

DEMIXING TRANSITION IN HARD-SPHERE MIXTURES

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OUTLINE

I. Introduction

II. Equation of state for hard-sphere mixtures

III. Demixing in binary mixtures of hard hyperspheres

IV. Concluding remarks

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I. Introduction

I.1. Entropy-driven transitions

- The second law of thermodynamics implies that a system that is not isolated tends to minimize its Helmholtz free energy

$$A = E - TS.$$

At constant temperature T , a system can lower its free energy either by *decreasing* its internal energy E or by *increasing* its entropy S .

- As a consequence, a phase transition from a *disordered* to a more *ordered* phase can only take place if the loss in entropy is compensated by the decrease in internal energy.

If the internal energy of the system depends *only* on the temperature and *not* on the density (as in **hard-core** systems), then a transition

Disordered state (high entropy) $\xrightarrow{\Delta S < 0}$ **Ordered state (low entropy)**

is forbidden.

- Does that mean that the freezing transition

Fluid \longrightarrow **Crystal**

is not possible for hard spheres?

- However, the freezing transition in hard-sphere systems can be observed in molecular dynamics simulations.

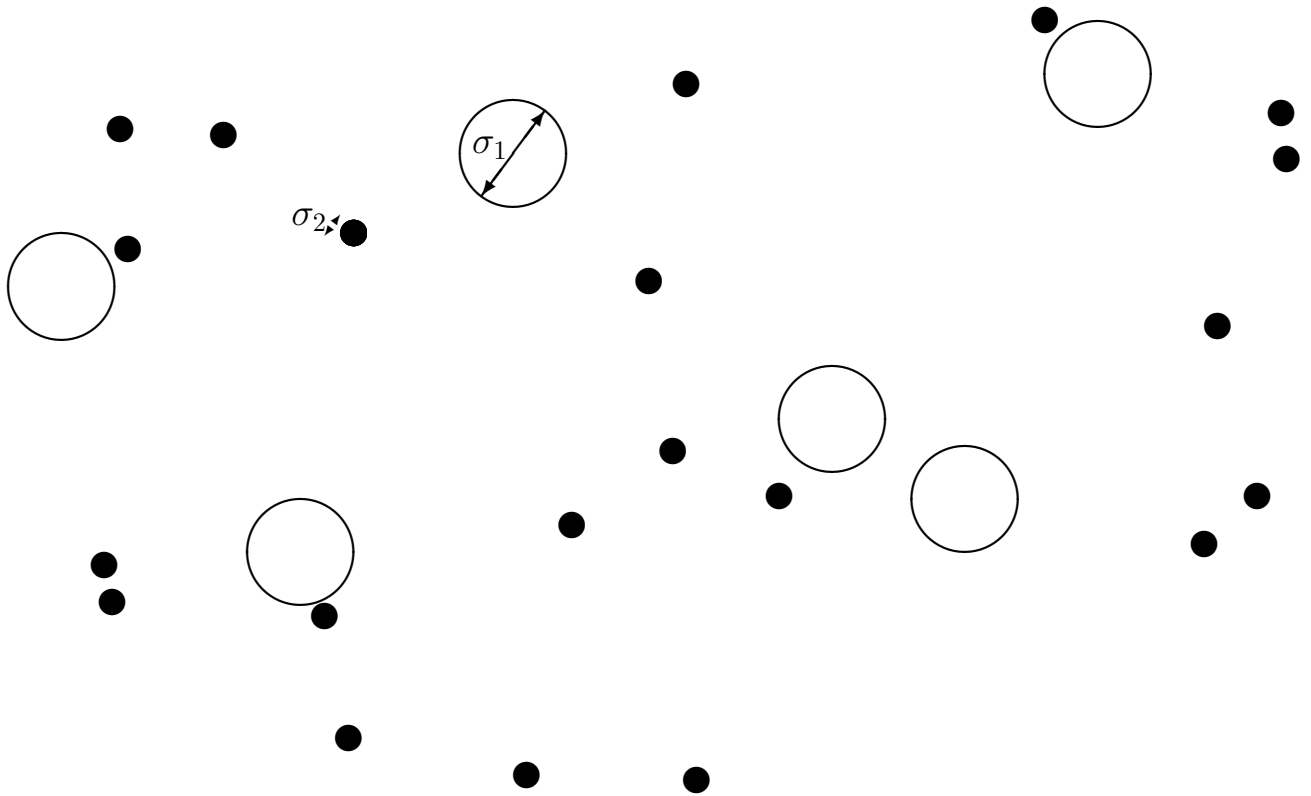
TABLE I. Volume fractions at close packing (η_{cp}) and at freezing (η_{f}).

