CRITICAL CONSOLUTE POINT IN HARD-SPHERE BINARY MIXTURES: EFFECT OF THE VALUE OF THE EIGHTH AND HIGHER VIRIAL COEFFICIENTS ON ITS LOCATION

Mariano LÓPEZ DE HARO[a,+], Anatol MALIJEVSKÝ[b1,*] and Stanislav LABÍK[b2]
[a] *Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain;*
e-mail: malopez@servidor.unam.mx
[b] *Department of Physical Chemistry, Institute of Chemical Technology, Prague and Center for Biomolecules and Complex Molecular Systems, Technická 5, 166 28 Prague 6, Czech Republic;*
e-mail: [1] anatol.malijevsky@vscht.cz, [2] stanislav.labik@vscht.cz

Received September 30, 2009
Accepted November 16, 2009

Dedicated to Professor Ivo Nezbeda on the occasion of his 65th birthday.

Various truncations for the virial series of a binary fluid mixture of additive hard spheres are used to analyze the location of the critical consolute point of this system for different size asymmetries. The effect of uncertainties in the values of the eighth virial coefficients on the resulting critical constants is assessed. It is also shown that a replacement of the exact virial coefficients in lieu of the corresponding coefficients in the virial expansion of the analytical Boublík–Mansoori–Carnahan–Starling–Leland equation of state, which still leads to an analytical equation of state, may lead to a critical consolute point in the system.
Keywords: Hard-sphere binary mixture; High virial coefficients; Fluid–fluid phase equilibrium; Thermodynamics; Equation of state.

The virial series was originally introduced by Kammerlingh–Onnes[1] to provide a mathematical representation of experimental pressure–density–temperature data of gases and liquids. If $Z \equiv p/\rho k_B T$ denotes the compressibility factor of the fluid, where p is the pressure, ρ is the number density, k_B is the Boltzmann constant and T the absolute temperature, the virial series reads

---

[+] On sabbatical leave from Centro de Investigación en Energía, Universidad Nacional Autónoma de México, Temixco, Morelos 62580, Mexico.

Collect. Czech. Chem. Commun. 2010, Vol. 75, No. 3, pp. 359–369

doi:10.1135/cccc2009510

$$Z = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1} \tag{1}$$

and thus such an expansion accounts for the deviation from ideal gas behavior in ascending powers of the density. In Eq. (*1*) the B_n are the virial coefficients which for simple fluids depend in general on temperature, while in the case of fluid mixtures they may depend on both temperature and composition. It is now well known that this representation for the equation of state can be derived rigorously in statistical mechanics and that the different virial coefficients are related to intermolecular interactions in a perfectly defined way. Unfortunately, irrespective of the intermolecular potential, the computation of the virial coefficients increases its complexity enormously as n grows and the radius of convergence of the series in Eq. (*1*) is not known. So it is not surprising that there is rather limited information on these virial coefficients even for the simplest models. Yet, this limited information has proved to be useful either to test empirical or semi-empirical proposals for the equation of state of a given system or to derive such proposals via numerical manipulation (Padé approximants or the like).

In this paper we will consider the demixing problem in a binary fluid mixture of $N = N_1 + N_2$ additive hard spheres of diameters σ_1 and σ_2 ($\sigma_1 > \sigma_2$). The thermodynamic properties of the mixture can be described in terms of the number density (which for this system is given by $\rho \equiv N/V$, with V the volume), the mole fraction of the big spheres $x \equiv N_1/N$, and the parameter $\gamma \equiv \sigma_2/\sigma_1$ which measures the size asymmetry. The Helmholtz free energy per particle $f \equiv f(\rho,x,\gamma)$ for this system reads

$$f = f_{\text{id}} + f_{\text{ex}} \tag{2}$$

with the ideal contribution f_{id} given by

$$\beta f_{\text{id}} = \ln(\rho\Lambda^3) - 1 + x\ln x + (1-x)\ln(1-x) \tag{3}$$

and the excess contribution f_{ex} given by

$$\beta f_{\text{ex}} = \sum_{n=1}^{\infty} \frac{1}{n} B_{n+1}(x,\gamma)\rho^n \; . \tag{4}$$

In the above formulae, $\beta \equiv 1/k_BT$ plays only the role of a scale factor, Λ is the thermal de Broglie wavelength of the particles, and $B_{n+1}(x,\gamma)$ are the virial coefficients of the mixtures.

