Study of phase-diagram domains

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Abstract

We propose a novel approach to calculate the thermodynamic phase diagrams. Differing from the conventional method in which the boundaries of the coexisting phases are the ultimate goal, the present work crosshatches the domains of the homogeneous phase and also the phases in coexistence. This was done by treating the separated phases as a composite system whose Helmholtz free energy density is expressed as the sum average of the constituent free energy densities which are weighed by their respective volume proportions. As a result, both the domains of the coexisting phases and the homogeneous single phase can be determined in addition to locating the phase boundaries, customarily obtained by imposing the thermodynamic equilibrium conditions of equal pressure and equal chemical potential. We illustrate the elegance of the theory by studying a thermally responsive microgel system.

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1. Introduction

Phase separation is an ubiquitous scenario. To describe this phenomenon theoretically, it is customarily in the literature to apply the thermodynamic equilibrium conditions by imposing the pressure $p$ and chemical potential $\mu$ of one phase (gas, liquid or solid) be equal to another phase (gas, liquid or solid). Mathematically, we require that the coexisting phases 1 and 2 satisfy $p_1 = p_2$ and $\mu_1 = \mu_2$. Depending on the control parameter which can be the temperature $T$ or the electrolyte concentration $n^{(s)}$, the solutions sought for are the two colloidal number densities $\rho_i$ and $\rho_j$, characterizing either the one phase, $i = j$, or the coexisting phases, $i \neq j$. For concreteness, let us consider a charged colloidal dispersion. For this physical system, one can apply the above-mentioned equilibrium conditions to locate the boundaries of a phase diagram, $T$ vs $\rho$ or $n^{(s)}$ vs $\rho$, if solutions exist for the coexisting colloidal densities $\rho_1$ and $\rho_2$ at each $T$ or initial $n^{(s)}$. This is the usual strategy often used in statistical thermodynamics for studying the phase transition. In this work, we draw attention to a novel means for understanding coexisting phases. The main idea is to view the coexisting phases as a composite system whose Helmholtz free energy density is taken to be the sum average of the constituent free energy densities which are weighed by their respective volume proportions. With the present approach, the domains of phase separation are crosshatched and the calculation leads naturally to the phase boundaries of demarcation. In addition, we obtain the volume proportion occupied by each of the phases in coexistence. This information on the volume proportions has much bearing on a thermally sensitive volume transition property observed [1,2] to occur in aqueous microgel dispersions. In view of this, we shall direct the present theory to the study of an aqueous dispersion of microgel particles thermally driven to undergo a volume transition. As demonstrated below for an aqueous poly-N-isopropylacrylamide (PNIPAM) dispersion, the calculated phase equilibrium behavior needs only the initial number density $\rho_1$ of colloids. Operationally, the methodology resembles

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the laboratory condition and is therefore experimentally appealing.

2. Theory

In this section, we describe the main idea behind the present calculation of phase diagram and give some essential details.

2.1. Theoretical framework

To present the theory in its most general form, we consider a homogeneous charged colloidal dispersion comprising of $N_i$ charged colloids and $N_i^{(s)}$ small ions (counterions and co-ions) embedded in a dispersive medium that is maintained at temperature $T$. These charged species are confined to a total volume $V$ giving the total number densities of colloids and small ions, $\rho_i = N_i/V$ and $\rho_i^{(s)} = N_i^{(s)}/V$ (> mM, assuming appreciable amounts), respectively. Suppose, under favorable thermodynamic conditions, the colloidal system undergoes phase separation into two coexisting subsystems. Let us assume $V_1$ and $V_2$ be their volumes. Inside $V_i$, $i = 1, 2$, we suppose that there are $N_i$ colloids; the corresponding number densities are $\rho_i = N_i/V_i$. Hereafter the subscripts $i = 1$ and 2 refer to phase-separated subsystems containing colloids of the same species. Denoting $x_i = V_i/V$ for the $i$th subsystem volume proportion, we proceed viewing the phase separation as a 'composite' system and write its Helmholtz free energy density as

$$f_m(\rho_1, \rho_2; \xi) = x_1 f_1(\rho_1, \xi) + x_2 f_2(\rho_2, \xi)$$

(1)