	2D	3D	4D	5D
η_{cp}	0.907	0.740	0.617	0.465
$\eta_{\text{f}}/\eta_{\text{cp}}$	0.76	0.67	0.50	0.42

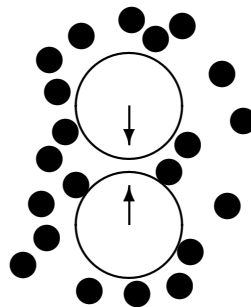
- The solution to the paradox lies in the fact that our intuitive concept of “order–disorder” does not necessarily coincide with the statistical one.
- The crystal *can* have a higher entropy than the fluid (at the same density and temperature). The entropy of the crystal *decreases* with respect to that of the fluid because the density is no longer uniform, but on the other hand it *increases* because the free-volume per particle is larger in the crystal than in the fluid. At sufficiently large densities ($\eta > \eta_{\text{f}}$), the second effect dominates and the equilibrium state is that of a crystal.
- The freezing transition in hard spheres (from “disorder” to “order”, intuitively speaking) is an example of *entropy-driven* transitions (in contrast to *energy-driven* ordering transitions).
- Another example of entropy-driven transition is the **isotropic** \rightarrow **nematic** transition in a three-dimensional system of *thin* hard rods. Here, the loss in orientational entropy can be compensated (at large enough densities) by the gain in translational entropy.

I.2. Demixing

- Could a fluid binary mixture of (additive) hard spheres separate into two phases of different composition due to entropic effects?



- The mechanism usually invoked to expect *demixing* is *osmotic depletion*: If the mole fraction x_1 of the large spheres and the size ratio $\alpha \equiv \sigma_2/\sigma_1$ are small enough, the small spheres can induce an effective *attraction* between the large spheres.



- In addition to its intrinsic interest, the study of the demixing transition (or of its existence) is relevant to the interpretation of experimental data on sterically stabilized colloidal suspensions, in which the interactions between the colloidal particles mimic those of a hard sphere system.
- Given a size ratio $\alpha \equiv \sigma_2/\sigma_1$, the equilibrium state of a binary mixture is characterized by the number densities $\rho_1 = N_1/V$, $\rho_2 = N_2/V$ [or, equivalently, by the total volume fraction $\eta = \eta_1 + \eta_2$ and the mole fraction $x_1 = N_1/(N_1 + N_2)$].
- The free energy of the mixture is

$$A(V, T, N_1, N_2) = V k_B T a(\rho_1, \rho_2), \quad (k_B T = 1).$$

– Pressure: $p = -\frac{\partial A}{\partial V} = -a + \sum_i \rho_i \frac{\partial a}{\partial \rho_i}$,

– Chemical potentials: $\mu_i = \frac{\partial A}{\partial N_i} = \frac{\partial a}{\partial \rho_i}$.

- If the equation of state of the mixture is known,

$$p = \rho k_B T Z_m(\eta, x_1),$$

the free energy per unit volume can be reconstructed from

$$a = \rho \left\{ -1 + \sum_i x_i \ln(\rho_i \lambda_i^d) + \int_0^\eta \frac{d\eta'}{\eta'} [Z_m(\eta', x_1) - 1] \right\},$$

$\lambda_i =$ (thermal) de Broglie wavelength of species i ,

$d =$ dimensionality of the system.

- The binary mixture becomes *unstable* with respect to demixing if the free energy per unit volume $a(\rho_1, \rho_2)$ ceases to be a convex function.