In general, one may express the virial coefficients of a binary hard-sphere mixture as

$$B_n(x,\gamma) = \sum_{m=0}^{n} B_n(m,n-m)\frac{n!}{m!(n-m)!}x^m(1-x)^{n-m} \tag{5}$$

where the partial virial (composition-independent) coefficients $B_n(m,n-m)$ ($m = 0, 1, \ldots n$) have been introduced. Analytical expressions are known for $B_2(x,\gamma)$ [2] and $B_3(x,\gamma)$ [3], while $B_4(x,\gamma)$ and up to $B_7(x,\gamma)$ have been evaluated numerically for various size ratios[4–8]. Very recently one of the present authors has developed an accurate algorithm to compute virial coefficients up to $B_8(x,\gamma)$ at a number of size ratios[9]. The specific values of the partial virial coefficients $\widetilde{B}_n(m,n-m)$ with $n = 4$–8 obtained for $\gamma = 0.05$, 0.1 and 0.2 are given in Table I. These most recent results, which apart from providing the new eighth virial coefficients improve on the numerical values of the lower ones, will be used later on. A very recent review on virial expansions, including an extensive list of references and a description of the difficulties associated with the computation of higher virial coefficients, has been written by Masters[10].

In order to make the paper self-contained, in section Theoretical we will briefly recall how to determine the critical consolute point in binary hard-sphere mixtures. This is followed in section Results by the presentation of the results of our calculations. The paper is closed in section Conclusions with further discussion of the results and some concluding remarks.

THEORETICAL

One convenient way to study demixing in binary hard-sphere mixtures is to look at the loss of convexity of the Helmholtz free energy per particle f. In the present thermodynamic representation, where ρ and x are the independent variables, the condition for the occurrence of a spinodal instability reads

$$\frac{\partial^2 f}{\partial\rho^2}\frac{\partial^2 f}{\partial x^2} - \left(\frac{\partial^2 f}{\partial\rho\partial x} - \frac{1}{\rho}\frac{\partial f}{\partial x}\right)^2 = 0 . \tag{6}$$

In two instances, namely the limiting cases of a pure hard-sphere system ($\gamma = 1$) and that of a binary mixture in which species two consists of point

Table I
Partial virial coefficients $\widetilde{B}_n(m,n-m) = B_n(m,n-m)/\sigma_1^{3(n-1)}$ of binary hard-sphere mixtures (n = 4–8) with size ratios γ = 0.05, 0.1 and 0.2