where $f_i$ is the $i$th subsystem free energy density which can be a solid, liquid or gas depending on the thermodynamic equilibrium conditions. The variable $\xi$ is the control parameter which can be the temperature $T$ or the electrolyte concentration. Now, if the combined operation of electrostatic and thermal effect were to induce phase separation in the colloidal dispersion, in that case the homogeneous system decomposes into $f_1(\rho_1, \xi)$ and $f_2(\rho_2, \xi)$, the composite free energy density $f_m$ given by Eq. (1) must have a lower energy value than the free energy densities $f_1$ and $f_2$ evaluated at the same initial number density $\rho_1$ and the control parameter $\xi$. The conservation constraints of volume and particle number then permit writing the subsystems $x_i$ as $x_1 = (\rho_1 - \rho_2)/(\rho_1 - \rho_2)$ and $x_2 = -(\rho_1 - \rho_2)/(\rho_1 - \rho_2)$. To ensure a lowest free energy density $f_m$, we require

$$\left(\frac{\partial f_m}{\partial \rho_1}\right)_{\rho_2, \xi} = 0$$

(2)

$$\left(\frac{\partial f_m}{\partial \rho_2}\right)_{\rho_1, \xi} = 0$$

(3)

subject to the conditions $x_1 + x_2 = 1$ and $x_1 \rho_1 + x_2 \rho_2 = \rho_1$. The latter constraints together with Eqs. (2) and (3) can be shown by the method of Lagrangian’s undetermined multipliers [3] to be equivalent to

$$\mu_i(\rho_1) = \mu_2(\rho_2)$$

(4)

$$p_i(\rho_1) = p_2(\rho_2)$$

(5)

which are two familiar thermodynamic conditions satisfied by two subsystems in coexistence [4,5]. Eqs. (4) and (5) are the necessary and sufficient thermodynamic equilibrium conditions for mapping out the boundaries of the $\xi - \rho$ phase diagram. Accordingly, one can employ Eq. (1) to crosshatch the domains (as well as the phase boundaries) of two coexisting phases of a colloidal dispersion either in the presence of salts in appreciable amounts or under the thermal effect at prescribed temperature by minimizing $f_m$ only. In other words, given $\rho_i$ and $\xi$ which are the usual initial input data in all colloidal experiments, Eq. (1) can be used to determine $(\rho_1, \rho_2; \xi)$ and hence the $\xi - \rho$ phase diagram. This feature of the present method is spectacular for $f_m$ yields naturally also the volume proportions of the subsystems in coexistence that are ubiquitously observed [6] and have actually been measured [7] for colloidal systems.

To illustrate the distinctiveness of the present approach, we have chosen to study the aqueous neutral microgel particles where $T$ is the control parameter. In this case Eq. (1) reads

$$f_m(\rho_1, \rho_2; T) = x_1 f_1(\rho_1, T) + x_2 f_2(\rho_2, T)$$

(6)

and we proceed by seeking solutions $\rho_i$ that minimize $f_m(\rho_1, \rho_2; T)$ subject to the conservation constraints of volume and particle number. To implement this method, we need the Helmholtz free energy densities for the liquid and solid phases to which we turn next.

2.2. Helmholtz free energy densities of a liquid and a solid

Within the first order thermodynamic perturbation theory [5], the Helmholtz free energy density $f_1$ for the $\lambda$ phase (liquid or solid) can be written, quite generally,

$$\beta f_1 = \beta f_1^{\text{hs}} + 12\eta^2 \int_{1}^{\infty} x^2 g_1^{\text{hs}}(x) (\beta u_A) \, dx$$

