

Universal law of fractionation for slightly polydisperse systems

R. M. L. Evans, D. J. Fairhurst and W. C. K. Poon

Department of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, U.K.
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By perturbing about a general monodisperse system, we provide a complete description of two-phase equilibria in *any* system which is slightly polydisperse in some property (*e.g.* particle size, charge, *etc.*). We derive a universal law of fractionation which is corroborated by comprehensive experiments on a model colloid-polymer mixture. We furthermore predict that phase separation is an effective method of reducing polydispersity only for systems with a skewed distribution of the polydisperse property.

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Complex fluids contain mesoscopic units that are almost inevitably polydisperse, *i.e.* colloidal or polymeric particles have some characteristic, such as radius, charge, mass or oblateness, which varies quasi-continuously from one to another. A truly polydisperse system contains infinitely many species with a distribution of properties, and could separate into arbitrarily many coexisting phases. The onset of phase separation is at the ‘cloud curve’, the boundary of coexistence with an infinitesimal amount of a second phase on the ‘shadow curve’. In contrast to simple systems, a complete description of phase equilibria entails determining not just these limiting curves, but also the different compositions (described by a distribution) of arbitrary coexisting phases.

Experimentally, phase equilibria have been completely determined for polydisperse polymers [1]. In contrast, most experiments on colloidal phase behavior have ignored polydispersity, despite pragmatic interest in using phase separation to fractionate suspensions [2]; limited data on particulate systems derives only from simulations [3,4]. Many calculations of two-phase equilibria have been attempted for specific polydisperse systems ([5] and references therein), especially polymers (which admit mean-field analysis). The popular but arbitrary method of discretizing the distribution [6], though efficacious, gives little insight. The infinity of coexistence conditions hampers the formulation of truly polydisperse statistical mechanics (discussed in [5,7,8]), especially in non-mean-field systems, for which exact phase calculations are consequently scarce [9]. The approach of Gualtieri et al. [5] to calculating two-phase coexistence is applicable to a large class of model systems, but gives rise to formidable non-linear equations. They calculate cloud/shadow curves for a polydisperse van der Waals model, but give no general result. We present a simpler treatment, applicable to real systems, and use it to solve the two-phase coexistence problem completely in the limit of small polydispersities. A universal law of fractionation is derived. We show significant consistency with comprehensive measurements of phase equilibria in a model polydisperse colloid.

Following Gualtieri et al. [5], we divide the total free energy, $F^{\text{tot}} = F^{\text{id}} + F^{\text{ex}}$ into two parts: the free energy of a polydisperse ideal gas of the given species distribution, and the excess due to interactions. The ideal part, F^{id} is a functional of the distribution $f(\varepsilon)$, where $f(\varepsilon)d\varepsilon$ particles have the polydisperse property ε in the range ε to $\varepsilon + d\varepsilon$. No matter what the system, F^{id} always takes the same form (in units of $k_B T$),

$$F^{\text{id}} = \int d\varepsilon f(\varepsilon) \left[\ln \frac{f(\varepsilon)}{V} - 1 \right] \quad (1)$$

where the integrand is the ideal gas free energy of each species in volume V . The total number of particles is $N = \int f(\varepsilon) d\varepsilon$. Non-trivially, Eq. 1 holds whether or not the members of each species are quantum-mechanically indistinguishable [8]. At equilibrium, the chemical potential for each species, $\mu(\varepsilon) \equiv \delta F^{\text{tot}} / \delta f(\varepsilon)$ is equal in any pair of coexisting phases. That is,

$$\Delta \mu(\varepsilon) = \Delta \mu^{\text{id}}(\varepsilon) + \Delta \mu^{\text{ex}}(\varepsilon) = 0 \quad \text{for all } \varepsilon, \quad (2)$$

which is an infinite number of equilibrium conditions (with Δ indicating difference between phases). From Eq. 1, the ideal part is $\mu^{\text{id}}(\varepsilon) = \ln[f(\varepsilon)/V]$. Applying the equilibrium constraints (Eq. 2) allows ratios of densities in coexisting phases A and B ,

$$\frac{f_A(\varepsilon)/V_A}{f_B(\varepsilon)/V_B} = \exp \Delta \mu^{\text{ex}}(\varepsilon) \quad (3)$$

to be found from F^{ex} . To reduce the infinity of simultaneous equations for coexistence to a finite set, Gualtieri et al. assumed F^{ex} was a function of finitely many moments. Recent work [8,10] has clarified the status of the moments neglected in F^{ex} in this type of approach, but the ‘finite moment’ assumption remains arbitrary, and is unlikely to be true for real systems.

