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Density functional theory of phase coexistence in weakly polydisperse fluids

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The recently proposed universal relations between the moments of the polydispersity distributions of a phase-separated weakly polydisperse system are analyzed in detail using the numerical results obtained by solving a simple density functional theory of a polydisperse fluid. It is shown that universal properties are the exception rather than the rule.

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Many, natural or manmade, systems are mixtures of similar instead of identical objects. For example, in a colloidal dispersion [1] the size and surface charge of the colloidal particles are usually distributed in an almost continuous fashion around some mean value. When this distribution is very narrow the system can often be assimilated [2] to a one-component system of identical objects. Such a system is usually called monodisperse whereas otherwise it is termed polydisperse. Since polydispersity is a direct consequence of the physicochemical production process it is an intrinsic property of many industrial systems. Therefore many authors [3] have included polydispersity into the description of a given phase of such systems. More recently, a renewed interest can be witnessed for the study of phase transitions occuring in weakly polydisperse systems [4]. The phase behavior of polydisperse systems is of course much richer than that of its monodisperse counterpart. It is also more difficult to study theoretically, essentially because one has to cope with an infinity of thermodynamic coexistence conditions [3]. Therefore several authors have proposed approximation schemes [5] which try to bypass this difficulty. In the present study we take the opposite point of view by solving numerically the infinitely many thermodynamic coexistence conditions for a simple model polydisperse system. On this basis we have studied the radius of convergence of the weak polydispersity expansion used in Ref. [4] and found that their ‘‘universal law of fractionation’’ and some of their conclusions have to be modified in several cases.

The statistical mechanical description of a polydisperse equilibrium system is equivalent to a density functional theory [6] for a system whose number density, $\rho(\mathbf{r},\sigma)$, depends besides the position variable $\mathbf{r}$ (assuming spherical particles) also on at least one polydispersity variable σ (which we consider to be dimensionless). Such a theory is completely determined once the intrinsic Helmholtz free-energy per unit volume, $f[\rho]$, has been specified as a functional of $\rho(\mathbf{r},\sigma)$ (for notational convenience the dependence on the temperature T will not be indicated explicitly). For the spatially uniform fluid phases considered here (and also implicitly in Ref. [4]) we have $\rho(\mathbf{r},\sigma)\rightarrow\rho(\sigma)$, and the pressure can be written as $p[\rho]=\int d\sigma\rho(\sigma)\mu(\sigma;[\rho])-f[\rho]$, where $\mu(\sigma;[\rho])=\delta f[\rho]/\delta\rho(\sigma)$ is the chemical potential of ‘‘species’’ σ. When a parent phase of density $\rho_0(\sigma)$ phase separates into n daughter phases of density $\rho_i(\sigma)$ $(i=1,\ldots,n)$ the phase coexistence conditions imply that $p[\rho_1]=p[\rho_2]=\cdots=p[\rho_n]$, and $\mu(\sigma;[\rho_1])=\mu(\sigma;[\rho_2])=\cdots=\mu(\sigma;[\rho_n])$. For simplicity we consider here only the case of two daughter phases $(n=2)$ and rewrite moreover $\rho_i(\sigma)=\rho_i h_i(\sigma)(i=0,1,2)$ in terms of the average density ρ_i and a polydispersity distribution $h_i(\sigma)$ such that $\int d\sigma h_i(\sigma)=1$. Since the ideal gas contribution to $f[\rho]$ is exactly known [6] one has $\mu(\sigma;[\rho])=k_BT\ln\{\Lambda^3(\sigma)\rho(\sigma)\}+\mu_{ex}(\sigma;[\rho])$, where k_B is Boltzmann's constant, $\Lambda(\sigma)$ is the thermal de Broglie wavelength of species σ, and μ_{ex} the excess (ex) contribution to μ. This allows us to rewrite the equality of the chemical potentials of the two daughter phases, as $h_1(\sigma)=h_2(\sigma)A(\sigma)$, where $A(\sigma)$ is a shorthand notation for

$$A(\sigma)=\frac{\rho_2}{\rho_1}\exp\beta\{\mu_{ex}(\sigma;[\rho_2])-\mu_{ex}(\sigma;[\rho_1])\} \tag{1}$$