(7)

where $\beta = 1/(k_B T)$ is the inverse temperature, $\eta = \pi \rho a^3/6$ is the microgel volume fraction in which $\rho$ and $a$ are the particle diameter and number density respectively, $u_A$ is the van der Waals attractive potential to be empirically determined by light scattering experiments, and $f_1^{\text{hs}}$ and $g_1^{\text{hs}}$ are the hard-sphere free energy density and the pair correlation function for the $\lambda$ phase, respectively. For a liquid (solid) $f_2 \rightarrow f_1(\xi \rightarrow f_0)$ in which $f_2^{\text{hs}} = f_1^{\text{hs}} (f_1^{\text{hs}} = f_s^{\text{hs}})$, the explicit form is given in Refs. [5,8], and for the quantity $g_1^{\text{hs}} = g_1^{\text{hs}} (g_2^{\text{hs}} = g_s^{\text{hs}})$, we use the Percus-Yevick [5] (modified Gaussian [9]) model. With these ingredients, $f_2$ are then

$$\beta f_2 = \left\{ \begin{array}{ll} \beta f_1 = \eta \left[ \ln \eta - 1 + \frac{4\eta - 3\eta^2}{(1 - \eta)} \right] - 12\eta^2 e^\eta \int_{1}^{\infty} x^{(2-n)} g_1^{\text{hs}}(x) \, dx & \text{(liquid)} \\ \beta f_s = -\eta \ln \left[ \frac{8}{\sqrt{\pi^3}} \left( \frac{\sqrt{x}}{\sqrt{\pi}} \right)^{1/3} - 1 \right]^3 - 12\eta^2 e^\eta \int_{1}^{\infty} x^{(2-n)} g_s^{\text{hs}}(x) \, dx & \text{(solid)} \end{array} \right.$$
where we have set $\beta u_A = -\varepsilon'(\sigma/r)^n$ with
\[
\varepsilon' = \gamma_A(T_0/T)(\sigma_0/\sigma)^{6+n}
\tag{9}
\]
In Eq. (9), $x = r/\sigma$ is the reduced distance, $\sigma_0$ is the particle diameter at the preparation condition, and $\gamma_A$ and $T_0$ are dimensionless constants. We should emphasize, that for the microgel particle, the Hamaker constant (see $\varepsilon'$ given above) is proportional to the square of the number density $\rho_{\text{polymer}}$ of the polymeric groups within each particle. The dispersion strength of attraction between microgel particles is therefore very much influenced by $\rho_{\text{polymer}}$ which in turn is dependent on the thermally responsive behavior of $\sigma$.

3. Numerical results

To proceed to numerical work, it is necessary to stipulate the parameters appearing in Eq. (9). For these quantities, we are guided by the static and dynamic light scattering results of the neutral PNIPAM particles carried out by Wu et al. [8]. Considering their experimental analysis, we set $\gamma_A = 0.43 \times 10^{-5}$, $T_0 = 293.002$ K, $n = 8$ and $\sigma_0 = 251.6$ nm. These values are determined by resorting to the osmotic second virial coefficients obtained from static light scattering measurements [8].

3.1. Liquid–solid and volume phase transition

Fig. 1(a) shows our predicted phase boundaries for a ‘line-domain’ judiciously selected at the fixed initial $\eta_1 = 0.56$. Increasing $T$ at this $\eta_1$, i.e. along the normal $\eta = \eta_1$, we proceeded by optimizing $f_m$ defined by Eq. (6). At each $T$, we search for the lowest energy value $f_m$. This was done by scanning all possible combinations of two phases in coexistence, the liquid–liquid, liquid–solid, solid–solid, etc. as well as the homogeneous vapor, liquid and solid phases at the same initial $\eta_1$. It was observed [8a,8b] that the PNIPAM particles are thermally sensitive, and as a result, swell (leading to an increase in $\sigma$) with decreasing $T$. To describe the thermal change of $\sigma(T)$, we use the modified Flory-Rehner theory [10] to account for the temperature dependence of $\sigma$; the reliability of $\sigma(T)$ obtained in this manner has been critically assessed in Fig. 1(b) against the static and dynamic light scattering data [8]. In Figs. 1(a) and (c), we depict, respectively, the $T$ vs $\eta$ and $T$ vs $x_i$ calculated at the fixed initial $\eta_1 = 0.56$. To proceed further, we give also in Figs. 2(a)–(d) more details of our calculated phase diagrams $T$ vs $\eta$ in order to exhibit the volume proportion which is a unique feature displayed by the PNIPAM microgel system. In these figures, we have chosen four initial volume fractions, namely, $\eta_1 = 0.25$, 0.35, 0.45 and 0.63 as parts of our phase-diagram domains to be investigated.