n	m	$\widetilde{B}_n(m,n-m)$		
		$\gamma = 0.05$	$\gamma = 0.1$	$\gamma = 0.2$
4	1	$0.1774860579(1) \times 10^{-7}$	$0.11970915337(1) \times 10^{-5}$	$0.84807580776(1) \times 10^{-4}$
4	2	$0.428997205793(1) \times 10^{-4}$	$0.404088381846(10) \times 10^{-3}$	$0.43324295130(1) \times 10^{-2}$
4	3	$0.55363065926(1) \times 10^{-1}$	$0.819065784669(1) \times 10^{-1}$	0.15893702101(1)
4	4	2.636218	2.636218	2.636218
5	1	$0.22303(9) \times 10^{-11}$	$0.11808(2) \times 10^{-8}$	$0.64707(5) \times 10^{-6}$
5	2	$0.780(2) \times 10^{-8}$	$0.5512(2) \times 10^{-6}$	$0.42481(3) \times 10^{-4}$
5	3	$0.19493(7) \times 10^{-4}$	$0.19596(2) \times 10^{-3}$	$0.23274(1) \times 10^{-2}$
5	4	$0.26587(2) \times 10^{-1}$	$0.43514(2) \times 10^{-1}$	$0.95860(4) \times 10^{-1}$
5	5	2.12139(1)	2.12139(1)	2.12139(1)
6	1	$0.2321(3) \times 10^{-15}$	$0.9758(4) \times 10^{-12}$	$0.42145(10) \times 10^{-8}$
6	2	$0.1013(5) \times 10^{-11}$	$0.5484(5) \times 10^{-9}$	$0.32007(9) \times 10^{-6}$
6	3	$0.357(1) \times 10^{-8}$	$0.2622(2) \times 10^{-6}$	$0.21746(4) \times 10^{-4}$
6	4	$0.9167(6) \times 10^{-5}$	$0.9740(3) \times 10^{-4}$	$0.12596(2) \times 10^{-2}$
6	5	$0.13212(2) \times 10^{-1}$	$0.23497(3) \times 10^{-1}$	$0.56988(7) \times 10^{-1}$
6	6	1.56691(1)	1.56691(1)	1.56691(1)
7	1	$0.2200(8) \times 10^{-19}$	$0.737(1) \times 10^{-15}$	$0.2523(2) \times 10^{-10}$
7	2	$0.108(2) \times 10^{-15}$	$0.458(2) \times 10^{-12}$	$0.2092(2) \times 10^{-8}$
7	3	$0.43(2) \times 10^{-12}$	$0.259(2) \times 10^{-9}$	$0.1618(1) \times 10^{-6}$
7	4	$0.165(2) \times 10^{-8}$	$0.1262(3) \times 10^{-6}$	$0.11294(7) \times 10^{-4}$
7	5	$0.4397(7) \times 10^{-5}$	$0.4906(4) \times 10^{-4}$	$0.6857(3) \times 10^{-3}$
7	6	$0.6705(3) \times 10^{-2}$	$0.12757(6) \times 10^{-1}$	$0.3351(1) \times 10^{-1}$
7	7	1.09916(3)	1.09916(3)	1.09916(3)
8	1	$0.196(3) \times 10^{-23}$	$0.524(4) \times 10^{-18}$	$0.1447(6) \times 10^{-12}$
8	2	$0.134(7) \times 10^{-19}$	$0.357(6) \times 10^{-15}$	$0.1271(5) \times 10^{-10}$
8	3	$0.50(2) \times 10^{-16}$	$0.220(7) \times 10^{-12}$	$0.1076(5) \times 10^{-8}$
8	4	$0.27(4) \times 10^{-12}$	$0.124(3) \times 10^{-9}$	$0.847(3) \times 10^{-7}$
8	5	$0.81(3) \times 10^{-9}$	$0.625(5) \times 10^{-7}$	$0.607(2) \times 10^{-5}$
8	6	$0.215(1) \times 10^{-5}$	$0.2497(9) \times 10^{-4}$	$0.3805(8) \times 10^{-3}$
8	7	$0.3441(5) \times 10^{-2}$	$0.693(1) \times 10^{-2}$	$0.1968(5) \times 10^{-1}$
8	8	0.7394(8)	0.7394(8)	0.7394(8)

particles ($\gamma = 0$) there is no fluid–fluid separation[11]. In the case of other size ratios, once γ is fixed, the lower critical consolute point, ρ_c and x_c, should be found by determining the minimum of the curve obtained from the use of Eq. (*6*). However, due to the fact that the virial coefficients beyond the eighth are unknown, the exact expression for $f(\rho,x,\gamma)$ is also unknown. Hence, either one truncates the series in Eq. (*4*) after the term with $n = 8$ or uses an approximate compressibility factor Z_{app} (in which case $\beta f_{\text{ex}} \cong \int_0^{\rho} \left((Z_{\text{app}} - 1)/\rho'\right) \mathrm{d}\rho'$) to approximate the true Helmholtz free energy.