- A sufficient condition for *spinodal instability* is

$$a_{11}a_{22} - a_{12}^2 = 0 \implies \text{spinodal line,} \quad a_{ij} \equiv \frac{\partial^2 a}{\partial \rho_i \partial \rho_j}.$$

- If a spinodal instability exists, this implies that the binary mixture will phase separate into two phases (A and B) of different composition. The *coexistence* conditions for the two phases are

$$\left. \begin{aligned} p(\rho_1^A, \rho_2^A) &= p(\rho_1^B, \rho_2^B) \\ \mu_1(\rho_1^A, \rho_2^A) &= \mu_1(\rho_1^B, \rho_2^B) \\ \mu_2(\rho_1^A, \rho_2^A) &= \mu_2(\rho_1^B, \rho_2^B) \end{aligned} \right\} \implies \text{binodal line.}$$

I.3. A brief historical perspective

- Computer simulations (molecular dynamics or Monte Carlo) are not determinant in elucidating the existence or not of the demixing transition because of severe ergodicity problems, even for a ratio $\alpha = 1/3$.
- In 1964, Lebowitz and Rowlinson proved that, within the Percus-Yevick approximation (which is exactly solvable), hard spheres ($d = 3$) of arbitrary size ratio mix in all proportions in the fluid phase.
- Moreover, the extremely accurate Boublík-Mansoori-Carnahan-Starling-Leland (1970) equation of state ($d = 3$) also predicts no demixing.
- The general belief was that mixtures of hard spheres never phase separate, until Biben and Hansen (1991), by numerically solving the Ornstein-Zernike equation with the Rogers-Young closure, gave strong *evidence* of phase separation for $\alpha \lesssim 0.2$.
- Frenkel and Louis (1992) found a demixing transition in a simple lattice model of binary hard-core mixture ($d = 2$). This model can be mapped onto a one-component lattice gas with attractive nearest neighbor interactions (Ising model).

Fig. 1 of Frenkel-Louis' paper

- By using a density functional theory, Cuesta (1996) found spinodal instability in a binary mixture of *parallel hard cubes* ($d = 3$) with $\alpha \lesssim 0.1$.
- Coussaert and Baus (1998) proposed an equation of state for the mixture ($d = 3$) that incorporated the *exact* first five virial coefficients (B_4 : 1996, B_5 : 1998). From there, they obtained demixing, but at such high pressures ($p\sigma_1^3 \sim 10^3$), that the fluid–fluid transition was metastable relative to freezing of the mixture into a partially ordered solid phase.

Fig. 3 of Coussaert-Baus' paper

I.4. Our approach

- In order to see the entropy-driven demixing transition in action, it seems that one has to use very sophisticated theories (integral equations for the pair correlation functions, effective one-component fluid theories with complicated depletion interactions, high-order virial coefficients, ...) or very artificial models (lattice models, parallel hard cubes, ...).
- It would be desirable to have systems in which the entropic effects responsible for a fluid–fluid transition were so “exaggerated”, that any reasonably simple equation of state should be able to predict demixing. From this approach, we could also learn some “regularities” of the transition that might be overlooked in treatments dealing with the elusive case of (three-dimensional) hard spheres.
- What is “closer” to a system of hard spheres: a system of hard cubes or a system of hard *hyperspheres*?
- H. L. Frisch and J. Percus, *High dimensionality as an organizing device for classical fluids*, Phys. Rev. E **60**, 2942 (1999):

[In high spatial dimensionality], fluctuations are reduced by high effective coordination number, so, e.g., interfaces tend to be even sharper, and *one generally expects clean caricatures of any thermodynamic phenomenology that indeed extends to higher dimensionality.*

II. Equation of state for hard-sphere mixtures

II.1 From a one-component fluid to a mixture. A simple recipe

- Given a multi-component hard-sphere system (in d dimensions) of diameters $\{\sigma_i\}$, mole fractions $\{x_i\}$, and packing fraction η , the compressibility factor $Z_m \equiv p/\rho k_B T$ is related to the contact values of the pair correlation functions, $g_{ij}^m(\sigma_{ij})$, by

$$Z^m(\eta, \{x_i\}) = 1 + 2^{d-1} \eta \sum_{i,j} x_i x_j \frac{\sigma_{ij}^d}{\langle \sigma^d \rangle} g_{ij}^m(\sigma_{ij}), \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \langle \sigma^n \rangle \equiv \sum_i x_i \sigma_i^n.$$

- Suppose we have a good equation of state $Z_s(\eta)$ for the single component case. Can we infer from this a “good” equation of state for the multi-component system? $Z_s(\eta) \Rightarrow Z_m(\eta, \{x_i\})$
- van der Waals one-fluid theory:

$$Z_m(\eta, \{x_i\}) = Z_s(\eta_{\text{eff}}(\{x_i\})), \quad \eta_{\text{eff}}(\{x_i\}) = \eta \sum_{i,j} x_i x_j \frac{\sigma_{ij}^d}{\langle \sigma^d \rangle}.$$

