Journal of Statistical Physics, Vol. 63, Nos. 3/4, 1991

Binary Nonadditive Hard-Sphere Mixtures at High Dimension

H.-O. Carmesin,[1,2] H. L. Frisch,[2,4] and J. K. Percus[1,3]

Received August 29, 1990; final December 3, 1990

At high spatial dimension, a suitably scaled classical system of interacting particles truncates at second virial terms. A binary mixture of nonadditive hard spheres with sufficiently repulsive interaction between unlike particles decomposes at sufficiently high density into two coexisting phases. The region around the critical density behaves classically.

KEY WORDS: Hard-sphere mixture; high dimensionality; phase separation; regular binary mixture.

1. INTRODUCTION

Understanding of the qualitative properties of statistical mechanical systems has traditionally been achieved by examination of suitable models which, to be sure, distort the microscopic structures of the system of interest, if indeed they pretend to represent it at all. One of the most useful elementary models in classical fluid equilibrium is that based upon the mean field approximation, although some aspects, such as nonclassical critical exponents, are totally missed in such models unless they are extrapolated from model hierarchies. While the idea of long-range force is often built into the concept of mean field, it has been known for a long time that increasing the number of internal degrees of freedom which enter into particle–particle coupling also leads to a mean field result by reducing relative fluctuations, and somewhat more recently that an increase in

[1] Courant Institute of Mathematical Sciences, New York University, New York, New York 10012.
[2] Chemistry Department, SUNY at Albany, New York, New York 12222.
[3] Universität Bremen, Postfach 330 440, 2800 Bremen 33, Germany.
[4] Physics Department, New York University, New York, New York 10003.

0022-4715/91/0500-0791$06.50/0

spatial dimensionality D can serve the same purpose.[1,2] Thus, asymptotically infinite spatial dimensionality maintains a considerable degree of phenomenology; we have recently shown[3] that the Onsager approximation for the spherocylinder nematic transition becomes exact in this limit. In the present note, we want to observe that, under suitable scaling, this type of limit gives rise to what is perhaps the most elementary model of phase separation, that associated with a hard-sphere mixture with non-additive exclusion lengths.

2. BACKGROUND

An appropriate format for our discussion is the standard Mayer diagrammatic expansion[4] of the excess free energy per unit volume (with respect to ideal gas) of a homogeneous mixture of simple classical fluids in a large volume. In this expansion, each term is of the form

$$I_{p,D}[n] = -\prod_{\gamma} n_\gamma^{p_\gamma} \int \prod_{(i,j)\in \Lambda} f_{\gamma_i\gamma_j}(|q_i - q_j|)\, dq_1^D \cdots dq_{p-1}^D \tag{1}$$

corresponding to p_γ particles of type γ and density n_γ, $p = \sum_\gamma p_\gamma$. Here, particle i at q_i in D space is of type γ_i, and $q_0 = 0$. Λ is a connected graph on p vertices with no articulation points, each edge of which contributes a weight $f_{\gamma_i\gamma_j}(|q_i - q_j|) = \exp - \beta\phi_{\gamma_i\gamma_j}(|q_i - q_j|) - 1$ for pair interaction $\phi_{\alpha\beta}(|q - q'|)$, assumed isotropic, and β is reciprocal temperature. If $p < D$, and $S_j = 2\pi^{j/2}/\Gamma(j/2)$ is the surface area of a j-dimensional unit sphere, $D - p + 1$ dimensions in (1) can be integrated out,[5] converting (1) to

$$\begin{aligned} I_{p,D}[n] = -\prod_1^p \left(\frac{S_{D-p+j}}{S_j}\right) \prod_\gamma n_\gamma^{p_\gamma} \int \prod_{(i,j)\in\Lambda} f_{\gamma_i\gamma_j}(|q_i - q_j|) \\ \times |\text{Det}\, q_{i,\alpha}|^{D-p+1}\, dq_1^{p-1} \cdots dq_{p-1}^{p-1} \end{aligned} \tag{2}$$