As already observed by Vlasov and Masters[8], and López de Haro and Tejero[12], truncation of a virial series (which is equivalent to truncating the series in Eq. (*4*)) can produce dramatic effects on the resulting critical behavior of the mixture. For instance, the well-known fact that the Boublík–Mansoori–Carnahan–Starling–Leland (BMCSL) equation of state[13,14] leads to no demixing should be contrasted with the result that a truncated virial expansion of the same equation of state leads to a critical consolute point. In this paper our aim is to gain some insight as to how to make the most profitable use of the available information on the virial coefficients of binary hard-sphere mixtures in the study of the demixing problem. For this purpose, we will initially assess several aspects of the effect of truncated virial expansions. First, we will truncate the density expansion in Eq. (*6*) up to $B_8(x,\gamma)$, compute the critical constants for the truncated series for three size ratios ($\gamma = 0.05$, 0.1 and 0.2) and compare with the results of truncating the virial series of the BMCSL equation of state and the approximation of Wheatley to the same order[15–20]. Since the difficulty in the computation of virial coefficients increases with the order beyond the eighth, as a second point we will consider the effect of keeping the first 'exact' eight virial coefficients and adding two extra ones $B_9(x,\gamma)$ and $B_{10}(x,\gamma)$ through either the BMCSL or the Wheatley approximation. As a third point in this regard, we will also extend the former calculation adding higher order virial coefficients up to $B_{30}(x,\gamma)$ as obtained from the BMCSL approximation.

As an alternative and complementary route to the preceding analysis, we will consider a different use of the available virial coefficients of the binary hard-sphere mixture. Starting from the BMCSL equation of state, we will assess, for the same values of γ as before, the effect on the demixing problem of replacing in this equation the k-th BMCSL virial coefficient by the 'exact' one (with $4 \le k \le 10$). In this case the ninth and tenth 'exact' virial coefficients will be those given by the Wheatley approximation while from the fourth to the eighth we will take the ones computed by Labík and Kolafa[9] whose values are reproduced in Table I. It is worth pointing out that for all three size ratios considered here, the differences between the 'exact' and the BMCSL virial coefficients are in the worst of cases of less than five per cent in the whole range of concentrations. As it will be shown below, the minor modifications to the BMCSL equation of state that these replacements imply are capable of leading to the presence of a critical consolute point in the system.

RESULTS

Table II presents the values of the critical constants as obtained from the truncated virial series by keeping N virial coefficients. Here we have introduced the critical packing fraction $\eta_c \equiv \frac{\pi}{6}\rho_c\sigma_1^3[x_c + (1-x_c)\gamma^3]$ and the reduced critical pressure $p_c^* \equiv \beta p_c\sigma_1^3$ to keep in line with previous work on this problem. The values in this table up to $N = 8$ complement the results obtained in ref.[12] for the three size ratios considered in this paper.

One can see from the results that for these size ratios, both the differences between the 'exact' values for the first eight virial coefficients[9] and the ones arising either from the BMCSL equation of state or from Wheatley's interpolation formula indeed have some influence on the location of the critical point. This influence seems to be small relatively speaking, with the BMCSL equation of state giving the worst performance. The addition of the higher virial coefficients for these size ratios, on the other hand, has a very strong influence, increasing substantially both the value of the reduced critical pressure and that of the critical packing fraction.

In Fig. 1 we illustrate the trend observed both for the reduced critical pressure and packing fraction as one adds one more 'exact' virial coefficient each step to the truncated virial series. No light is thrown by the present results either on the convergence of the series or on the character (either stable, metastable with respect to freezing or nonexistent) of demixing in these binary hard-sphere mixtures. However would the observed trend continue whenever higher virial coefficients become available, and so far this has proved to be the case, it would strongly suggest that demixing does not occur in these systems.

