Soft depletion in binary fluids

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We show theoretically that a binary fluid characterized on a mesoscopic scale by purely repulsive short-range interactions without cores possesses an effective attraction between like particles. This *"soft depletion effect"* is a generic phenomenon driving a mixing-demixing transition in a binary system with pure repulsions.

PACS number(s): 05.20.Jj, 61.20.Gy, 64.75.+g

Interactions in complex fluids on a mesoscopic scale are conventionally modeled by *soft potentials*—short-range repulsions without cores with the range given by a cutoff radius (for a recent review see Ref. [1]). The "particles" in this picture represent liquid elements or lumps of molecules rather than atoms in a simple fluid. Soft potentials are successfully used in polymer theory where the underlying physics is based on the fractal nature of the objects such as polymer coils, star polymers, and dendrimers [2]. For example, interaction between the centers of mass of polymer coils in an athermal solvent is adequately described by a "Gaussian core model" (GCM) [3], where the repulsive potential

$$u(r) = \epsilon \exp(-r^2/r_c^2), \qquad \epsilon > 0, \qquad (1)$$

is finite for all separations r and characterized by a cutoff distance of the order of r_c, the radius of gyration of the coils; ϵ sets the energy scale. The mesoscopic approach is also used in computer simulations of large-scale phenomena in fluids within the dissipative particle dynamics (DPD) method [4] where the interactions between fluid "particles" are usually described by a parabolic model (PM)

$$u(r) = \begin{cases} \epsilon\left(1 - \dfrac{r}{r_c}\right)^2, & 0 \le r \le r_c \\ 0, & r \ge r_c, \end{cases}$$

which can be obtained by averaging the molecular field over the rapidly fluctuating motions of atoms during short time intervals [5].

In the framework of this coarse-grained description, we consider a *binary fluid mixture* of species a and b characterized by purely repulsive soft potentials $u_{\tau_1\tau_2}(r_{ij})$, $\tau_1,\tau_2 = a,b$ with the energy scales $\epsilon_{\tau_1\tau_2}$ and length scales $r_{c_{\tau_1\tau_2}}$. In the present paper, we show that such a system possesses an effective attraction between like particles for sufficiently strong unlike interactions. This effect can be termed soft depletion by analogy with hard-core depletion in colloidal systems [6]. The theory we develop is insensitive to a particular form of soft potentials $u_{\tau_1\tau_2}$.

The Helmholtz free energy of the system of N_a particles of species a and N_b particles of species b in the volume V at a temperature T is

$$e^{-\beta\mathcal{F}} = \int d\mathbf{R}^{N_a}\, e^{-\beta U_{aa}} \int d\mathbf{r}^{N_b}\, e^{-\beta[U_{bb} + U_{ab}]}, \qquad (2)$$

where $U_{aa}(\mathbf{R}^{N_a}) = \sum_{1 \le i < j \le N_a} u_{aa}(R_{ij})$, $U_{bb}(\mathbf{r}^{N_b}) = \sum_{1 \le i < j \le N_b} u_{bb}(r_{ij})$ are the bare Hamiltonians of particles a and b, respectively, $U_{ab}(\mathbf{R}^{N_a}, \mathbf{r}^{N_b}) = \sum_{i=1}^{N_a}\sum_{j=1}^{N_b} u_{ab}(|\mathbf{R}_i - \mathbf{r}_j|)$ is the total energy of unlike interactions, $\beta = 1/(k_B T)$, k_B is the Boltzmann constant. Introducing $\mathcal{F}'(\mathbf{R}^{N_a}; T, \rho_b)$,

$$e^{-\beta\mathcal{F}'} = \int d\mathbf{r}^{N_b} e^{-\beta[U_{bb}(\mathbf{r}^{N_b}) + U_{ab}(\mathbf{R}^{N_a},\mathbf{r}^{N_b})]}, \qquad (3)$$

we can write Eq. (2) as

$$e^{-\beta\mathcal{F}} = \int d\mathbf{R}^{N_a}\, e^{-\beta\mathcal{H}_{\text{eff}}},$$

where

$$\mathcal{H}_{\text{eff}}(\mathbf{R}^{N_a}; \rho_b, T) = U_{aa}(\mathbf{R}^{N_a}) + \mathcal{F}'(\mathbf{R}^{N_a}; \rho_b, T) \qquad (4)$$