with $\beta=1/k_BT$. The polydispersity distributions are further constrained by the relation $x_1h_1(\sigma)+x_2h_2(\sigma)=h_0(\sigma)$, which expresses particle number conservation. The number concentration of phase 1, $x_1=1-x_2$, is given by the lever rule: $x_1=[\rho_1/(\rho_1-\rho_2)]\cdot[(\rho_0-\rho_2)/\rho_0]$. Combining these two relations one finds

$$h_2(\sigma)-h_1(\sigma)=h_0(\sigma)\cdot H(\sigma), \tag{2}$$

where $H(\sigma)\equiv[1-A(\sigma)]/[x_2+x_1A(\sigma)]$. Equation (2) is the starting point to relate the difference between the moments of the daughter phases, $\Delta_k=\int d\sigma\,\sigma^k[h_2(\sigma)-h_1(\sigma)]$, to the moments, $\xi_k=\int d\sigma\,\sigma^k h_0(\sigma)$ $(k=0,1,2,\ldots)$, of the parent phase distribution $h_0(\sigma)$. Indeed, when σ is chosen such that $h_0(\sigma)$ tends to the Dirac delta function $\delta(\sigma)$ in the monodisperse limit, Δ_k can be obtained from Eq. (2) by expanding $H(\sigma)$ around $\sigma=0$, $H(\sigma)=\Sigma_{l=0}^{\infty}a_l\sigma^l$, yielding for a weakly polydisperse system, $\Delta_k=\Sigma_{l=0}^{\infty}a_l\xi_{l+k}$. The normalization of the $h_i(\sigma)$ $(i=0,1,2)$ implies $\Delta_0=0$, $\xi_0=1$ or $a_0=-\Sigma_{l=1}^{\infty}a_l\xi_l$, and eliminating a_0 from Δ_k yields the general moment relation

$$\Delta_k=a_1\xi_{k+1}+\sum_{l=2}^{\infty}a_l(\xi_{k+l}-\xi_l\xi_k), \tag{3}$$

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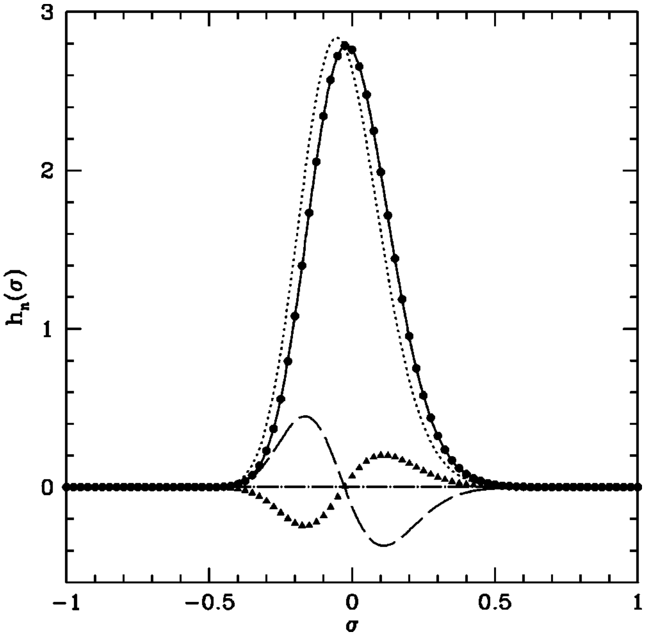

FIG. 1. The polydispersity distributions $h_n(\sigma)$ of the parent phase ($n=0$: full curve) (a Schulz distribution with the width parameter $\alpha=50$), the low-density ($n=1$: dotted curve) and the high-density ($n=2$: circles) daughter phases, as obtained by numerically solving the coexistence conditions of the van der Waals model of Eq. (4) for $t=1$, $\eta_0=0.5$. The corresponding dimensionless densities of the coexisting daughter phases are $\eta_1=0.106, \eta_2=0.521$ whereas for the monodisperse system one has $\eta_1=0.103, \eta_2=0.608$. Also shown are $h_1(\sigma)-h_0(\sigma)$ (dashed curve) and $[h_2(\sigma)-h_0(\sigma)]\cdot 50$ (triangles).

