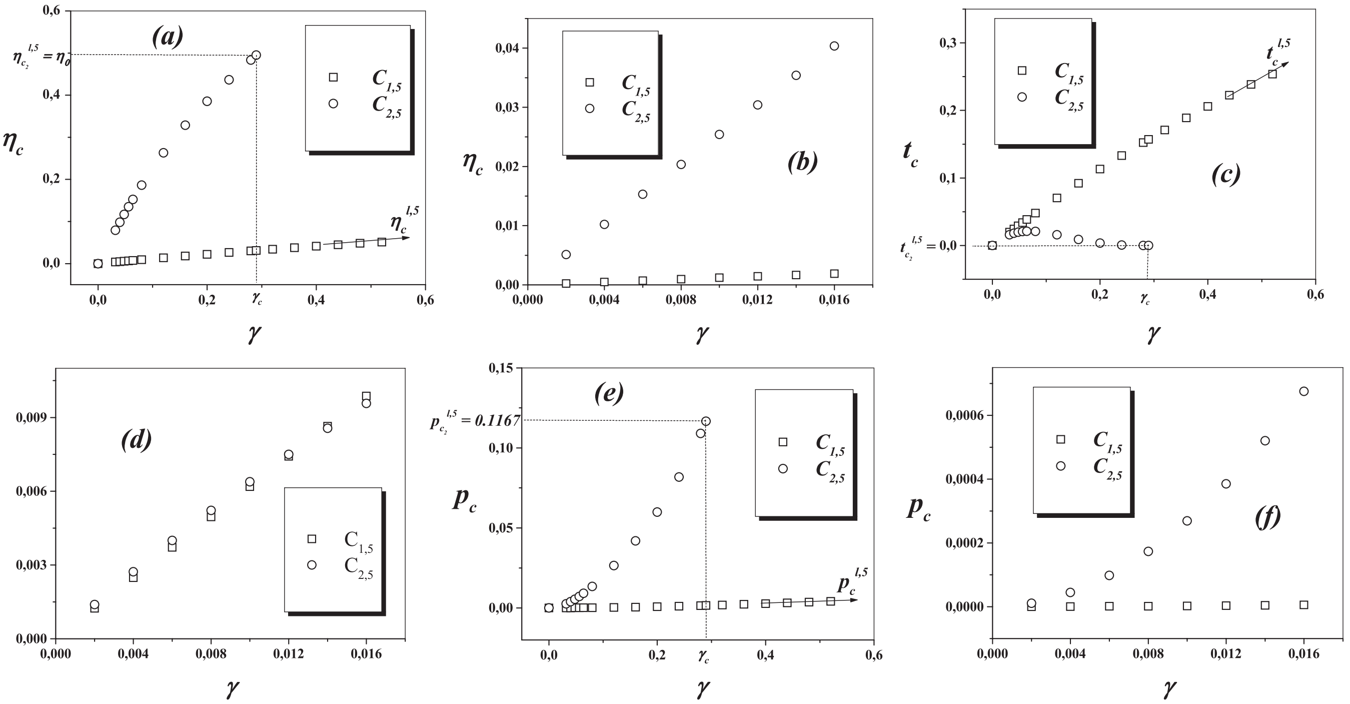

Fig. 3. Behaviour of the density (a), temperature (c) and pressure (e) of the low-density critical point $C_{1,5}$ (squares), and the high-density critical point $C_{2,5}$ (dots) as a function of the parameter γ with $n = 5$. The limiting critical point $C_5^l(\eta_c^{l,5}, t_c^{l,5}, p_c^{l,5}) = (0.1650, 0.8800, 0.0545)$ corresponds to a γ approaching infinity; and the behaviour of the same quantities $\eta_{c_i}^5$(b), $t_{c_i}^5$(d) and $p_{c_i}^5$(f) of $C_{1,5}$ (squares), and $C_{2,5}$ (dots) as a function of γ approaching zero.

3.2 Effect of n on the phase transitions

The potential adopted here has an important advantage. Because it is really flexible, without counting the impact of γ on the phase diagram by keeping n constant, it enables us to study the evolution of the position of the low-density critical point $C_{1,\gamma}\left(\eta_{c_1}^{\gamma}, t_{c_1}^{\gamma}, p_{c_1}^{\gamma}\right)$ and the high-density critical point $C_{2,\gamma}\left(\eta_{c_2}^{\gamma}, t_{c_2}^{\gamma}, p_{c_2}^{\gamma}\right)$ when γ is fixed. We find that varying the power n does not affect the critical densities $\left(\eta_{c_1}^{\gamma}, \eta_{c_2}^{\gamma}\right)$, indeed, they remain constant. On the other hand, we note that the critical temperatures $\left(t_{c_1}^{\gamma}, t_{c_2}^{\gamma}\right)$ and pressures $\left(p_{c_1}^{\gamma}, p_{c_2}^{\gamma}\right)$ decrease when n increases. Table 1 contains a few examples that illustrate our comments. Figures 4a, 4b represent respectively the behaviour of the temperature and pressure of the low-density critical point and high-density critical point as a function of the potential power n.