is the effective Hamiltonian of a particles in the presence of the b component, $\rho_b = N_b/V$. From the form of Eq. (3), it is clear that $\mathcal{F}'(\mathbf{R}^{N_a}; T, \rho_b)$ is the Helmholtz free energy of b particles in the external field imposed by a fixed configuration $\mathbf{R}^{N_a}$ of the a component. Using the *algebraic perturbation theory* [7] based on Ruelle's rigorous expansion [8], one can write $\mathcal{F}'$ in the exact form

$$\mathcal{F}' = \mathcal{F}_b - k_B T \sum_{n=1}^{\infty} \frac{\rho_b^n}{n!} \xi_n, \qquad (5)$$

where $\mathcal{F}_b(N_b, V, T)$ is the free energy of the pure b system and

$$\xi_n = \int d\mathbf{r}^n \left(\prod_{k=1}^{n} f_{\text{ext}_k}^{\mathbf{R}^{N_a}}\right) h_b^{(n)}(\mathbf{r}^n; \rho_b, T).$$

Here $h_b^{(n)}(\mathbf{r}^n; \rho_b, T)$ are algebraic combinations of the correlation functions of orders $1-n$ of the pure b system and

$$f_{\text{ext}_k}^{\mathbf{R}^{N_a}} = \exp\left[-\beta \sum_{i=1}^{N_a} u_{ab}(|\mathbf{R}_i - \mathbf{r}_k|)\right] - 1$$

is the Mayer function of the b particle in the external field of all a particles. We emphasize that Eq. (5) is not a virial-type expression due to the dependence of $h_b^{(n)}$ on ρ_b for $n \ge 2$. The structure of $h_b^{(n)}$ provides convergence of the integrals:

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$h_b^{(1)} \equiv 1$ and for all $n \geq 2$ the functions $h_b^{(n)}(\mathbf{r}^n)$ vanish at large interparticle separations. For ξ_1 and ξ_2, we have [7] $\xi_1 = \int d\mathbf{r}_1 f_{\text{ext}_1}^{\mathbf{R}^{N_a}}$, $\quad \xi_2 = \int d\mathbf{r}_1 d\mathbf{r}_2 \, f_{\text{ext}_1}^{\mathbf{R}^{N_a}} f_{\text{ext}_2}^{\mathbf{R}^{N_a}} h_b(r_{12})$, $\quad$ where $h_b(r_{12}; \rho_b, T)$ is the total pair correlation function of the pure b system.

The energy scale of a potential depends on a system under study. For example, for polymers the renormalization group analysis and simulation studies [1] show that ϵ in Eq. (1) is of the order of $k_B T$ and decreases with increasing degree of polymerization or with worsening of solvent quality. It is therefore plausible to study the case of small $\beta \epsilon_{ab}$, the assumption that enables to facilitate model calculations (note that the inverse case $\beta \epsilon_{ab} \rightarrow \infty$ corresponds to the hard-core limit). Expanding $f_{\text{ext}_k}^{\mathbf{R}^{N_a}}$, to the second order in βu_{ab} we obtain

$$\xi_1 = N_a \int d\mathbf{r} \left\{ -\beta u_{ab}(r) + \frac{1}{2}\beta^2 [u_{ab}(r)]^2 \right\}$$
$$+ \beta^2 \sum_{1 \leq i < j \leq N_a} \int d\mathbf{r} \, u_{ab}(r) u_{ab}(|\mathbf{r} + \mathbf{R}_{ij}|), \quad (6)$$

$$\xi_2 = \beta^2 N_a \int d\mathbf{r}_1 d\mathbf{r}_2 \, u_{ab}(r_1) u_{ab}(r_2) h_b(r_{12})$$
$$+ 2\beta^2 \sum_{1 \leq i < j \leq N_a} \int d\mathbf{r}_1 d\mathbf{r}_2 \, u_{ab}(|\mathbf{R}_i - \mathbf{r}_1|) u_{ab}(|\mathbf{R}_j - \mathbf{r}_2|) h_b(r_{12}). \quad (7)$$

From Eqs. (5), (6), and (7), $\mathcal{F}'$ reads

$$\mathcal{F}' = \mathcal{F}_b + \mathcal{F}_{\text{self}} + \sum_{1 \leq i < j \leq N_a} \Delta u(R_{ij}; \rho_b, T). \quad (8)$$