Our *ab initio* approach imposes no special structure on F^{ex} . Our starting point is the observation that an *almost* pure ensemble (one with a narrow normalized distribution $p(\varepsilon) \equiv f(\varepsilon)/N$) should behave similarly to a monodisperse system (for which $p(\varepsilon) = \delta(\varepsilon)$, the Dirac delta function), despite having a very different formal

description (being a mixture of infinitely many species). Therefore, although a general polydisperse system could separate into arbitrarily many coexisting phases (see *e.g.* [10]), we may restrict our attention to two-phase coexistence. We apply thermodynamic perturbation theory to a monodisperse reference system [11], using ε_i as a small, dimensionless variable assigned to each particle $i = 1 \dots N$. We ascribe no specific physical meaning to ε_i at this stage but it may be, *e.g.*, the fractional deviation of a particle's radius from the mean. With this approach, we derive a number of results which are exact and universal in the limit of a narrow distribution. Such distributions are ubiquitous, being the typical product of chemical syntheses aimed at producing monodisperse systems. Details of the calculations are given elsewhere [12]. One universal (but perhaps unsurprising) result to emerge is that, to *first* order in polydispersity, the shadow and cloud curves are not perturbed from the coexistence boundary (the binodal) of the monodisperse reference system. Coexisting polydisperse phases in general exhibit *fractionation* and have different distributions from the parent sample, *e.g.* the denser phase might favor larger particles. We derive universal results relating the moments in the daughter phases to those of the parent, using the location of the monodisperse binodal as an input parameter.

We begin by noting [8,10,13] that ‘moment densities’,

$$\rho_\alpha \equiv \frac{1}{V} \int_{-\infty}^{\infty} \varepsilon^\alpha f(\varepsilon) d\varepsilon, \quad (4)$$

being linear combinations of conserved species densities, are themselves conserved and, accordingly, respect the usual equilibrium conditions. For instance, each ‘moment chemical potential’, defined by $\mu_\alpha \equiv \partial(F/V)/\partial\rho_\alpha$, is equal in coexisting phases. This is clear from expanding the species chemical potential in partial derivatives

$$\mu(\varepsilon) \equiv \frac{\delta F}{\delta f(\varepsilon)} = \sum_{\alpha=0}^{\infty} \frac{\partial F}{\partial \rho_\alpha} \frac{\delta \rho_\alpha}{\delta f(\varepsilon)} = \sum_{\alpha=0}^{\infty} \mu_\alpha \varepsilon^\alpha. \quad (5)$$

Thus, equality of $\mu(\varepsilon)$ in coexisting phases requires equality of μ_α . Note that $\rho_\alpha = \overline{\varepsilon^\alpha} \rho$, so that ρ_0 is the overall particle density ρ . The mean α th power of ε , $\overline{\varepsilon^\alpha}$, is the α th moment of the *normalized* distribution $p(\varepsilon)$.

Substituting Eq. 5 into 3 and demanding that, at coexistence, the distributions in the two phases *A* and *B* sum to the parent $f_P(\varepsilon)$ from which they came yields

$$f_A(\varepsilon) = \frac{f_P(\varepsilon)}{1 + \frac{V_B}{V_A} \exp[-\sum_{\alpha=0}^{\infty} \Delta\mu_\alpha^{\text{ex}} \varepsilon^\alpha]} \quad (6)$$

which expresses a daughter distribution in terms of the parent and excess moment chemical potentials in the daughter phases. Here $\Delta\mu_\alpha^{\text{ex}} = \mu_{\alpha(B)}^{\text{ex}} - \mu_{\alpha(A)}^{\text{ex}}$ and $V_{A,B}$ are the phase volumes. Eq. 6 was expressed in Ref. [5]

in terms of species chemical potentials. It simply ensures equality of all chemical potentials in the coexisting phases. We can obtain all $\rho_{\alpha(A)}$ from Eqs. 4 and 6, given $\{\mu_0^{\text{ex}}, \mu_1^{\text{ex}}, \dots\}$, for which we require F^{ex} .