In this study, the liquid-liquid transition has the same physical origin as that in [14]. However, in reference [14], it is the range of the attraction which is a function of density that leads towards this transition. The precise choice of the potential suggested here is more judicious, because it is based in an effective interaction fitted to some experimental systems such as colloidal systems and liquid metals [16]. Moreover, this potential will enable us to make a suitable study of the influence of the parameter n in equation (4) on the position of the critical points. So we fixed the value of γ and varied n. This situation would correspond to the variation of the parameter $n(0)$ in reference [14]. It is easy to verify in [14] that by increasing $n(0)$, the critical densities and temperatures remain unchanged, whereas the critical pressures decrease. The behaviour of the critical densities $\left(\eta_{c_1}^{\gamma}, \eta_{c_2}^{\gamma}\right)$ and pressures $\left(p_{c_1}^{\gamma}, p_{c_2}^{\gamma}\right)$ is similar to reference [14]. However, the critical temperatures $\left(t_{c_1}^{\gamma}, t_{c_2}^{\gamma}\right)$ decrease as n increases. Table 1 shows, as described above, that when γ approaches zero, the low-density critical point $C_{1,\gamma}\left(\eta_{c_1}^{\gamma}, t_{c_1}^{\gamma}, p_{c_1}^{\gamma}\right)$ decreases towards $(0, 0, 0)$ more quickly than the high-density critical point $C_{2,\gamma}\left(\eta_{c_2}^{\gamma}, t_{c_2}^{\gamma}, p_{c_2}^{\gamma}\right)$. This still suggests that $C_{1,\gamma}$ would disappear and $C_{2,\gamma}$ would remain just before the crystallization.

4 Conclusion

It is known that the effective interaction of some systems such as colloidal dispersions and liquid metals depend on density and/or temperature. For these systems, the thermodynamic properties can be affected by this dependence. Consequently, the appearance of a second critical point in the fluid phase should be possible. In this work we proved that the phase diagram of systems interacting via density dependent potentials, with a constant excluded volume, can exhibit two phase transitions: gas-liquid and liquid-liquid.

Before the onset of crystallization and for the systems treated here, we have found three distinct types of diagram. In the first type of phase diagram ($\gamma > \gamma_c$) we have found the usual gas-liquid critical point. In the second type

Table 1. Some values of the low-density critical point $C_{1,\gamma}$ $(\eta_{c_1}^{\gamma}, t_{c_1}^{\gamma}, p_{c_1}^{\gamma})$ and the high-density critical point $C_{2,\gamma}$ $(\eta_{c_2}^{\gamma}, t_{c_2}^{\gamma}, p_{c_2}^{\gamma})$ when γ is fixed.

	$\gamma = 0.006$	$\gamma = 0.008$	$\gamma = 0.01$	$\gamma = 0.02$	$\gamma = 0.03$	$\gamma = 0.04$
η_{c_1}	0.0007	0.0010	0.0012	0.0024	0.0035	0.0047
η_{c_2}	0.0153	0.0203	0.0254	0.0503	0.0746	0.0983
t_{c_1}	$0.0074/(n-3)$	$0.0099/(n-3)$	$0.0124/(n-3)$	$0.0246/(n-3)$	$0.0368/(n-3)$	$0.0488/(n-3)$
t_{c_2}	$0.0080/(n-3)$	$0.0104/(n-3)$	$0.0128/(n-3)$	$0.0229/(n-3)$	$0.0202/(n-3)$	$0.0361/(n-3)$
p_{c_1}	$1.6 \times 10^{-6}/(n-3)$	$2.9 \times 10^{-6}/(n-3)$	$4.6 \times 10^{-6}/(n-3)$	$1.8 \times 10^{-5}/(n-3)$	$4.1 \times 10^{-5}/(n-3)$	$7.1 \times 10^{-5}/(n-3)$
p_{c_2}	$1.9 \times 10^{-4}/(n-3)$	$3.5 \times 10^{-4}/(n-3)$	$5.4 \times 10^{-4}/(n-3)$	$2.1 \times 10^{-3}/(n-3)$	$3.6 \times 10^{-3}/(n-3)$	$7.8 \times 10^{-3}/(n-3)$