Here, $\mathcal{F}_{\text{self}}$ is the average energy of noninteracting a particles in the external field of the other species and therefore can be termed as the "self-energy":

$$\mathcal{F}_{\text{self}} = N_a u_{\text{self}}(\rho_b, T), \quad (9)$$

$$u_{\text{self}}(\rho_b, T) = \rho_b \int d\mathbf{r} \left\{ u_{ab}(r) - \frac{1}{2}\beta [u_{ab}(r)]^2 \right\}$$
$$- \frac{1}{2}\beta \rho_b^2 \int d\mathbf{r}_1 d\mathbf{r}_2 \, u_{ab}(r_1) u_{ab}(r_2) h_b(r_{12}). \quad (10)$$

Note that Eq. (10) takes into account fluctuations of this field. $\mathcal{F}_{\text{self}}$ is similar to the "volume term" encountered in the models of charged colloidal suspensions [9]. The last contribution to $\mathcal{F}'$ contains $\Delta u = \Delta u_1(R_{ij}; \rho_b, T) + \Delta u_2(R_{ij}; \rho_b, T)$ with

$$\Delta u_1 = -\beta \rho_b \int d\mathbf{r} \, u_{ab}(r) u_{ab}(|\mathbf{r} + \mathbf{R}_{ij}|),$$

$$\Delta u_2 = -\beta \rho_b^2 \int d\mathbf{r}_1 d\mathbf{r}_2 \, u_{ab}(|\mathbf{R}_i - \mathbf{r}_1|) u_{ab}(|\mathbf{R}_j - \mathbf{r}_2|) h_b(r_{12}).$$

Summarizing, we obtain from Eqs. (4) and (8)

$$\mathcal{H}_{\text{eff}}(\mathbf{R}^{N_a}; \rho_b, T) = \mathcal{F}_b + \mathcal{F}_{\text{self}} + \sum_{i < j} u_{\text{eff}}(R_{ij}; \rho_b, T), \quad (11)$$

where

$$u_{\text{eff}}(R_{ij}; \rho_b, T) = u_{aa}(R_{ij}) + \Delta u(R_{ij}; \rho_b, T) \quad (12)$$

is the effective pair potential of a particles in the presence of b particles. Note that Δu appears in the second-order (in u_{ab}) perturbation theory, whereas in the first-order theory, interaction between a particles remains unchanged.

Calculation of Δu requires the knowledge of $h_b(r; \rho_b, T)$. That is why we first discuss *thermodynamics of a pure system* setting $r_c = 1$ and omitting the subscript (a or b). The isothermal compressibility χ_T is related to $h(r)$ via the compressibility equation of state: $\rho k_B T \chi_T = 1 + \rho \tilde{h}(k=0)$, which using the Ornstein-Zernike equation yields

$$\frac{1}{k_B T}\frac{dp}{d\rho} = 1 - \rho \tilde{c}(k=0). \quad (13)$$

Here, p is the pressure, $\tilde{h}(k)$ and $\tilde{c}(k)$ are the Fourier transforms of $h(r)$ and the direct correlation function $c(r)$, respectively. We apply the random phase approximation (RPA) setting $c(r) = -\beta u(r)$. Monte Carlo simulations of GCM demonstrated that RPA accounts well for pair correlations and equation of state [10,11]. One can expect this to be also true for other soft potentials. The Fourier transforms of $c(r)$ for GCM and PM read, respectively,

$$\tilde{c}_{\text{GCM}}(k) = -\pi^{3/2}\beta\epsilon \exp\left(-\frac{1}{4}k^2\right),$$

$$\tilde{c}_{\text{PM}}(k) = -8\pi\beta\epsilon \left[\frac{k \cos k - 3 \sin k + 2k}{k^5}\right].$$

Integrating Eq. (13), we obtain

$$p/(k_B T) = \rho + \kappa\beta\epsilon\rho^2 \quad (14)$$

with $\kappa_{\text{GCM}} = \frac{1}{2}\pi^{3/2}$ and $\kappa_{\text{PM}} = \pi/15$. The absence of a core has an important impact on the thermodynamic behavior: the pressure increases very slowly with the density, $p_a \sim \rho_a^2$. This statement is confirmed by the DPD simulations of PM [4], where the equation of state was found to be of the type (14) with $\kappa_{\text{PM}}^{\text{DPD}} \approx 0.202 \pm 0.002$, which is in a very good agreement with our $\kappa_{\text{PM}} \approx 0.209$. The function $h(r)$ is given by the inverse Fourier transform:

$$h(r; \rho, T) = \frac{1}{2\pi^2 r}\int_0^\infty dk \left[\frac{k\tilde{c}(k)}{1 - \rho\tilde{c}(k)}\right]\sin(kr). \quad (15)$$