Let us now restrict our attention to hard-core interactions, so that f becomes a step function,

$$f_{\alpha\beta}(r) = -\varepsilon(R_{\alpha\beta} - r) \tag{3}$$

where $R_{\alpha\beta}$ is the α, β separation at contact. A conservative estimate of (2) is readily made. If $R = \max R_{\alpha\beta}$, then $|\text{Det}\, q_{i,\alpha}|/(p-1)!$ is bounded by the volume of a regular polytope of side R, namely $R^{p-1}/(p-1)!$. Hence we can write

$$v_D(R)\, |I_{p,D}[n]| \leqslant \prod_1^p \left(\frac{S_{D-p+j}}{S_j}\right) |\tilde{I}_{p,p-1}[\rho]| \tag{4}$$

where in $\tilde{I}$, all distances are measured in units of R. Here, $v_D(R) = \pi^{D/2}R^D/(D/2)!$ is the volume of a D-dimensional sphere of radius R, and in terms of the scaled densities

$$\rho_\gamma = n_\gamma v_D(R) \tag{5}$$

the D dependence of (4) is restricted to the numerical coefficient of $\tilde{I}$. We want to compare (4) with the leading, $p=2$, terms of (1), which can be written as

$$v_D(R)\, I_{2,D}[n] = \rho_\alpha \rho_\gamma \left(\frac{v_D(R_{\alpha\gamma})}{v_D(R)}\right) \tag{6}$$

for each pair α, γ. Clearly the factors of the form $S_D \sim (2\pi e/D)^{D/2}$ annihilate (4) for $p>1$ as $D \to \infty$, whereas (6) is unchanged in this scaling. It is of course the core volume rather than its radius which is held fixed during the process, so that $\tilde{I}$ in this limit[5] becomes a single-species hard-core system.

3. ANALYSIS OF THE MODEL

We conclude that if the Mayer series converges, then only the first term in the excess free energy per molecular volume survives as $D \to \infty$ (if not, we are solving a limiting model, not the limit of a model). Including the ideal gas contributions, we then have for the total free energy f per molecular volume $v_D(R)$

$$\beta f = \sum \rho_\alpha[\ln \rho_\alpha - 1 + \ln v_D(R)] + \tfrac{1}{2} \sum \rho_\alpha \rho_\gamma \tau_{\alpha\gamma} \tag{7}$$

where

$$\tau_{\alpha\gamma} = v_D(R_{\alpha\gamma})/v_D(R)$$

We will restrict our consideration to a binary, AB, mixture of hard cores. It has been known for a long time that such a mixture can decompose into an A-rich and a B-rich phase when the interaction of two unlike particles is sufficiently repulsive. This was proved in two dimensions[(6)] for the pure Widom–Rowlinson[(7)] case ($R_{AA} = R_{BB} = 0$), exhibiting a non-classical critical point, and considered more generally by Ahn and Lebowitz.[(8)] It is to be noted that in order to have a well-defined non-vanishing relative core volume $\tau_{\alpha\gamma}$ as $D \to \infty$, we must scale the radius difference as

$$R_{\alpha\gamma} = \left(1 - \frac{1}{D}\Delta_{\alpha\gamma}\right) R \tag{8}$$

[5] For a detailed analysis of $\tilde{I}(D)$ an unpublished paper of the first author is available.

and then indeed

$$\tau_{\alpha\gamma} = e^{-\Delta_{\alpha\gamma}} \tag{9}$$

For superadditive two-component diameters, $\Delta_{AB} < \frac{1}{2}(\Delta_{AA} + \Delta_{BB})$, we have

$$\tau_{AB}^2 > \tau_{AA}\tau_{BB} \tag{10}$$

The limiting primitive model, in which $\tau_{AA} = \tau_{BB} = 0$, has previously been discussed by Rowlinson.[9]

Now we want to study phase coexistence in the binary mixture represented by (7) at $p = 2$, i.e., between states characterized by (ρ_A, ρ_B, T) and (ρ'_A, ρ'_B, T). In general, this requires equal pressures and chemical potentials: $P(\rho_A, \rho_B, T) = P(\rho'_A, \rho'_B, T)$, $\mu_A(\rho_A, \rho_B, T) = \mu_A(\rho'_A, \rho'_B, T)$, $\mu_B(\rho_A, \rho_B, T) = \mu_B(\rho'_A, \rho'_B, T)$, and results in the coexistence planes $[\rho_A(\lambda, T), \rho_B(\lambda, T)]$, $[\rho'_A(\lambda, T), \rho'_B(\lambda, T)]$ parametrized by T and some λ. For hard core interactions, there is no T dependence, and so one has only a coexistence line, parametrized, e.g., by $\rho = \rho_A + \rho_B$. The analysis simplifies, while maintaining the phenomenology, in the symmetric case