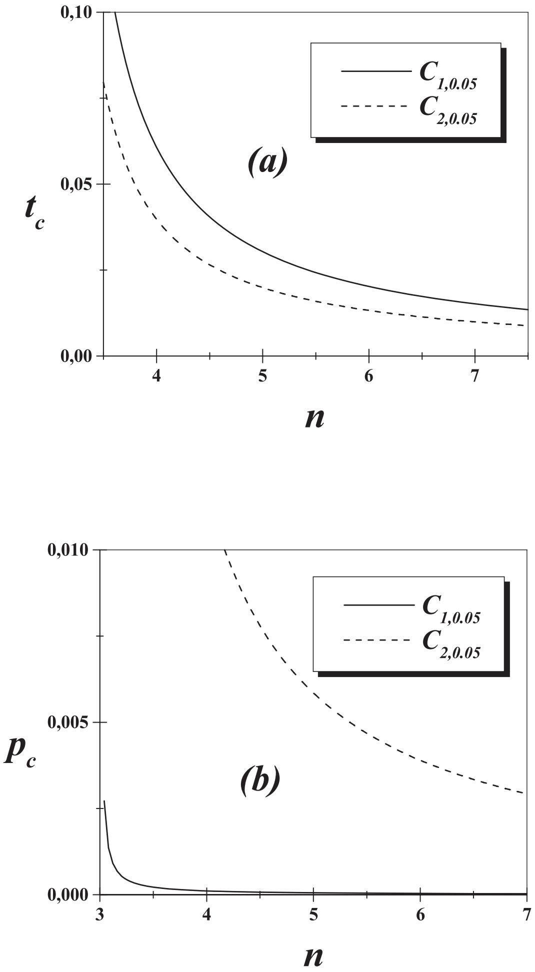

Fig. 4. Behaviour of the temperature (a) and pressure (b) of the low-density critical point $C_{1,0.05}$ and high-density critical point $C_{2,0.05}$ as a function of the potential power n with $\gamma = 0.05$.

of the phase diagram ($\gamma \leq \gamma_c$), the two critical points: gas-liquid and liquid-liquid are present. Finally, in the third phase diagram (γ approaches zero) we have found just a single liquid-liquid critical point.

An effective interaction strength that depends on the density and the variation of the relative attraction strength versus repulsion would explain the modification that the phase diagram undergoes. Energetic aspects can be behind the manifestation of the second critical point in the fluid phase resulting from a phase transition between a low density liquid (LDL) and a high density liquid (HDL).

We thank A. Rusi El Hassani for stimulating discussions.

References

1. J.P. Hansen, I.R. McDonald, *Theory of simple Liquids*, 1st edn. (Academic Press, London, 1976)
2. G. Monaco, S. Falconi, W.A. Crichton, M. Mezouar, Phys. Rev. Lett. **90**, 255701 (2003); Y. Katayama, T. mizutani, W. Utsumi, O. shimomura, M. Yamakata, K. Funakashi, Nature **403**, 170 (2000)
3. Y.D. Fomin, V.N. Ryzhov, E.E. Tareyeva, e-print `arXiv:cond-mat/0512640`
4. A. Skibinsky, S.V. Buldyrev, G. Franzese, G. Malescio, H.E. Stanley, Phys. Rev. E **69**, 061206 (2004)
5. G. Malescio, G. Franzese, A. Skibinsky, S.V. Buldyrev, H.E. Stanley, Phys. Rev. E **71**, 061504 (2005)
6. G. Franzese, G. Malescio, A. Skibinsky, S.V. Buldyrev, H.E. Stanley, Phys. Rev. E. **66**, 051206 (2002)
7. G. Malescio, G. Franzese, G. Pellicane, A. Skibinsky, S.V. Buldyrev, H.E. Stanley, J. Phys.: Condens. Matter. **14**, 2193 (2002)
8. S.V. Buldyrev, G. Franzese, N. Giovambattista, G. Malescio, M.R. Sadr-Lahijany, A. Scala, A. Skibinsky, H.E. Stanley, Physica A **304**, 23 (2002)
9. Y. Senda, F. Shimojo, K. Hoshino, Journal of Non-Crystalline Solids **312**, 80 (2002)
10. G. Franzese, G. Malescio, A. Skibinsky, S.V. Buldyrev, H.E. Stanley, Nature **409**, 692 (2001)
11. S. Harrington, R. Zhang, P.H. Poole, F. Sciortino, H.E. Stanley, Phys. Rev. Lett. **78**, 2409 (1997)
12. S.V. Buldyrev, H.E. Stanley, Physica A **330**, 124 (2003)
13. A. Daanoun, C.F. Tejero, M. Baus, Phys. Rev. E **50**, 2913 (1994)
14. C.F. Tejero, M. Baus, Phys. Rev. E **57**, 4821 (1998)
15. N.G. Almarza, E. Lomba, G. Ruiz, C.F. Tejero, Phys. Rev. Lett. **86**, 2038 (2001)
16. S. Amokran, M. Bouaskarne, Phys. Rev. E **65**, 051501 (2002); M. Bouaskarne, S. Amokran, C. Regnaut, J. Chem. Phys. **111**, 2151 (1999)
17. T. Coussard, M. Baus, Phys. Rev. E **52**, 862 (1995)
18. C.F. Tejero, A. Daanoun, H.N.W. Lekkerkerker, M. Baus, Phys. Rev. Lett. **73**, 752 (1994); C.F. Tejero, A. Daanoun, H.N.W. Lekkerkerker, M. Baus, Phys. Rev. E **51**, 558 (1995)
19. P. Bolhuis, D. Frenkel, Phys. Rev. Lett. **72**, 2211 (1994); P. Bolhuis, M. Hagen, D. Frenkel, Phys. Rev. E **50**, 4880 (1994)