Now we have all the necessary ingredients to study the effective potential given by Eq. (12). It is sensitive to the range and energy scales of interactions, as well as to the temperature and density. If the unlike interactions are stronger than the like ones and/or more long ranged, one can expect the *effective attraction between like particles* at sufficiently low temperatures, the effect which can be termed "soft depletion," since it is similar (but not identical) to
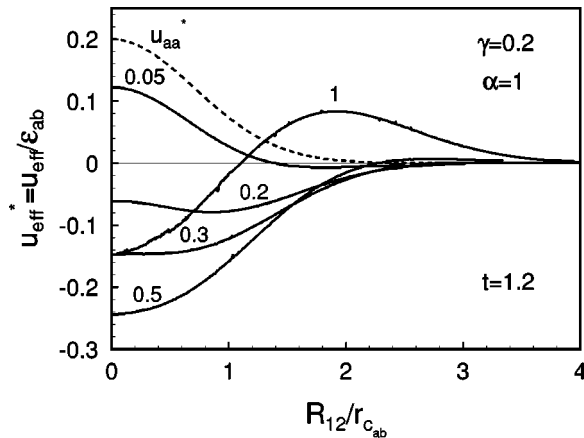
FIG. 1. Effective interaction between *a* particles for the Gaussian core model at $t=k_BT/\epsilon_{ab}=1.2$ for various ρ_b (solid lines). The curves are labeled by the value of $\rho_b r_{c_{ab}}^3$. Also shown is the pure potential $u_{aa}^*=u_{aa}/\epsilon_{ab}$ (dashed line).

FIG. 2. Effective interaction between *a* particles for the parabolic model. Notations are the same as in Fig. 1.

depletion in a mixture of hard-core particles. In the models proposed by several authors [6], the effective attraction in a system of mutually repelling particles was discussed for hard-sphere interactions where this effect is of entropic origin. For particles without cores, both entropic and energetic contributions to the free energy are important. Figure 1 shows the effective potential of *a* particles in a "symmetric" GCM mixture ($\epsilon_{aa}=\epsilon_{bb}$, $r_{c_{aa}}=r_{c_{bb}}$) at the temperature $t=k_BT/\epsilon_{ab}=1.2$. The values of interaction parameters are $\gamma=\epsilon_{aa}/\epsilon_{ab}=0.2$, and $\alpha=r_{c_{aa}}/r_{c_{ab}}=1$. Curves are labeled by the value of the reduced *b* particle density $\rho_b^*=\rho_b r_{c_{ab}}^3$. At low densities, $\rho_b<0.45$, interaction $u_{\rm eff}(R_{12})$ between *a* particles is repulsive at short distances, reaches a minimum, beyond which it becomes attractive tending asymptotically to zero at large R_{12}. The increase in ρ_b results in stronger attractive forces (given by the slope of the potential curves) which at the same time become more short ranged. For $\rho_b>0.45$, the potential curves show oscillatory behavior: beyond the point R_m^*, where $u_{\rm eff}$ is at its maximum (e.g., for $\rho_b=1$, $R_m^*\approx1.9$), the attractive part is followed by a repulsive tail. Soft depletion does not occur in the case when unlike repulsion is weaker than repulsion between like particles, i.e., when $\gamma>1$. The same qualitative features albeit for different values of ρ_b^* are shared by PM as shown in Fig. 2. The appearance of the oscillatory part in $u_{\rm eff}$ at high ρ_b suggests that the multibody terms in effective interaction may be important at high ρ_b, while at low ρ_b they are insignificant.

Soft depletion manifests itself by driving a phase transition. To study the phase behavior of the binary system with the Hamiltonian (11), we consider its free energy

$$\mathcal{F}=\mathcal{F}_{\rm eff}([u_{\rm eff}])+\mathcal{F}_{\rm self}(N_a,\rho_b,T)+\mathcal{F}_b(N_b,V,T). \quad (16)$$

Here, $\mathcal{F}_{\rm eff}$ is the free energy of the system of *a* particles interacting via $u_{\rm eff}(R)$; $\mathcal{F}_{\rm eff}$ can be found by thermodynamic integration [12]. To this end, we introduce an auxiliary interaction potential $u^{(\nu)}(R_{ij})=u_{aa}(R_{ij})+\nu\Delta u(R_{ij})$, where $0\leq\nu\leq1$ is the coupling parameter; at $\nu=0$, it reduces to the