To find F^{ex} , let us write the polydisperse Hamiltonian as $H_{\text{poly}} = H_{\text{mono}} + H_1$, the sum [14] of a monodisperse reference and a perturbation. Using Eq. 1, the free energy is evaluated from a configurational integral [12] as

$$F_{\text{poly}}^{\text{ex}} = F_{\text{mono}}^{\text{ex}} - \ln \langle \exp -H_1 \rangle_{\text{mono}}, \quad (7)$$

which resembles the usual expression [15] for the free energy of a perturbed system, but applies *only to the excess parts*. Thermal averages with respect to the monodisperse reference system are denoted $\langle \dots \rangle_{\text{mono}}$. Assuming the Hamiltonian $H_{\text{poly}}(\{\mathbf{r}_i, \varepsilon_i\})$ is differentiable with respect to the ε_i s, we expand it to first order to find

$$H_1 = \sum_{j=1}^N \varepsilon_j K_j(\{\mathbf{r}_i\}) \quad (8)$$

where $K_j(\{\mathbf{r}_i\}) = (\partial H_{\text{poly}}/\partial \varepsilon_j)|_{\{\varepsilon_i\}=\{0\}}$ and $\{\mathbf{r}_i\}$ are the particle positions. We have not assumed *any* special properties of the Hamiltonian (not even pairwise additivity of interactions) except differentiability. K_j is a property of particle j . Substituting Eq. 8 into 7 gives $F_{\text{poly}}^{\text{ex}} = F_{\text{mono}}^{\text{ex}} + \sum_{j=1}^N \varepsilon_j \langle K_j(\{\mathbf{r}_i\}) \rangle_{\text{mono}} + O(\varepsilon^2)$. As the thermal average is taken in the reference system of identical particles, it is independent of j . We write $\langle K_j \rangle_{\text{mono}} = \langle K \rangle_{\text{mono}}$, which is the mean rate of change of total energy from varying the property ε of *any* particle. Eq. 7 therefore yields

$$F_{\text{poly}}^{\text{ex}}/V = F_{\text{mono}}^{\text{ex}}/V + \langle K \rangle_{\text{mono}} \rho_1 + O(\varepsilon^2). \quad (9)$$

A strength of the perturbative approach is that high moments are of high order in small quantities, so $F_{\text{poly}}^{\text{ex}}$ truncates naturally. (We have stopped at first order.) In previous approaches [5,10] such truncation was necessary but arbitrary. Since $\mu_\alpha \equiv \delta F^{\text{ex}}/\delta \rho_\alpha = 0$ for $\alpha > 1$, the infinite sum in Eq. 6 becomes finite, and the equations are tractable. Eq. 9 yields $\{\mu_0^{\text{ex}}, \mu_1^{\text{ex}}\}$ in terms of $\{\rho_0, \rho_1\}$, thus, with Eqs. 4 and 6, solving the problem. The solution involves linearising the factor multiplying $f_P(\varepsilon)$ in Eq. 6, but *not* in any way approximating $f_P(\varepsilon)$ itself. Consequently, so long as the distribution is narrow, it can have any shape, including the case of some components appearing in finite amounts (contributing delta spikes), which was treated separately in Ref. [5].

Defining the origin of ε so its mean vanishes in the parent, $\overline{\varepsilon_P} \equiv 0$, we find that normalized distributions in the daughter phases differ by $\Delta p(\varepsilon) \rightarrow -\varepsilon p_P(\varepsilon) \Delta \langle K \rangle_{\text{mono}}$. Hence their α th moments differ by

$$\Delta \overline{\varepsilon^\alpha} \rightarrow -\overline{\varepsilon_P^{\alpha+1}} \Delta \langle K \rangle_{\text{mono}} \quad (10)$$

as $\overline{\varepsilon_P^2} \rightarrow 0$, which is proportional to the *next* moment of the parent distribution. Eq. 10 constitutes a full solution

[16] of the two-phase coexistence problem to lowest order in polydispersity. Taking $\alpha = 1$, we find that the separation $\Delta\bar{\varepsilon}$ of daughter distributions is proportional not to the *width*, but to the *variance* of the parent. For $\alpha = 2$, Eq. 10 prescribes the daughters' variances. (In fact Eq. 10, with closure by conservation of matter [16], gives the *second moments* of the phases, $\overline{\varepsilon^2}_{A,B}$. To lowest order, 'variance' $\sigma^2 \equiv \overline{\varepsilon^2} - \bar{\varepsilon}^2$, and 'second moment' are interchangeable since the difference, $\bar{\varepsilon}^2_{A,B}$, is of fourth order in the width of the parent.) Eq. 10 asserts that purification (which requires one daughter to have a smaller variance than the parent, resulting [16] in a finite $\Delta\bar{\varepsilon}^2$) of a slightly polydisperse sample by phase separation (*e.g.* [2]) is ineffective unless the sample's distribution is strongly skewed, $\bar{\varepsilon}_P^3 \neq 0$.