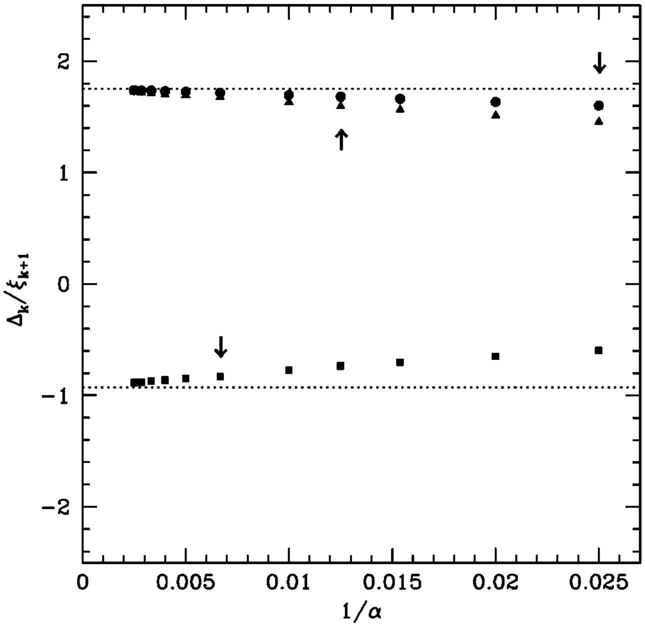

FIG. 2. The ratio Δ_k/ξ_{k+1} ($k=1,2,3$) versus $1/\alpha$ as obtained from the numerical solution of the van der Waals model of Eq. (4) for $t=1$, $\eta_0=0.5$ and a Schulz distribution for $h_0(\sigma)$. The symbols are as follows: circles ($k=1$), squares ($k=2$), and triangles ($k=3$). The dotted lines indicate their asymptotic ($\alpha\to\infty$) values. The arrows indicate for each case the radius of convergence of the weak polydispersity expansion of Eq. (3).

where we took, moreover, into account that σ can always be chosen such that $\xi_1=0$. When only the first term in the right-hand side of Eq. (3) is retained we recover the universal law $\Delta_k/\Delta_l=\xi_{k+1}/\xi_{l+1}$, put forward in Ref. [4]. The question left unanswered by the study of Ref. [4] concerns the radius of convergence of the weak polydispersity expansion (3). In order to study this problem in more detail we now consider a simple model system for which we can determine the $h_i(\sigma)(i=1,2)$ numerically and compare the results with Eq. (3). The free energy density functional chosen here corresponds to a simple van der Waals (vdW) model [7] for the liquid-vapor transition in polydisperse systems of spherical particles of variable size:

$$f[\rho]=k_BT\int d\sigma\rho(\sigma)\left\{\ln\left(\frac{\Lambda^3(\sigma)\rho(\sigma)}{E[\rho]}\right)-1\right\}+\tfrac{1}{2}\int d\sigma\int d\sigma' V(\sigma,\sigma')\rho(\sigma)\rho(\sigma'), \tag{4}$$