- However, this is inconsistent with the exact property (binary case)

$$Z_m(\eta, x_1) \xrightarrow{\sigma_2/\sigma_1 \rightarrow 0} x_1 Z_s(\eta) + \frac{x_2}{1 - \eta}.$$

- Our proposal [A.S., S. B. Yuste, M. López de Haro, Mol. Phys. **96**, 1 (1999)] consists of

1. $g_{ij}^m(\sigma_{ij})$ depends on $\{\sigma_k\}$ and $\{x_k\}$ only through the parameter

$$\gamma_{ij} \equiv \frac{\sigma_i \sigma_j \langle \sigma^{d-1} \rangle}{\sigma_{ij} \langle \sigma^d \rangle},$$

2. $g_{ij}^m(\sigma_{ij})$ is a *linear* function of γ_{ij} (Percus-Yevick approximation in 3D):

$$g_{ij}^m(\sigma_{ij}) = \frac{1}{1-\eta} + \left[g^s(\sigma) - \frac{1}{1-\eta} \right] \gamma_{ij}.$$

- Consequently,

$$Z_m(\eta, \{x_i\}) = 1 + [Z_s(\eta) - 1] 2^{1-d} \Delta_0(\{x_i\}) + \frac{\eta}{1-\eta} \left[1 - \Delta_0(\{x_i\}) + \frac{1}{2} \Delta_1(\{x_i\}) \right],$$

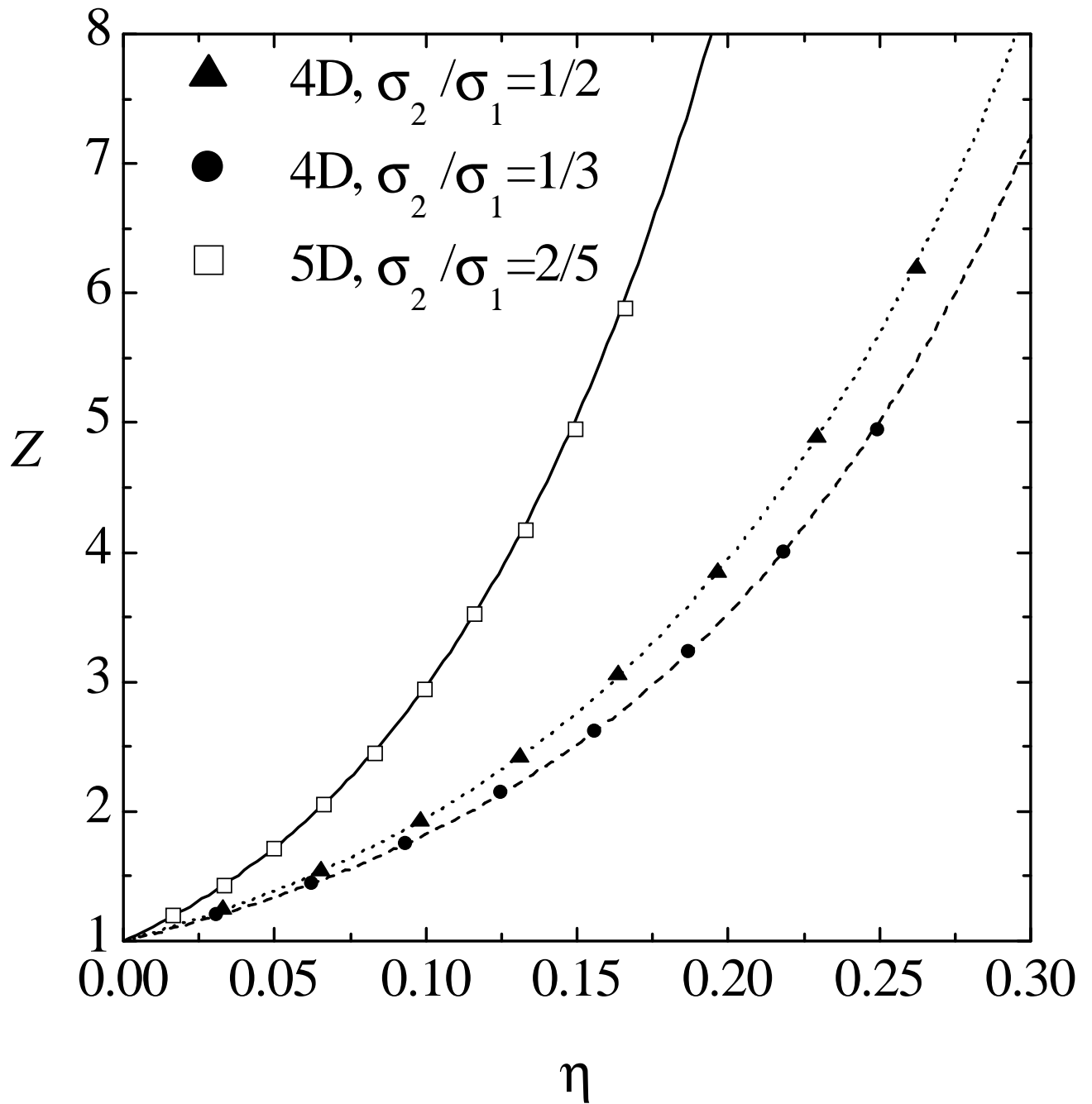
$$\Delta_n(\{x_i\}) \equiv \frac{\langle \sigma^{d+n-1} \rangle}{\langle \sigma^d \rangle^2} \sum_{m=n}^{d-1} \frac{(d+n-1)!}{m!(d+n-1-m)!} \langle \sigma^{m-n+1} \rangle \langle \sigma^{d-m} \rangle.$$