Once we have dealt with various aspects of truncated virial series, now we address the question of whether a different use of the available virial coefficients may also tell us something about the demixing problem. Let us recall that the BMCSL compressibility factor is given by

$$Z_{\mathrm{BMCSL}}(\eta) = \frac{1}{1-\eta} + \frac{\xi_1\xi_2}{\xi_3}\frac{3\eta}{(1-\eta)^2} + \frac{\xi_2^3}{\xi_3^2}\frac{\eta^2(3-\eta)}{(1-\eta)^3} \qquad (7)$$

TABLE II

Critical constants p_c^*, x_c, and η_c as obtained from the truncation of the virial series after the *N*-th virial coefficient for different γ values. The labels are as follows: E indicates exact results; L corresponds to taking the values of the approximate fourth to eighth virial coefficients from ref.[9]; the label BMCSL corresponds to the BMCSL equation of state; W refers to the approximate formula for virial coefficients by Wheatley[15] and the combinations L+BMCSL and L+W indicate that the first eight virial coefficients are those of ref.[9] while from the ninth to the *N*-th they are either taken from the BMCSL equation of state or from the interpolation formula of Wheatley, respectively

N	Label	$\gamma = 0.05$			$\gamma = 0.1$			$\gamma = 0.2$		
		p_c^*	x_c	η_c	p_c^*	x_c	η_c	p_c^*	x_c	η_c
2	E	23.23	0.0304	0.2759	19.55	0.0368	0.2741	17.33	0.0561	0.3386
3	E	50.84	0.0294	0.4284	38.68	0.0365	0.3941	28.48	0.0525	0.3814
4	L	95.20	0.0254	0.5295	67.16	0.0333	0.4760	44.64	0.0498	0.4317
5	L	154.5	0.0223	0.5981	102.7	0.0308	0.5340	64.05	0.0488	0.4762
6	L	227.5	0.0198	0.6453	144.1	0.0289	0.5758	86.28	0.0482	0.5124
7	L	313.7	0.0179	0.6789	191.3	0.0272	0.6068	111.2	0.0473	0.5413
8	L	412.4	0.0162	0.7034	243.4	0.0255	0.6300	138.5	0.0463	0.5648
8	BMCSL	417.8	0.0156	0.7002	248.4	0.0246	0.6283	144.0	0.0465	0.5726
8	W	409.9	0.0168	0.7080	242.9	0.0274	0.6400	140.5	0.0517	0.5822
10	L+BMCSL	656.0	0.0133	0.7345	366.6	0.0225	0.6637	204.4	0.0439	0.6032
10	L+W	646.1	0.0137	0.7378	363.3	0.0233	0.6670	202.1	0.0455	0.6063
30	L+BMCSL	5692.4	0.0061	0.8515	3036.3	0.0176	0.8275	1861.5	0.0560	0.8160

where, for ease of presentation, we have written it in terms of the packing fraction $\eta \equiv \frac{\pi}{6}\rho\sigma_1^3[x+(1-x)\gamma^3]$ and the moments $\xi_n = \sigma_1^n[x+(1-x)\gamma^n]$ ($n = 1$, 2, 3) instead of in terms of ρ, x and γ which will nevertheless remain as our chosen thermodynamic variables. In turn, the excess Helmholtz free energy per particle corresponding to the BMCSL equation of state reads

$$\beta f_{\text{ex}}^{\text{BMCSL}} = -\ln(1-\eta) + \frac{\xi_1\xi_2}{\xi_3}\frac{3\eta}{1-\eta} + \frac{\xi_2^3}{\xi_3^2}\left[\frac{\eta}{(1-\eta)^2} + \ln(1-\eta)\right] \tag{8}$$

so that the approximate Helmholtz free energy per particle used in connection with Eq. (*6*) reads

$$\beta f_{\text{app}} = \beta f_{\text{id}} + \beta f_{\text{ex}}^{\text{BMCSL}} + \sum_{n=3}^{n_{\max}} \frac{1}{n}(B_{n+1} - B_{n+1}^{\text{BMCSL}})\rho^n \tag{9}$$