$$\tau_{AA} = \tau_{BB} = \tau \tag{11}$$

for then it is readily seen that $\rho'_A = \rho_B$, $\rho'_B = \rho_A$; hence $\rho' = \rho$, and only the relative concentration $c = \rho_A/\rho$ differs in the two phases, satisfying $c + c' = 1$, as well as $\mu_A(\rho, c) = \mu_B(\rho, c)$. Hence we can choose $R_{AB} = R$, so that $\tau_{AB} = 1$, $\tau < 1$, and reduce (7) to

$$\begin{aligned}\beta f = {} & \rho[c \ln c + (1-c)\ln(1-c) - 1 + \ln\rho + \ln v_D(R)] \\ & + \tfrac{1}{2}\rho^2[\tau c^2 + 2c(1-c) + \tau(1-c)^2]\end{aligned} \tag{12}$$

The discussion then maps onto that of standard symmetric regular binary mixture theory[10] with nonideal (second virial) components. Since $\partial f/\partial\rho_A = \mu_A$, $\partial f/\partial\rho_B = \mu_B$, then

$$\frac{1}{\rho}\frac{\partial\beta f}{\partial c} = \beta(\mu_A - \mu_B) = \ln\frac{c}{1-c} + \rho(1-\tau)(1-2c) \tag{13}$$

At coexistence, (13) must vanish, with f a stable minimum. We see as well that

$$\begin{aligned}\frac{1}{\rho}\frac{\partial^2\beta f}{\partial c^2} &= \frac{1}{c} + \frac{1}{1-c} - 2\rho(1-\tau) \\ \frac{1}{\rho}\frac{\partial^3\beta f}{\partial c^3} &= \frac{2c-1}{c^2(1-c)^2}\end{aligned} \tag{14}$$

Clearly, f is always stationary at the 1:1 mixture $c = 1/2$. If $4 - 2\rho(1 - \tau) > 0$, or

$$\rho < \rho_0 = \frac{2}{1 - \tau} \tag{15}$$

this is a stable minimum. But if ρ exceeds the critical density ρ_0, then $c = 1/2$ yields a maximum, and two new minima, at $c > 1/2$ and $c' = 1 - c$, appear, which are indeed the predicted consistent A-rich and B-rich phases. The transition is of course first order.

To home in on the details of the transition, we can expand about the critical point, at which the transition is second order. If $m = c - 1/2$, this yields to order m^4 the Landau-type Hamiltonian

$$\frac{1}{\rho} \beta f(m, \rho) = \frac{1}{\rho} \beta f(0, \rho) + (\rho_0 - \rho)(1 - \tau)\, m^2 + \frac{4}{3} m^4 \tag{16}$$

The critical exponents and amplitudes which follow[11] from (16) are now classical, unlike the two-dimensional result.

ACKNOWLEDGMENTS

We would like to thank a referee for drawing our attention to relevant earlier work. This work was supported in part by the Alexander von Humboldt Foundation, the Department of Energy, the National Science Foundation, and the Petroleum Research Fund of the American Chemical Society.

REFERENCES

1. H. L. Frisch, N. Rivier, and D. Wyler, *Phys. Rev. Lett.* **54**:2061 (1985).
2. H. L. Frisch and J. K. Percus, *Phys. Rev. A* **35**:4696 (1987).
3. H.-O. Carmesin, H. L. Frisch, and J. K. Percus, *Phys. Rev. B* **40**:9416 (1989).
4. J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, New York (1947).
5. J. K. Percus, *Commun. Pure Appl. Math.* **XL**:449 (1987).
6. D. Ruelle, *Phys. Rev. Lett.* **27**:1040 (1971).
7. B. Widom and J. S. Rowlinson, *J. Chem. Phys.* **52**:1670 (1970).
8. S. Ahn and J. L. Lebowitz, *J. Chem. Phys.* **60**(2):523 (1974).
9. J. S. Rowlinson, *Adv. Chem. Phys.* **41**:1 (1980).
10. J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures* (Butterworth, London, 1982).
11. S. K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, New York, 1976).