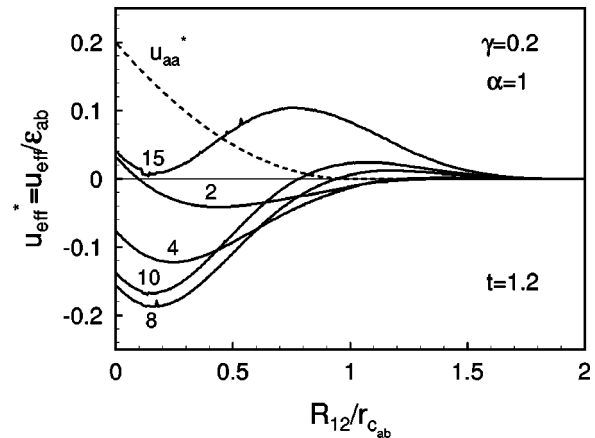*a*-*a* interaction $u^{(\nu=0)}(R_{ij})=u_{aa}(R_{ij})$, while at $\nu=1$ we recover $u_{\rm eff}$: $u^{(\nu=1)}(R_{ij})=u_{\rm eff}(R_{ij})$. Using the standard argument, we obtain

$$\mathcal{F}_{\rm eff}=\mathcal{F}_a+\frac{1}{2}\rho_a^2\int_0^1 d\nu\int d\mathbf{R}_1 d\mathbf{R}_2\,\Delta u(R_{12})g^{(\nu)}(R_{12}),$$

where $\mathcal{F}_a$ is the free energy of the pure *a* system, $\rho_a=N_a/V$, and $g^{(\nu)}(R)$ is the pair correlation function of the system with the potential $u^{(\nu)}$ at the density ρ_a and temperature T. To be consistent with the second-order (in u_{ab}) perturbation theory, we keep in $\mathcal{F}_{\rm eff}$ the term linear in Δu, thus replacing $g^{(\nu)}(R)$ with $g^{(\nu=0)}(R)=g_a(R)$, the pair correlation function of the pure *a* system. Integration over ν yields $\mathcal{F}_{\rm eff}=\mathcal{F}_a+\Delta\mathcal{F}$ with

$$\Delta\mathcal{F}=2\pi N_a\rho_a r_{c_{ab}}^3\int_0^\infty dx\,x^2\Delta u(x;\rho_b)g_a(x;\rho_a), \quad (17)$$

where $x=R_{12}/r_{c_{ab}}$ and $g_a=h_a+1$ with h_a given by Eq. (15).

Let us study first the behavior of the mixture at a *fixed density of b* particles. Then, $\mathcal{F}_b$ in Eq. (16) is an additive constant and can be omitted. What we are left with is a single-component system with interactions $u_{\rm eff}$ in the external field whose average energy per particle is $u_{\rm self}$. The effective pressure $\bar{p}_a$ is found from Eqs. (9), (14), and (17),

$$\frac{\bar{p}_a}{k_BT}=\rho_a\left[1+\rho_b\frac{\partial\beta u_{\rm self}}{\partial\rho_b}\right]+\rho_a^2\bar{B},$$

where

$$\frac{\bar{B}(\rho_a,\rho_b,T)}{r_{c_{ab}}^3}=\kappa\beta\epsilon_{aa}\left(\frac{r_{c_{aa}}}{r_{c_{ab}}}\right)^3+2\pi\int_0^\infty dx\,x^2\left[\beta\Delta u g_a\right.$$
$$\left.+\rho_b\frac{\partial\beta\Delta u}{\partial\rho_b}g_a+\beta\Delta u\rho_a\frac{\partial g_a}{\partial\rho_a}\right].$$

Monte Carlo simulations of a *pure* GCM system [11] show that at high densities, it behaves as a weakly correlated "mean-field fluid." This implies that at high ρ_a, g_a shows an

ideal-gas-like behavior and $\bar{B}$ becomes virtually independent of ρ_a resulting in the equation of state of the form (14); the important difference from a pure system, however, is that the quadratic term can be both positive and negative. For $\bar{B} > 0$, the system is stable and homogeneous. If $\bar{B} < 0$, the system collapses. In a special case of $\bar{B} = 0$, the pressure scales linearly with ρ_a; hence, for $\bar{B} = 0$ the system *at high* ρ_a behaves as an ideal gas with the renormalized density $\rho_a[1 + \rho_b \partial \beta u_{\text{self}} / \partial \rho_b]$. These features make the effective system qualitatively different from a van der Waals fluid in which at high densities the excluded volume effect always dominates attractions thus being a stabilizing factor. The effective system does not possess the liquid-vapor transition with a characteristic van der Waals loop.