4. Discussion

Let us scrutinize Fig. 1(a). The first striking feature is that the coexisting phases predicted using Eq. (6) agree excellently with the phase boundaries obtained by matching the thermodynamic equilibrium conditions of equal pressure and equal chemical potential thus lending great credence to the present theory. Coming to Figs. 2(a)–(d), there are two aspects that merit emphasis. First, it is seen that the microgel particles undergo phase separation into a (very) low density liquid coexisting with a (f.c.c.) solid for $309 < T < 310$ K if the system is prepared at a lower initial $\eta_1 (< 0.1)$. If, however, we begin with a higher $\eta_1 (> 0.2)$ (see, for example, Fig. 2(a)), it will change from a (very) low-density-liquid–solid transition for $309 < T < 310$ K to a higher-density-liquid–solid transition for $T < 309$ K. This kind of the two-stages phase-transition scenario (Figs. 2(a)–(d)) is more conspicuously manifested if we proceed along the normal at a larger $\eta_1 (> 0.3$, say). Second, for very low initial $\eta_1 (< 0.1)$, it can be inferred from the trend displayed in Figs. 2(a)–(d) that the vapor-like phase occupies a distinctly large volume proportion; however, as $\eta_1$ is increased ($0.25 \rightarrow 0.35 \rightarrow 0.45 \rightarrow 0.63$), the microgel particles undergo subtle changes in their occupation of volume. The system is driven first shifting from $x_1 \gg x_2$ for $\eta_1 < 0.1$ (hereafter $x_1$ and $x_2$ refer to the volume proportions of the phases at a lower and a higher densities, respectively) to the volume proportion ratio $x_1:x_2 = 0.62:0.38$ (liquid:solid) at $\eta_1 = 0.25$, narrowing the ratio reversely to

Fig. 1. (a) Domain of microgel phase diagram (open triangles) calculated at an initial $\eta_1 = 0.56$ along the normal where $T$ decreases. At each $T$, we search for the lowest $f_m$. The boundaries of the coexisting phases (open circles for low density fluid and solid circles for high-density solid) agree excellently with results (full curves) obtained by the conditions of matching the pressure and chemical potential; (b) Variation of the microgel particle radius with temperature $T$ calculated using the modified Flory-Rehner theory [10] compared with experimental data (solid circles) taken from Wu et al. [8]; (c) Temperature $T$ versus volume proportion $x_i$ for the microgel dispersion that corresponds to (a) calculated at initial $\eta_1 = 0.56$. 
\[ x_1 : x_2 = 0.48 : 0.52 \] at \( \eta_1 = 0.35 \), then widening still the reversed ratio at \( \eta_1 = 0.45 \) to \( x_1 : x_2 = 0.33 : 0.67 \), and finally at \( \eta_1 = 0.63 \) approaching the volume transition scenario with the solid occupying a much larger volume than the coexisting liquid. Accordingly, there is a subtle shift-over in the volumes occupied by the coexisting fluid and solid phases if one prepares the initial \( \eta_1 \) from a small value (<0.1) to a large one (>0.4). One sees, in particular, that the solid phase is thermally induced and it changes from a crystalline phase in sparse island-like distribution for \( \eta_1 \) < 0.1 to one that occupies space for >90% for \( \eta_1 \) > 0.63.