$n_{\max}$ being successively 3, 4, 5, 6, 7, 8 and 9. In Table II, we present the critical constants computed using the Helmholtz free energy per particle given in Eq. (*9*). It must be pointed out here that, contrary to what happens in the case of truncated virial expansions, the solution of Eq. (*6*) in this instance is not single valued. However, we have checked that the one we have

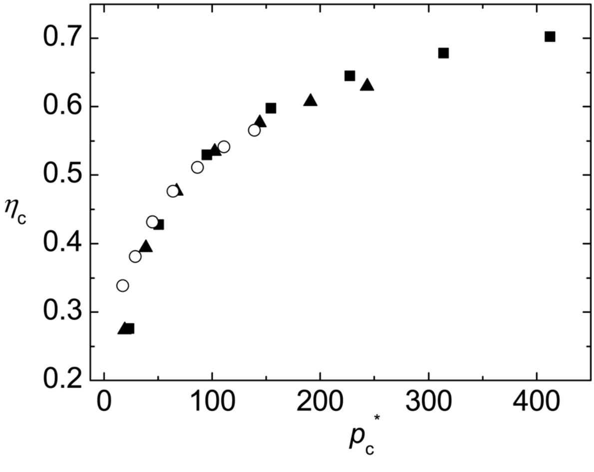

FIG. 1
Critical packing fraction η_c vs reduced critical pressure p_c^* in binary hard-sphere mixtures of different size ratios γ as computed from truncated virial expansions keeping successively 2–8 'exact' virial coefficients. γ = 0.05 (■), 0.1 (▲), 0.2 (○)

TABLE III

Critical constants p_c^*, x_c, and η_c for $\gamma = 0.05$, 0.1 and 0.2 as obtained from the replacement of k 'exact' virial coefficients from $k = 4$ up to $k = 10$ in the BMCSL equation of state

k	$\gamma = 0.05$			$\gamma = 0.1$			$\gamma = 0.2$		
	p_c^*	x_c	η_c	p_c^*	x_c	η_c	p_c^*	x_c	η_c
4	3743.8	0.0001	0.2467	–	–	–	–	–	–
5	3364.8	0.0003	0.3095	1419.0	0.0008	0.3670	–	–	–
6	3501.4	0.0004	0.3727	1413.4	0.0012	0.4041	1624.7	0.0028	0.5674
7	3867.8	0.0005	0.4249	1489.6	0.0014	0.4281	1270.0	0.0038	0.5573
8	4104.9	0.0005	0.4574	1522.1	0.0014	0.4331	1225.5	0.0050	0.5730
9	4486.1	0.0006	0.4861	1690.4	0.0014	0.4454	1337.6	0.0059	0.5946
10	4724.7	0.0007	0.5152	1852.7	0.0013	0.4477	1458.9	0.0070	0.6176

chosen corresponds to the minimum of the free energy. What one immediately notices from Table III is that for the smallest size ratio that we have considered in this paper ($\gamma = 0.05$) already the replacement of the 'exact' fourth virial coefficient in the BMCSL equation of state produces demixing. This has been confirmed independently by Kolafa[21] using his NSK software package. For the other two size ratios we also get demixing, but it requires the replacement of both the fourth and the fifth virial coefficients in the case of $\gamma = 0.1$ and of the fourth, fifth and sixth virial coefficients in the case of $\gamma = 0.2$. All the critical constants increase their value as one replaces more 'exact' virial coefficients and the growth seems to be diminishing each time, but no convergence may be ascertained at this stage.

CONCLUSIONS

The results of the previous section deserve further consideration. To begin with, we find that the location of the critical consolute point of a binary hard-sphere fluid mixture as derived from the truncated virial series is indeed sensitive to small variations in the values of the first eight virial coefficients, some of which have to be obtained numerically and are therefore subject to errors. This might explain why, as exhibited in ref.[12], different equations of state that are reasonably accurate when compared to simulation data, but differ in their estimates for $B_n(x,\gamma)$ for $n \geq 4$, lead to quite different predictions for the critical constants. While our results based on the truncated virial series suggest that eventually demixing will not occur for the size ratios we have considered, a deeper assessment is precluded at this stage and in this respect at least must await the determination of still higher virial coefficients or the knowledge of the convergence properties of the virial series to either confirm or reject this suggestion.

