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A DFT study of self-assembly in symmetric binary Gaussian mixtures

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Overview

- Density-functional theory (DFT) is the method of choice in the study of inhomogeneous phases. Usually, for bulk phases the density profile $\rho(\mathbf{r})$ is assumed to have a given analytical form, depending on a small number of free parameters.
- However, the phase behavior of soft-matter systems can be very complex, even for isotropic interactions. Thus, it may be difficult to make a good guess on $\rho(\mathbf{r})$.
- We have then developed a parameter-free minimization procedure of the free-energy functional, and applied it to the study of microphase formation in binary Gaussian mixtures.

Theory

Simple, mean-field-like grand potential functional, accurate for systems interacting via soft-core repulsive potentials.

$$\Omega[\rho(\mathbf{r})] = \int d^3\mathbf{r}\,\rho(\mathbf{r})\{f[\rho(\mathbf{r})] - \mu\} + \frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\,w(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r})\rho(\mathbf{r}')$$

Helmholtz free energy per particle of the reference system (here: ideal gas) — perturbation (here: full interaction)

We assume from the outset that $\rho(\mathbf{r})$ is periodic

$$\rho(\mathbf{r}+\mathbf{h}_i) = \rho(\mathbf{r})$$

$\{\mathbf{h}_i\}$=set of vectors defining a Bravais lattice

express $\rho(\mathbf{r})$ as a Fourier series over the reciprocal lattice vectors $\mathbf{k}_m$

$$\rho(\mathbf{r}) = \sum_{\mathbf{m}} e^{-i\mathbf{k_m}\cdot\mathbf{r}}\hat{\rho}_{\mathbf{m}}$$

$$\hat{\rho}_{\mathbf{m}} = \int_Q d^3\mathbf{s}\; e^{2\pi i\mathbf{m}\cdot\mathbf{s}}\,\rho(\mathbf{s})$$

Q=unit cube defined by $-1/2 \le s_j < 1/2$, j=1,2,3

and w(**r**) (which is non-periodic!) via its Fourier transform in the continuum

$$\tilde{w}(\mathbf{r}) = \int d^3\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} w(\mathbf{r})$$

$$\frac{\Omega[\rho(\mathbf{r})]}{V} = \int_Q d^3\mathbf{s}\,\rho(\mathbf{s})\{f[\rho(\mathbf{s})] - \mu\} + \frac{1}{2}\sum_{\mathbf{m}} |\hat{\rho}_{\mathbf{m}}|^2\,\tilde{w}(\mathbf{k_m})$$

The information on the lattice enters only via the $\mathbf{k}_m$ at which the potential is evaluated

We discretize $\rho(\mathbf{s}) \to \rho_{\mathbf{n}}$ and minimize $\omega=\Omega/V$ with respect to both $\rho_{\mathbf{n}}$ and the lattice vectors $\mathbf{h}_i$. The minimization algorithm is a refinement of the basic steepest descent

$$\rho_{\mathbf{n}}^{(k+1)} = \rho_{\mathbf{n}}^{(k)} - \lambda \left.\frac{\partial\omega}{\partial\rho_{\mathbf{n}}}\right|_k \qquad \mathbf{h}_i^{(k+1)} = \mathbf{h}_i^{(k)} - \delta \left.\frac{\partial\omega}{\partial\mathbf{h}_i}\right|_k$$

which includes:

- pre-conditioning (a la Jacobi)
- conjugate gradients
- adaptive stepsize

Binary, symmetric, athermal Gaussian mixture

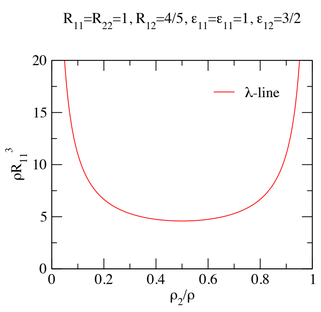
$$\beta w_{ij}(r) = \epsilon_{ij}\exp[-(r/R_{ij})^2] \qquad \epsilon_{11}=\epsilon_{22} \qquad R_{11}=R_{22}$$

The mixture may experience either demixing into two bulk phases *(spinodal line)*, or formation of periodic microphases *(λ–line)*.