- How good is the above prescription?
 - It is consistent with the exact property in the limit $\sigma_2/\sigma_1 \rightarrow 0$.
 - In 1D, it yields the exact result $Z_m(\eta, \{x_i\}) = Z_s(\eta)$.
 - In 2D and 3D, it gives excellent results when one takes any accurate equation of state $Z_s(\eta)$ for the single component case.
- What about 4D and 5D?

II.2 Comparison with numerical and simulation results for 4D and 5D

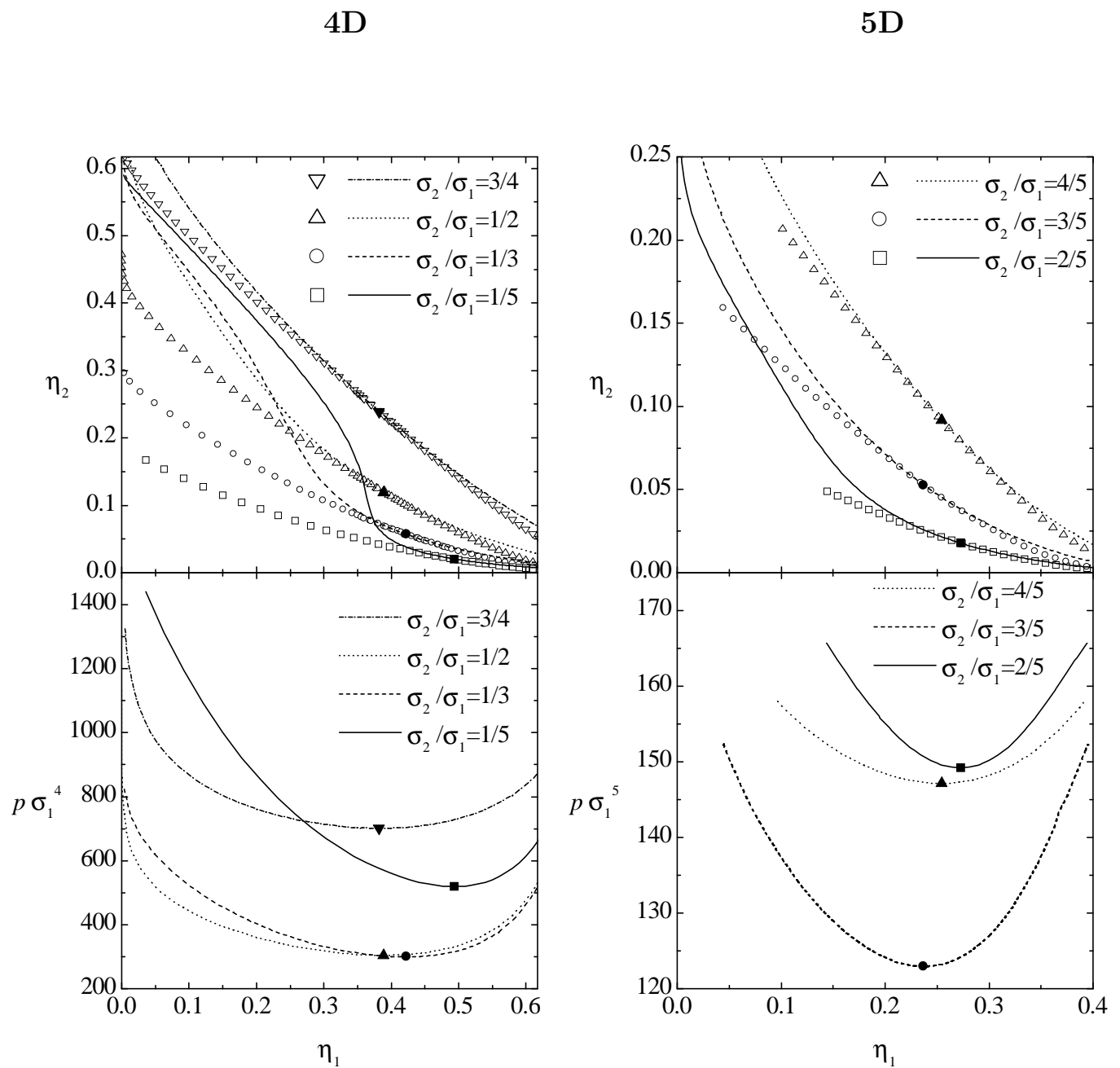
- Third and fourth virial coefficients for $d = 4$ and $\sigma_2/\sigma_1 = 1/2$ [E. Enciso, N. G. Almarza, M. A. González, and F. J. Bermejo, submitted to Phys. Rev. E]:

