Erratum: Virial Approach to Hard-Sphere Demixing [Phys. Rev. Lett. 79, 1881 (1997)]

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In our Letter, we argued that the negative values found in [1] for the fifth virial coefficient (B_5) of a binary hard-sphere mixture could provide an alternative explanation for hard-sphere demixing. Meanwhile it has been shown [2] that the values of [1] for B_5 are in error (those for B_4 remaining correct), while the revised B_5 values are no longer negative. We now find that, using the new B_5 values of [2] and computing the free energy of the mixture as a perturbation to the Carnahan-Starling (CS) result as in our Letter, there is no spinodal instability. Physically this is fairly obvious since by changing the sign of B_5 the effective attraction of our Letter has been turned into a repulsion. Note also that, with the negative B_5 values of [1], our perturbation approach was forced upon us if we wanted to avoid negative pressures at high densities. At present, with the positive B_5 values of [2], such a perturbative approach is no longer necessary and we can use instead the rescaled virial expansion of [3] which should yield better results for high densities. Within the rescaled virial expansion of [3], the compressibility factor Z is approximated by (see our Letter for the notation)

$$Z_n = \left\{\sum_{i=0}^{n-1} c_i(\xi_3)^i\right\} \Big/ (1 - \xi_3)^3, \tag{1}$$

with the n coefficients, $c_i = c_i(x_1;\gamma)$, fixed in such a manner that Z_n will reproduce the first n virial coefficients exactly. In doing so, we find [4] that Z_3, which is comparable to the CS approximation, does show no spinodal instability, whereas Z_4 (using the B_4 data of [1]) and Z_5 (using, moreover, the B_5 data of [2]) do lead to a spinodal instability as shown in the figure. This reinforces again the idea that the presence or absence of demixing in this system hinges on very small changes with respect to the CS approximation. The new spinodals obtained from Eq. (1) correspond to much higher η_2 values than in our Letter. At such high densities the demixing transition can still be pre-empted by other phase transitions as shown in our Letter. Note, however, that, when n of (1) increases above the CS level ($n > 3$) or γ decreases, these spinodals rapidly move towards the low η_2 region (see Fig. 1). Consequently, Eq. (1) should provide a description of the binary hard-sphere fluid which remains meaningful for all partial densities and γ values and which describes a thermodynamically stable demixing for sufficiently low values of γ [4].

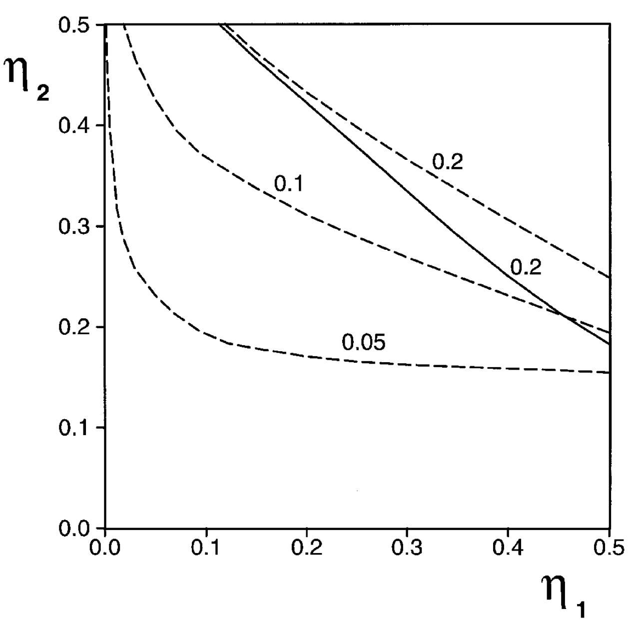

FIG. 1. The spinodals of binary hard-sphere mixtures of diameter ratio $\gamma = \sigma_2/\sigma_1$ in the η_1-η_2 plane, with $\eta_i = (\pi/6)\sigma_i^3\rho_i$ being the partial packing fraction of species i ($i = 1, 2$), as obtained from Eq. (1) and the data for B_4 given in [1] together with the data for B_5 at $\gamma = 0.2$ given in [2]. The spinodals obtained from Z_4 [see Eq. (1)] correspond to the dashed lines (for the value of γ indicated), the spinodal obtained from Z_5 for $\gamma = 0.2$ to the full line.

[1] F. Saija, G. Fuimara, and P. V. Giaquinta, Mol. Phys. **87**, 991 (1996); Mol. Phys. **89**, 1181 (1996).
[2] E. Enciso, N. G. Almarza, D. S. Calzas, and M. A. Gonzalez, Mol. Phys. **92**, 173 (1997); R. J. Wheatley, F. Saija, and P. V. Giaquinta (to be published).
[3] M. Baus and J. L. Colot, Phys. Rev. A **36**, 3912 (1987); J. L. Barrat, H. Xu, J. P. Hansen, and M. Baus, J. Phys. C **21**, 3165 (1988).
[4] T. Coussaert and M. Baus (to be published).