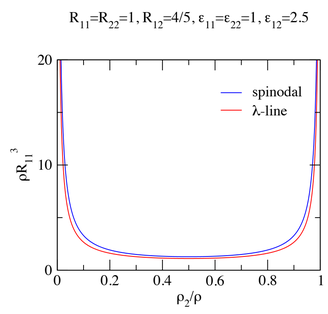
The existence and relative location of the spinodal and λ–line depend on the parameters $\alpha=(R_{11}/R_{12})^2$ and $H=(\varepsilon_{11}R^3_{11}/\varepsilon_{12}R^3_{12})$.

- The spinodal line exists for $H < 1$.
- The λ-line exists for $1 < \alpha < 2$, $H^2 > (2-\alpha)/\alpha$ and for $\alpha > 2$, any H.

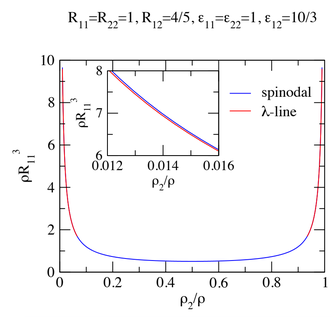
If the λ-line is there, three situations may occur:



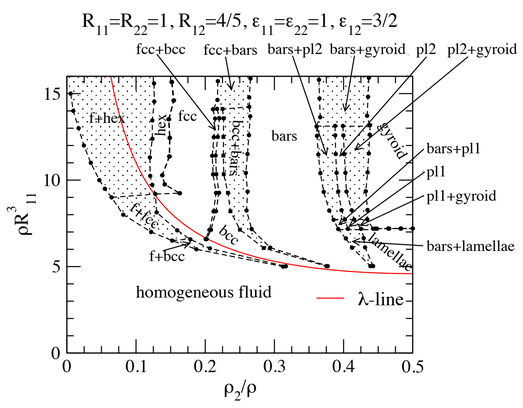
a) H>1: no spinodal



b) 1/α < H < 1: the spinodal lies above the λ-line

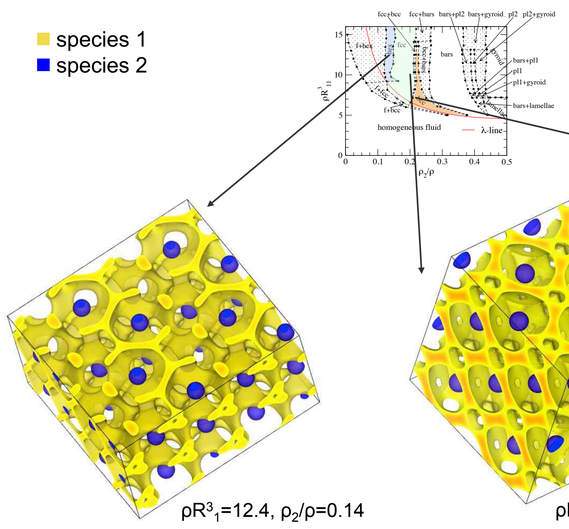


c) H < 1/α: the λ-line bifurcates from the spinodal



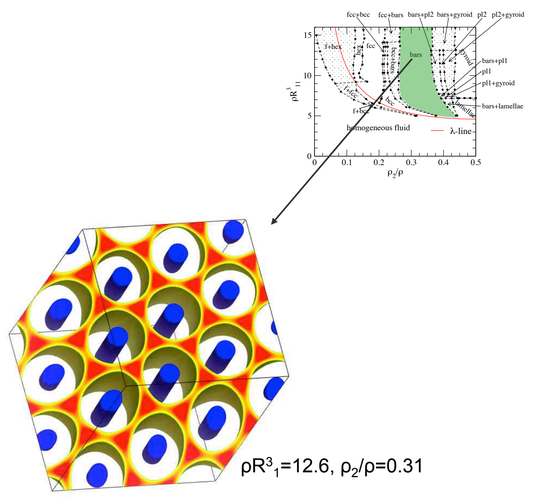
We have used DFT to study in detail the phase diagram of case a).