- Compressibility factor for three equimolar mixtures in 4D and 5D [M. González, J. Alejandro, and M. López de Haro, submitted to J. Chem. Phys.]:



III. Demixing in binary mixtures of hard hyperspheres

- Spinodal curves (upper panels: lines) and binodal curves (upper panels: symbols; lower panels: lines). The filled symbols are the critical consolute points [S. B. Yuste, A. S., and M. López de Haro, Europhys. Lett. (in press)].



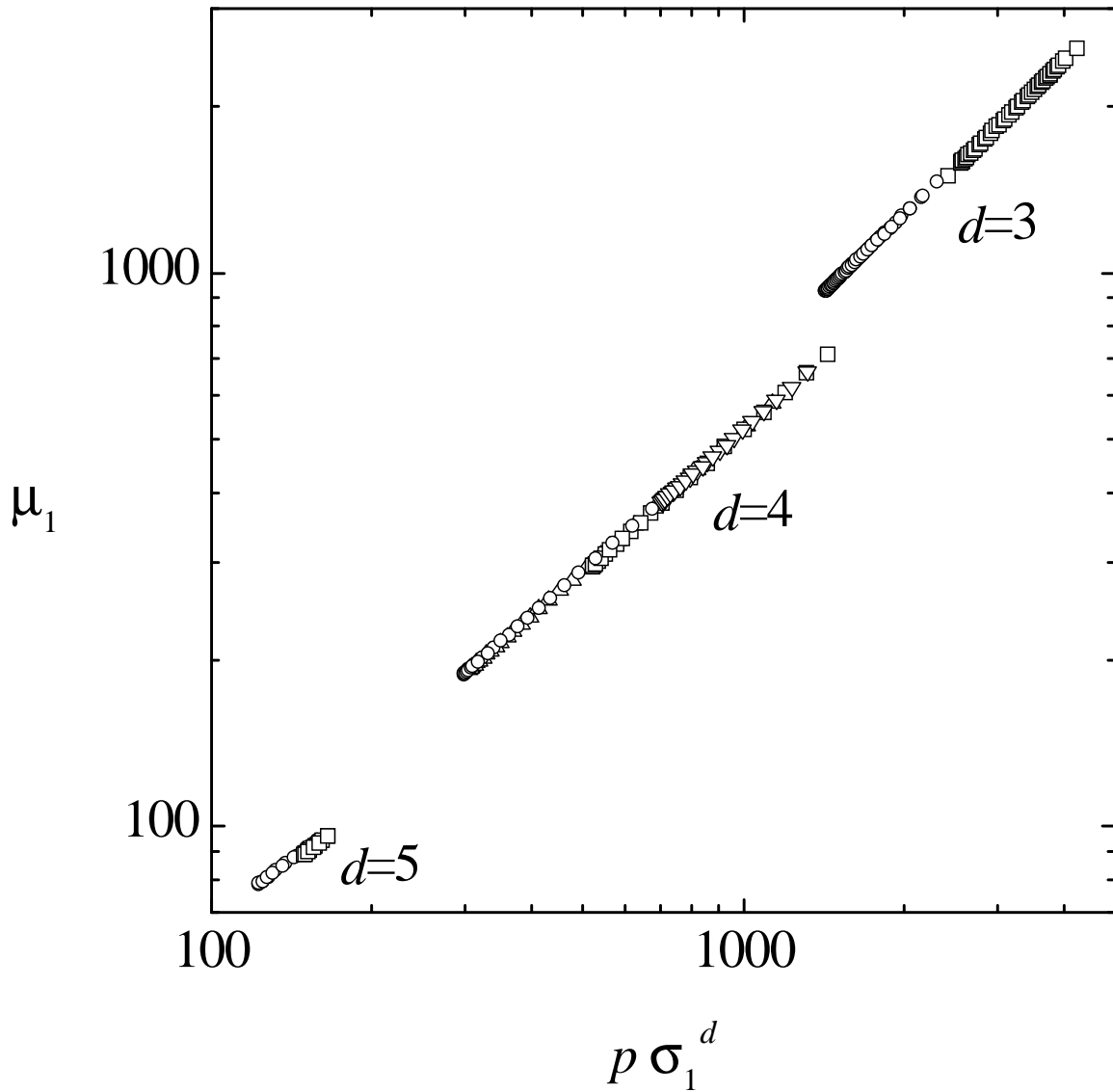
- Some observations

- Our simple equation of state leads to an analytical expression for the free energy of the mixture in 4D and 5D. From here, we find spinodal instability for any size ratio.
- The pressure of the critical point does not decrease monotonically as the asymmetry increases.

	3D	4D	5D
$p_c \sigma_1^d _{\min}$	$\sim 10^3$	≈ 300	≈ 120
$\alpha _{\min}$	≈ 0.3	≈ 0.4	≈ 0.6