The system-dependent constant of proportionality $\Delta\langle K \rangle_{\text{mono}}$ in Eq. 10 is a function of properties of the two coexisting phases, but not of α [17]. Hence, to lowest order, the ratio of differences of any two moments in the daughter phases,

$$\Delta\bar{\varepsilon}^\alpha / \Delta\bar{\varepsilon}^\beta = \overline{\varepsilon_P^{\alpha+1}} / \overline{\varepsilon_P^{\beta+1}} \quad (11)$$

is, surprisingly, independent of any properties of the phases themselves (even the nature of the interactions). It relies only on the parent from which they came. As Eq. 11 contains no system-dependent parameters, it constitutes a universal law of slightly polydisperse systems. We restate that the small number ε may be *any* distinguishing property of the particles, such as relative size, charge or mass, expressed dimensionlessly. Having identified no particular physical scale for the property, we must clarify what constitutes 'small'. Linearization of the distribution's prefactor in Eq. 6, and of Eq. 7 to produce Eq. 9, is a good approximation over some range of ε . This range defines the maximum width of $p(\varepsilon)$ for which the calculation is valid. The *extra* assumption that the Hamiltonian may be expanded as Eq. 8 is not vital to the final result. Even hard spheres, whose interactions are non-differentiable, have a linearizable excess free energy (as Eq. 9). Their moments therefore obey Eq. 10, but with $\Delta\langle K \rangle_{\text{mono}}$ an *unknown* [12] constant of proportionality, which still cancels to give Eq. 11.

Eqs. 10 and 11 can, in principle, be tested by observing phase equilibria in *any* slightly polydisperse system. Here we report results obtained from colloidal suspensions with polydisperse particle radius R . We define the deviation of the i th particle ε_i by $R_i \equiv \overline{R_P}(1 + \varepsilon_i)$, with $\overline{R_P}$ the mean radius in the parent sample. To date, experiments on polydisperse colloids have concentrated on characterisation by static or dynamic light scattering; little data on polydisperse colloidal phase equilibria exist. We have performed comprehensive measurements on two-phase coexistence in a model system: mixtures of sterically-stabilised polymethylmethacrylate (PMMA) particles and random-coil polystyrene (PS) dispersed in

cis-decahydronaphthalene (cis-decalin). The particles behave as nearly-perfect hard spheres. Exclusion of polymer molecules from the region between the surfaces of nearby PMMA particles creates an imbalance in osmotic pressure, pushing the particles together [18]. The resultant effective 'depletion' pair potential between the particles is attractive, and a function of individual colloidal radii. The topology of the phase diagram of such a mixture with *monodisperse* components depends on the polymer-colloid size ratio, $\xi = r_g/R$ [19]. When $\xi \gtrsim 0.25$, the phase behavior resembles that of a simple atomic substance (*e.g.* argon). In particular, samples with suitable concentrations of colloid and polymer show coexistence between colloidal gas and liquid phases. To test Eq. 11 for $\alpha = 2$, $\beta = 1$, a parent stock of polydisperse PMMA colloid was first characterised by measuring the sizes of 830 particles from a dried sample imaged in a transmission electron microscope. To check that our counting was representative, we also measured the form factor by static light scattering, and compared it [20] to the average form factor calculated using the measured particle size distribution [21]. These measurements gave for the stock an average radius $\overline{R_P} = 167\text{nm}$, a polydispersity $\sigma_P \equiv \overline{\varepsilon_P^2}^{1/2} = 0.18$, and third to second moment ratio $\overline{\varepsilon_P^3} / \overline{\varepsilon_P^2} = -0.113 \pm 0.012$. The PS used has molecular weight $M_w = 6.85 \times 10^6$ amu. Its polydispersity, given by $M_w/M_n \approx 1.07$, does not impinge upon this study [22]. In cis-decalin at the experimental temperature ($20 \pm 2^\circ\text{C}$), the PS has mean radius of gyration $\overline{r_g} \approx 94\text{nm}$. Addition of sufficient PS to the colloidal stock brings about separation into coexisting colloidal gas and liquid phases [23]; the high stock polydispersity precluded formation of colloidal crystals [24]. Several samples were prepared in the gas-liquid coexistence region. In each case, when phase separation was complete, the two phases were separately extracted and the particle size distribution in each was analysed, by fitting a Schultz distribution to measured form factors. This procedure allows us to estimate the difference in variances of the distributions, $\Delta\sigma^2$, and the fractional difference in the means, $\Delta\overline{R}/\overline{R_P}$, in each pair of coexisting phases. In Fig. 1, $\Delta\sigma^2$ is plotted against $\Delta\overline{R}/\overline{R_P}$, the error bars reflecting the tolerance of the fit. Eq. 11 predicts a line of proportionality with slope $\overline{\varepsilon_P^3} / \overline{\varepsilon_P^2}$ which, from our measurements of the stock colloid, is not only of the right *sign* and order of magnitude, but is close to the slope of best fit, weighted by inverse-square uncertainties.