A tour of the phase diagram



Clusters

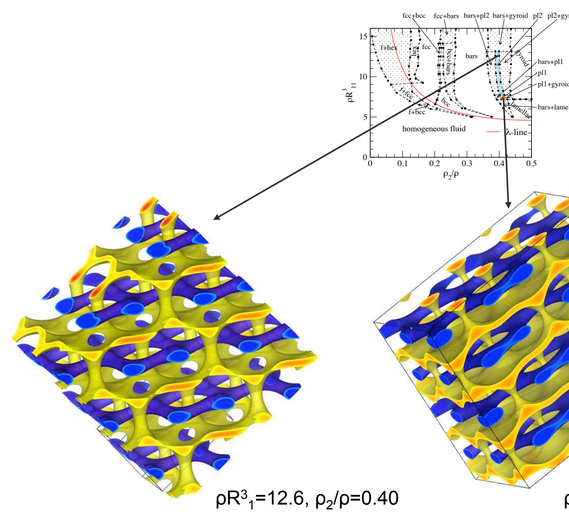
ρR^3_1=12.4, ρ_2/ρ=0.14 — ρR^3_1=10.3, ρ_2/ρ=0.21 — ρR^3_1=7.13, ρ_2/ρ=0.23



Bars

For both clusters and bars, the species at lower concentration is localized at the lattice sites, while the species at higher concentration is distributed non-uniformly in the remaining region, forming a percolating network.

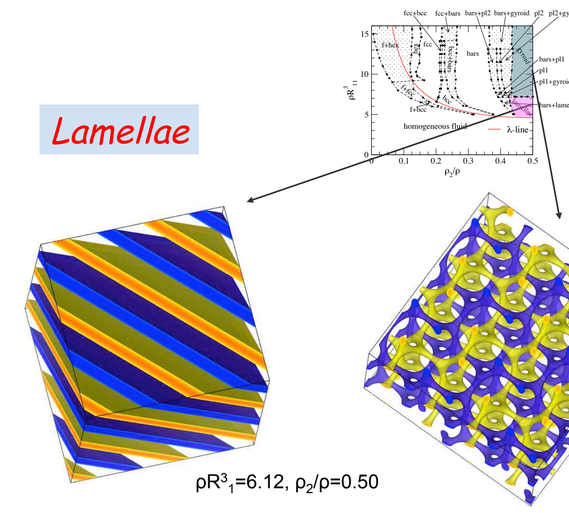
ρR^3_1=12.6, ρ_2/ρ=0.31



Pillared + perforated lamellae

As the difference in the concentrations of species 1 and 2 decreases, the distinction between localized and percolating structures blurs. Here, the two species arrange into alternating layers, but the layers of the more abundant species are connected by tubes piercing those of the less abundant species.

ρR^3_1=12.6, ρ_2/ρ=0.40 — ρR^3_1=7.18, ρ_2/ρ=0.41



Lamellae — *Gyroid*

For similar concentrations, the two species arrange into the same structure, forming a lamellar phase at low density and double-gyroid phase at higher density.

ρR^3_1=6.12, ρ_2/ρ=0.50 — ρR^3_1=10.5, ρ_2/ρ=0.50

Conclusions

- Binary Gaussian mixtures can form rather complicated structures, most of which we would not have been able to pick out from the outset. The parameter-free minimization used here was instrumental in bringing them forward.
- When the difference in the concentrations of the two species is large, the species at lower concentration arranges into localized clusters, whereas the species at larger concentration percolates into the remaining region.
- As the concentration difference decreases, the distinction between localized and percolating structures is lost. Eventually, the structure becomes the same for both species.
- Clusters, bars, lamellae, and bicontinuous phases such as the gyroid are found in other microphase-forming systems, e.g., block copolymers and fluids with competing attractive and repulsive interactions.
- However, in those systems the gyroid is stable only in a narrow domain squeezed between the bar and lamellar phases, while here it takes up most of the central region normally occupied by lamellae. Moreover, we found other exotic phases at slightly lower concentrations.