where $E[\rho]=1-\int d\sigma v(\sigma)\rho(\sigma)$ describes the average excluded volume correction for particles of radius R_σ and volume $v(\sigma)=(4\pi/3)R_\sigma^3$, while $V(\sigma,\sigma')=\int d\mathbf{r}V(r;\sigma,\sigma')$ is the integrated attraction between two particles of species σ and σ', for which we took the usual vdW form $V(r;\sigma,\sigma')=-\epsilon_0(R_\sigma+R_{\sigma'})^6/r^6$ for $r\geqslant R_\sigma+R_{\sigma'}$ and zero otherwise, ϵ_0 being the amplitude of the attraction at the contact of the two particles. The size polydispersity can be described in terms of the dimensionless variable, $\sigma=R_\sigma/R-1$, with R the mean value of R_σ in the parent phase, hence $\xi_1=\int d\sigma\,\sigma h_0(\sigma)=0$. The thermodynamics is given in terms of $h_0(\sigma)$, the dimensionless temperature $t=k_BT/\epsilon_0$ and the dimensionless density $\eta=v_0\rho$, with $v_0=(4\pi/3)R_0^3$ and R_0 the value of R_σ in the monodisperse limit. The coexistence conditions are integral equations which can be solved numerically using, for instance, an iterative algorithm [8] for any t, $\eta_0=v_0\rho_0$ and $h_0(\sigma)$. For $h_0(\sigma)$ we took a Schulz distribution [3] with zero mean. The normalized distribution is given, for $-1\leqslant\sigma<\infty$, by $h_0(\sigma)=\alpha^\alpha(1+\sigma)^{\alpha-1}e^{-\alpha(1+\sigma)}/\Gamma(\alpha)$, with $\Gamma(\alpha)$ the gamma function and $1/\alpha$ a width parameter which measures the distance to the monodisperse limit, $h_0(\sigma)\to\delta(\sigma)$ when $\alpha\to\infty$. We then have: $\xi_0=1$, $\xi_1=0$, $\xi_2=1/\alpha$, $\xi_3=2/\alpha^2$, $\xi_4=3/\alpha^2+6/\alpha^3$, $\xi_5=20/\alpha^3+24/\alpha^4$, etc. For a weakly polydisperse system we retain only the dominant terms of Eq. (3) in a $1/\alpha$ expansion. From Eq. (3) we obtain then: $\Delta_1=a_1(\infty)\xi_2+O(1/\alpha^2)$, $\Delta_2=a_1(\infty)\xi_3+a_2(\infty)(\xi_4-\xi_2^2)+O(1/\alpha^3)=\{a_1(\infty)+a_2(\infty)\}\xi_3+O(1/\alpha^3)$, $\Delta_3=a_1(\infty)\xi_4+O(1/\alpha^3)$, etc, where $a_l(\infty)$ are the values of a_l for $\alpha\to\infty$. Using the vdW expression (4) to evaluate Eq. (1) one finds, for example, for $t=1.0$ and $\eta_0=0.5$, $a_1(\infty)=1.75$ and $a_2(\infty)=-2.68$. Using the corresponding numerical solutions found for $h_1(\sigma)$ and $h_2(\sigma)$ (see Fig. 1) it can be seen from Fig. 2 that $\Delta_1/\xi_2\approx1.75$, $\Delta_2/\xi_3\approx-0.93$, and $\Delta_3/\xi_4\approx1.75$ are obeyed to within ten percent for α larger than, respectively, 40, 80, and 150. We can conclude thus that the weak polydispersity expansion (3) is valid (to dominant order) for Schulz distributions $h_0(\sigma)$ with a dispersion $[(\xi_2-\xi_1^2)^{1/2}]$ smaller than, say, 0.1 ($\alpha\approx100$). These values do, of course, depend on the thermodynamic state but the case considered here $(t=1,\eta_0=0.5)$ is representative of other t,η_0 values. Note also that we have verified numerically that the radius of convergence of Eq. (3) with respect to $1/\alpha$ is fairly sensitive to the total amount of polydispersity present. Allowing, for instance, the amplitude ϵ_0 of the pair potential $V(r;\sigma,\sigma')$ to depend on σ and σ' does reduce the radius of convergence of Eq. (3) considerably. From the above it follows that Δ_3/Δ_1 follows the universal law, $\Delta_3/\Delta_1=\xi_4/\xi_2$, put forward in Ref. [4] whereas Δ_2/Δ_1 follows the nonuniversal law, $\Delta_2/\Delta_1=\{1+a_2(\infty)/a_1(\infty)\}\xi_3/\xi_2$. We have verified that similar results can be obtained for different $h_0(\sigma)$ distributions. Taking, for instance, a Gaussian for $h_0(\sigma)$, similar results are found, although $\xi_3=0$ for this case. This invalidates the conclusion of Ref. [4] that a particular importance should be attached to the skewness of $h_0(\sigma)$. In conclusion, the general moment relation (3) can yield useful information about the phase behavior of weakly polydisperse systems but this information is in general not universal.

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