In order to search for possible phase transitions, we return to the full binary mixture description introducing the reduced total density $\rho_t = (\rho_a + \rho_b) r_{c_{ab}}^3$, the fractions of components $\phi_a = N_a / N$, $\phi_b = N_b / N$, $N = N_a + N_b$ satisfying $\phi_a + \phi_b = 1$, and interaction parameters $\gamma_a = \epsilon_{aa} / \epsilon_{ab}$, $\gamma_b = \epsilon_{bb} / \epsilon_{ab}$, $\alpha_a = r_{c_{aa}} / r_{c_{ab}}$, $\alpha_b = r_{c_{bb}} / r_{c_{ab}}$. Let us consider the reduced free energy per particle

$$f = \frac{\mathcal{F}}{N k_B T}.$$

The combined contribution of the pure a and b systems to f is obtained by integration of their equation of state (14):

$$f^{\text{pure}} = \phi_a \ln \phi_a + \phi_b \ln \phi_b + \frac{\rho_t \kappa}{t}(\gamma_a \alpha_a^3 \phi_a^2 + \gamma_b \alpha_b^3 \phi_b^2) + \ln \rho_t,$$

where the term with the irrelevant de Broglie thermal wavelength is omitted. The contributions f^{self} and f^{Δ} from $\mathcal{F}_{\text{self}}$ and $\Delta \mathcal{F}$ are obtained using Eqs. (9), (10), (15)–(17): $f^{\text{self}} + f^{\Delta} = \Psi(\phi_b, \rho_t; t) \phi_a \phi_b$, where $\Psi(\phi_b, \rho_t; t)$ is calculated numerically (the details are presented elsewhere [13]). Thus, the reduced free energy can be written as a function of $\phi = \phi_b$ and ρ_t at a given t:

$$f(\phi, \rho_t) = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \frac{\kappa \rho_t}{t}[\gamma_a \alpha_a^3 (1 - \phi)^2$$
$$+ \gamma_b \alpha_b^3 \phi^2] + \Psi(\phi, \rho_t; t) \phi (1 - \phi) + \ln \rho_t. \quad (18)$$

In the case of a symmetric mixture, $\gamma_a = \gamma_b = \gamma$, $\alpha_a = \alpha_b = \alpha$, Eq. (18) is simplified to

$$f_{\text{sym}}(\phi, \rho_t) = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi(\phi, \rho_t; t) \phi (1 - \phi) + \left[\frac{\kappa \rho_t \gamma \alpha^3}{t} + \ln \rho_t \right], \quad (19)$$

where $\chi(\phi, \rho_t; t) = -2 \kappa \rho_t \gamma \alpha^3 / t + \Psi(\phi, \rho_t; t)$. If we assume that ρ_t is approximately constant, then apart from the constant term in the square brackets, Eq. (19) has the form of the Flory-Huggins expression for the free energy $\mathcal{F}_{\text{FH}}$ of a polymer mixture [14] if we identify f_{sym} with $\mathcal{F}_{\text{FH}} / k_B T$ and χ with the Flory χ-parameter (the possibility of the free energy density mapping to the Flory-Huggins model was pointed out in Ref. [4]). Possible phase transitions are of liquid-liquid and liquid-solid type. Applying the standard stability analysis, one can conclude that below a critical temperature $T_c(\rho_t)$, the system is separated into the a-rich and b-rich phases. The striking feature is that this mixing-demixing transition is caused by purely repulsive interactions. Note that our model does not invoke any *a priori* assumptions about the unlike correlation functions $c_{ab}(r)$ and $h_{ab}(r)$. This feature may be important since it is these interactions that are responsible for the soft depletion.

In conclusion, the theory presented in this paper predicts the effect of soft depletion—an effective attraction between like particles in a binary fluid with soft repulsive potentials - which occurs when the unlike repulsion is stronger than the repulsion between like particles. This effect is a generic phenomenon driving the phase separation. We expect that at high densities, the oscillatory part in u_{eff} will probably be smoothed out by successive multibody terms in effective interactions so that soft depletion will become more pronounced—a problem to be explored in future work.

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