These two aspects are intimately related and they can be understood by examining the thermal change of \( \sigma(T) \). In this essentially collapsed state, there is a significant increase of \( \rho_{\text{polymer}} \) inside the microgel particles. As pointed out above (see remarks made below Eq. (9)), this would lead to a strong increment of the strength of attraction. At a low \( \eta_1 \), the microgel particles can form a sparse island-like crystal energetically induced by this strong short-ranged attraction. However, the low \( \eta_1 \) environment has considerably limited its large scale formation. For a higher \( \eta_1 \), the average inter-particle distance is relatively smaller. Now, the swelling of microgel particles for decreasing \( T \) has an additional feature, however. On the one hand, at higher \( \eta_1 \), it accelerates the crystalline phase formation, but on the other hand, it enhances also the possibility of the microgel particles being driven to become a liquid phase at a lower \( T \) when \( u_A \) is getting small. The higher density liquid formation therefore arises from the swelling of microgel particles and may be physically traced to the accompanying decrease of \( \rho_{\text{polymer}} \) with decreasing \( T \). It is interesting to note that in the temperature range \( 307 < T < 310 \) K considered here a drastic change in \( x_i \) occurs when the temperature falls below \( T_v \) corresponding to a volume transition which is approximately 309.07 K (Fig. 2(f)) for \( \eta_1 = 0.35 \) and 308.9 K (Fig. 2(g)) for \( \eta_1 = 0.45 \). Apparently, \( T_v \) decreases further if we start with a larger \( \eta_1 \). There is thus a direct dependence of the attractive strength \( u_A \) and the hard-sphere-like repulsion on \( \eta_1 \) as \( T \) decreases. In view of this fluctuation in magnitude for the attraction and repulsion, it is perhaps worthwhile to delve further into the lower \( T \) regime. Let us return to Fig. 1(c) and scrutinize the \( x_i \) calculated at \( \eta_1 = 0.56 \). For \( T > 307.125 \) K, the fluid (solid) occupies less (more) than 20\% (80\%) of the total volume. These spatial occupancies can again be interpreted in terms of the swelling property thermally reflected in microgel particles. Perhaps more interesting is the scenario where the microgel system crosses \( T = 307.125 \) K in the direction of decreasing \( T \). Now, it is seen that the liquid (solid) occupies more (less) space in contrast to \( T > 307.125 \) K. We attri-
bute this volume transition phenomenon to the significant swelling in size of each microgel particle (Fig. 1(b)) and that will result in a drastic decrease of \( \rho_{\text{polymer}} \) and hence drive the microgel particles to resemble hard spheres as indeed observed \[8\].

5. Conclusion

In this work we present a theoretical means to study phase diagrams. The distinctive feature of the theory is that it can be generalized, in principle, to crosshatch the domains of multi-phases in coexistence which are either a formidable task to obtain or rather tedious to implement numerically with an approach as resorting to Eqs. (4) and (5). Quite similar line of thought as the present work has been independently advanced by Bodnář and Oosterbaan \[7\] and Renth et al. \[11\] in their studies of colloid-polymer mixtures. To summarize, our present studies suggest the following:

(a) The phases in coexistence can be accurately obtained by optimizing the ‘composite’ Helmholtz free energy in terms of the constituent densities pertaining to the coexisting phases. Since the calculation does not need to evaluate the derivatives of the thermodynamic functions, reliability of numerical results is ensured.

(b) Using the present method, both the domains and the phase boundaries of phase separation of microgel particles are determined. In crosshatching the domains of the coexisting phases, the volume proportions occupied by microgel particles in each coexisting phase are predicted as well. It is found here that the swelling property of microgel particles with temperature has important bearing on the calculated phase diagram, notably the volume transition.

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References

[10] T. Hino, J.M. Prausnitz, Polymer 49 (1998) 3279. In using formulas (Eqs. (8), (11) and (13)) given in this reference to calculate \( \sigma \) at each \( T \), we make the tacit assumption that the microgel particles are homogeneous spheres with an effective radius defined by \( (\sqrt{5/3}R_g + R_H)/2 \) (see Ref. \[8b\]), \( R_g \) and \( R_H \) being the measured radius of gyration and hydrodynamic radius, respectively. The introduction of an effective radius is for two reasons. First, it was experimentally observed in static light scattering measurement (Fig. 2(a) of Ref. \[8b\]) that \( R_g \) changes drastically with \( T \) near the volume transition temperature due to the inhomogeneity of microgel particles resulting in a nonuniform volume change within individual particles [T. Hu and C. Wu, Phys. Rev. Lett. 83 (1999) 4105], whereas from the dynamic light scattering measurement, \( R_H \) is observed to be less sensitive to \( T \) in the same temperature range of volume transition due to the dangling chains outside. Second, to proceed to the theoretical calculation, we need to account for the excluded volume of microgel particles at each prescribed \( T \) and, to minimize numerical uncertainties, a continuous variation of the effective radius (and hence \( \sigma \)) is preferred. As illustrated in Fig. 1(b), the calculated effective radius is reasonably well reproduced using the modified Flory-Rehner theory. The interested readers are referred to Ref. \[8b\] for further experimental details.