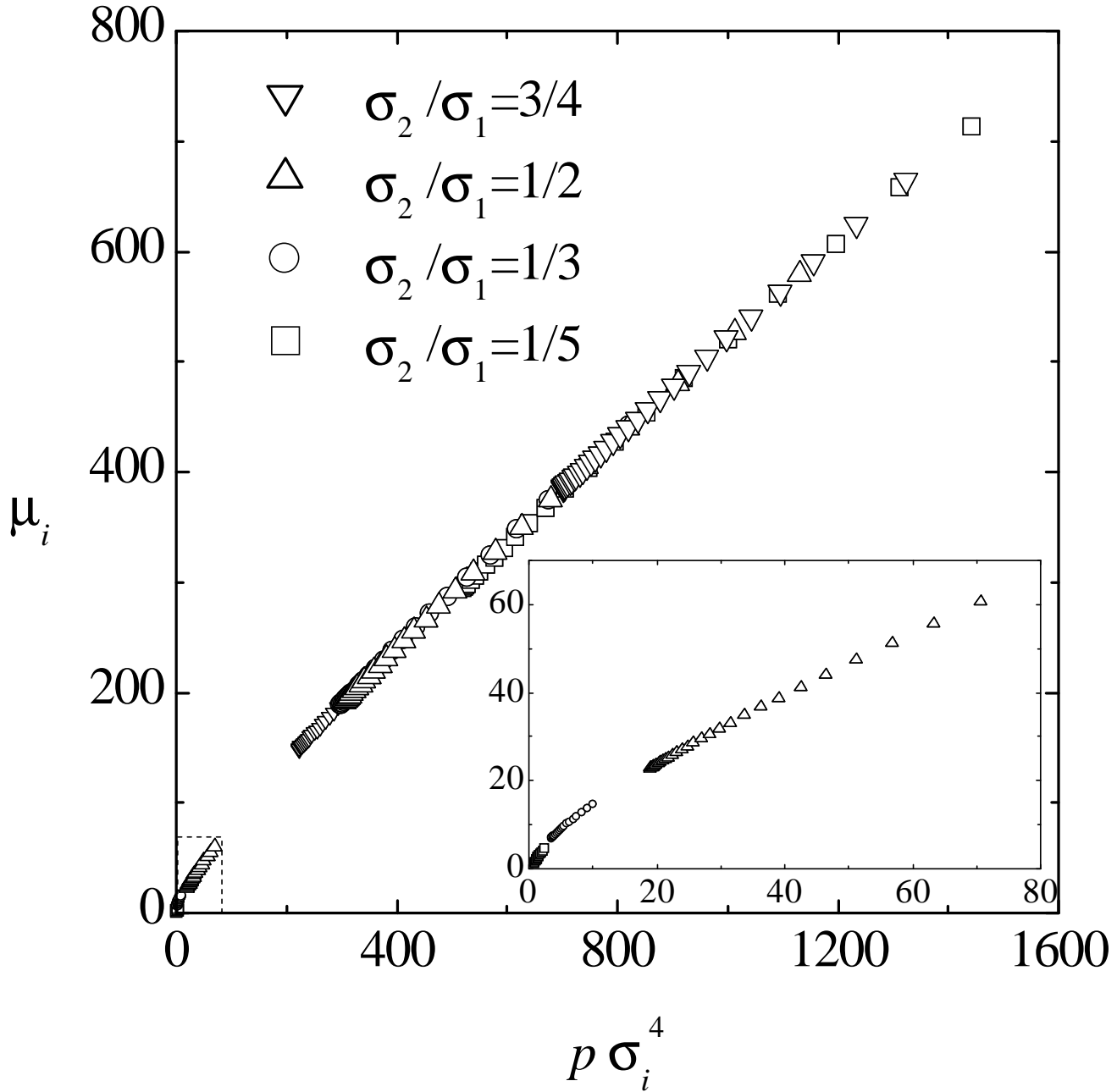
- There is a remarkable similarity between the binodal curves represented in the $p\sigma_i^d-\eta_1$ and in the $\mu_i-\eta_1$ planes (with $\lambda_i = \sigma_i$). If we eliminate the parameter η_1 , how do the binodal curves look in the $\mu_i-p\sigma_i^d$ plane?

- Binodal curves in the μ_1 vs $p\sigma_1^d$ plane for $d = 3$ (circles: $\sigma_2/\sigma_1 = 1/5$, squares: $\sigma_2/\sigma_1 = 1/10$), $d = 4$ and $d = 5$. Note that for each size ratio the binodal curve is restricted to $p \geq p_c$.



- For a given dimensionality, the binodal lines corresponding to different size ratios seem to lie on a common line: “universality” property!

- Binodal curves in the μ_i vs $p\sigma_i^4$ plane for a 4D system.



- The curves $\mu_1 = F_1(p\sigma_1^d)$ and $\mu_2 = F_2(p\sigma_2^d)$ seem to probe different different regions of the plane but otherwise overlap reasonably well.

IV. Concluding remarks

- The geometrical effects of osmotic depletion become more important as the dimensionality increases in much the same way that in 3D they are more important for parallel hard cubes than for hard spheres.
- The universal behavior of the binodal lines is not an artifact of our equation of state or of a high dimensionality. It reveals the existence of a certain *geometrical* regularity that might characterize the entropy driven transitions. One could then state that all binary hard (hyper)sphere mixtures belong to the same *universality class* since, for fixed d , there are some properties such as the binodal curves in which the asymmetry is to a certain extent irrelevant.
- We also find an upper quasi-universality: for the range of common values, the universal curve in 3D lies close but somewhat above the universal curve in 4D, and in turn this latter lies above the one in 5D. All three curves approach straight lines of slopes 0.44 ($d = 3$), 0.45 ($d = 4$), and 0.43 ($d = 5$) in the region of their higher values.
- It is likely that the demixing fluid–fluid transition in 4D and 5D is metastable with respect to a fluid–solid transition. However, since the pressure at the freezing transition for the single component fluid does not change appreciably with the dimensionality, while the demixing critical pressure decreases as d increases, there might be a threshold dimensionality d_{th} above which the fluid–fluid transition in hard hypersphere mixtures becomes stable.