As for the replacement of BMCSL virial coefficients with 'exact' ones, it is clear that a minor correction to this very accurate equation of state can produce a radically different critical behavior. Unfortunately, the rate of convergence is rather slow, so one cannot conclude anything solid on the grounds of these results alone. However, the extremely high values of the reduced critical pressure that we have obtained are probably an indication that if demixing occurs in these mixtures it will be probably metastable with respect to a freezing transition. However, further work is required again before the problem gets settled.

Two of us (A. Malijevský and S. Labík) would like to thank the Ministry of Education, Youth and Sports of the Czech Republic for financial support through Grants No. LC512 and No. 604 613 7307.

M. López de Haro acknowledges the financial support of Ministerio de Educación y Ciencia (Spain) through Grant No. FIS200760977 (partially financed by FEDER funds) and by the Junta de Extremadura through Grant No. GRU09038.

REFERENCES AND NOTES

1. Kammerlingh Onnes H.: *Commun. Phys. Lab. Univ. Leiden* **1901**, *71*, 3.
2. Kihara T.: *Rev. Mod. Phys.* **1955**, *27*, 412.
3. Kihara T., Miyoshi K.: *J. Stat. Phys.* **1975**, *13*, 337.
4. Saija F., Fiumara G., Giaquinta P. V.: *Mol. Phys.* **1996**, *87*, 991.
5. Enciso E., Almarza N. G., Calzas D. S., González M. A.: *Mol. Phys.* **1997**, *92*, 173.
6. Enciso E., Almarza N. G., González M. A., Bermejo F. J.: *Phys. Rev. E* **1998**, *57*, 4486.
7. Wheatley R. J., Saija F., Giaquinta P. V.: *Mol. Phys.* **1998**, *94*, 877.
8. Vlasov A. Yu., Masters A. J.: *Fluid Phase Equilib.* **2003**, *212*, 183.
9. Labík S., Kolafa J.: *Mol. Phys.*, submitted.
10. Masters A. J.: *J. Phys.: Condens. Matter* **2008**, *20*, 283102.
11. For the latter system this was proved by Vega C.: *J. Chem. Phys.* **1998**, *108*, 3074.
12. López de Haro M., Tejero C. F.: *J. Chem. Phys.* **2004**, *121*, 6918.
13. Boublík T.: *J. Chem. Phys.* **1970**, *53*, 471.
14. Mansoori G. A., Carnahan N. F., Starling K. F., Leland T. W.: *J. Chem. Phys.* **1971**, *54*, 1523.
15. a) Wheatley R. J.: *J. Chem. Phys.* **1999**, *111*, 5455; see also b) Barrio C., Solana J. R. in: *Theory and Simulation of Hard-Sphere Fluids and Related Systems, Lecture Notes in Physics* (A. Mulero, Ed.), Vol. 753, p. 133. Springer, Berlin, Heidelberg 2008.
16. The formulae by Wheatley require as input the virial coefficients of a pure hard-sphere fluid. Here we have used the values reported by van Rensburg[17], Labík[18] and Clisby and McCoy[19,20].
17. van Rensburg E. J.: *J. Phys. A: Math. Gen.* **1993**, *26*, 4805.
18. Labík S., Kolafa J., Malijevský A.: *Phys. Rev. E* **2005**, *71*, 021105.
19. Clisby N., McCoy B. M.: *Pramana* **2005**, *64*, 775.
20. Clisby N., McCoy B. M.: *J. Stat. Phys.* **2006**, *122*, 15.
21. Kolafa J.: Private communication. We are grateful to Prof. J. Kolafa for checking out our result. The software NSK is a graphically-oriented software for calculating phase equilibrium phenomena of binary mixtures described by classical equations of state. It is accessible through Prof. Kolafa's personal webpage: http://www.icpf.cas.cz/jiri/