Work is in progress to test a particular case of Eq. 10, namely $\Delta\bar{\varepsilon} \propto \sigma_P^2$, using a variety of parent colloidal suspensions. This power law is somewhat surprising, as one might expect the distance between daughters $\Delta\bar{\varepsilon}$ to scale with the width σ_P of the parent, since σ_P restricts the available range of species. The reason for the *extra* factor σ_P stems from Eq. 3. The excess chemical potential,

deriving from interactions, causes the concentrations of the two phases to differ. It is a function of species property ε . If it depends only weakly on ε , we may expect

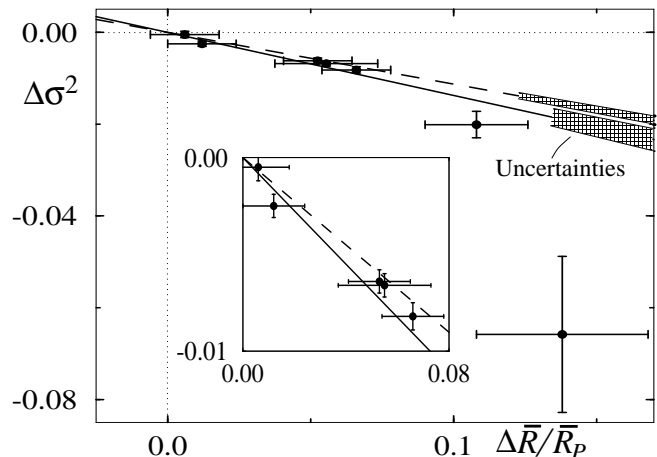


FIG. 1. Difference in variances of distributions in daughter phases *versus* fractional difference in mean particle radii, for various fluid-fluid separations of the same parent sample. Line: Best fit through origin (& uncertainty). Dashed: Gradient $\overline{\varepsilon}_P^3 / \overline{\varepsilon}_P^2$ (& uncertainty). Inset: Enlarged near origin.

little fractionation between phases, as all species feel approximately the same driving force. So it is *differences* in $\Delta\mu^{\text{ex}}$ for different ε s which bias the shapes of the distributions, making one species partition itself differently from another. As all species are similar, these differences are small (of order $\sigma_P d\Delta\mu^{\text{ex}}/d\varepsilon$). This small ‘biasing force’ on the shapes of the distributions is the source of the extra factor σ_P in the power law. So Eq. 10 is understood for $\alpha = 1$. Heuristically, Eq. 10 is at least reasonable for $\alpha = 2$. For a symmetric parent, the biasing force happens to leave the variances of both daughters equal to that of the parent. One phase may prefer large particles, accentuating the high- ε end of its distribution, but this is exactly balanced by loss from the low- ε end. It seems reasonable, however, that the daughters’ widths should differ if one end of the parent distribution is more ‘compact’ than the other. That is, one daughter will be purer than the other if their parent is skewed.

To summarise, we have derived universal laws governing two-phase coexistence in slightly polydisperse systems (Eqs. 10 and 11), which show that skewness in the parent is required for purification and that fractionation, $\Delta\overline{\varepsilon}$, is dependent on variance rather than width. Experimental results provide support for Eq. 11, and demonstrate how measurements of one moment permit the inference of another. It is remarkable that the complexities of polydisperse statistical mechanics should give rise to universal results of such mathematical simplicity and experimental utility.

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- [16] The value of a moment $\overline{\varepsilon}^\alpha$ in *each* phase (*A,B*) is calculable from the difference $\Delta\overline{\varepsilon}^\alpha$ by appealing to conservation of matter, expressed as $N_A \overline{\varepsilon}_A^\alpha + N_B \overline{\varepsilon}_B^\alpha = N \overline{\varepsilon}_P^\alpha$, with $N_{A,B}$ the number of particles in each phase [10,12].
- [17] For a central, pairwise-additive, isotropic, symmetric interaction potential $U(r, \varepsilon_1, \varepsilon_2)$, dependent on the properties $\varepsilon_1, \varepsilon_2$ of two particles of separation r , $\langle K \rangle_{\text{mono}} = 4\pi\rho \int_0^\infty r^2 \frac{\partial U(r, \varepsilon, 0)}{\partial \varepsilon} \Big|_{\varepsilon=0} g(r) dr$ with $g(r)$ the monodisperse radial distribution function [12].
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