Non-monotonic temperature response of polymer mediated interactions

Xie, Fei; Woodward, Clifford E; Forsman, Jan

Published in:
Soft Matter

DOI:
10.1039/c5sm02420j

2016

Citation for published version (APA):
Xie, F., Woodward, C. E., & Forsman, J. (2016). Non-monotonic temperature response of polymer mediated interactions. *Soft Matter*, *12*, 658-663. https://doi.org/10.1039/c5sm02420j

Total number of authors:
3

Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Non-monotonic temperature response of polymer mediated interactions[†]

Fei Xie,[*a] Clifford E. Woodward,[b‡] and Jan Forsman [a]

Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

In a recent publication, Feng et al. [Feng *et al., Nature Mater.*, 2015, 14, 61] reported very interesting re-entrant solidification behaviour of colloidal particles in an aqueous solution containing polyethylene oxide (PEO). In this system, a crystalline colloidal phase, which is present at low temperatures, melts to a homogeneous fluid upon increasing the temperature. Further raising the temperature, however, eventually gives rise to a flocculated colloidal phase. Feng et al. proposed that the low-temperature crystalline phase is caused by polymer depletion while, at higher temperature, an increased attraction between polymers and particles leads to bridging attractions, and colloidal flocculation. The intermediate temperature regime sees the colloidal interactions dominated by charge repulsion, giving rise to a fluid phase. In the model by Feng et al., polymers are treated as hard spheres, which interact with the colloids via a phenomenological, temperature dependent potential. In this work, we develop a more detailed polymer density functional treatment, based on a model for aqueous PEO solutions that was originally developed by Karlström [Karlström *The Journal of Physical Chemistry*, 1985, 89, 4962] for bulk solutions. In this model, monomers are assumed to be in either of two states, labelled *A* and *B*, where *B* is more solvophobic than *A*. On the other hand, the degeneracy of the *B* state exceeds that of *A*, causing the population of solvophobic monomers to increase with temperature. If the colloidal particles are also solvophobic, then this model displays the same qualitative temperature response as was observed by Feng et al. That is, at low temperatures, *A* type monomers predominate and one observes depletion interactions, whereas polymer bridging dominates at higher temperatures, due to the attraction between *B*-type monomers and the colloidal surface. Interestingly, the intermediate temperature regime is characterized by a polymer mediated interaction between colloids which is *repulsive*. That is, according to our model the homogeneous fluid phase would form even in the absence of repulsive electrostatic interactions. We emphasize that our model does *not* rely upon any temperature-dependent interactions. Furthermore, *all* possible polymer configurations are accounted for, subject to a mean-field Boltzmann weight. Finally, we show that interactions between colloids, mediated by neutral non-grafted polymers, generally follow the trend: attraction => repulsion (or vanishing interaction) => attraction as the surface affinity toward monomers proceeds from repulsive to attractive.

The large parameter space spanned by the myriad of possible interactions between large particles, polymers and solvent molecules implies a rich phase behaviour in these systems. For example, polymer solutions may induce particle flocculation or act as stabilizers depending upon these factors. Varying conditions can influence stability, allowing some degree of control. This versatility has created significant interest in this field, which is both academic and application-based.

It is well-known that high concentrations of non-adsorbing polymers can destabilize particle dispersions via so-called depletion attractions. Alternatively, if polymers adsorb to particle surfaces, they may cause flocculation via the formation of bridges. Polymer mediated *repulsive* interactions between particles can be obtained by grafting one end of non-adsorbing polymer molecules onto the particle surfaces. The resultant "hairy" particles will repel each other, due to the configurational entropy cost associated with confining polymers between approaching surfaces. However,

---

[a] *Theoretical Chemistry, Lund University, P.O.Box 124, S-221 00 Lund, Sweden. Fax: +46468225; Tel.:+46462220381; E-mail: fei.xie@teokem.lu.se*

[b] *School of Physical, Environmental and Mathematical Sciences, University College, University of New South Wales, ADFA, Canberra ACT 2600, Australia.*

[†] Electronic Supplementary Information (ESI) available: [In the ESI, we show how the lower critical solution temperature varies with polymer length, and demonstrate the validity of a thermodynamic consistency rule. We furthermore show that there is a regime between adsorbing and non-adsorbing surfaces, where polymer mediated interactions are either repulsive or essentially vanishing. This is demonstrated for ideal chains, in which case the results are exact, as well as for excluded volume polymers ("good solvent").].

for non-grafted polymers, a well-known theorem by deGennes[1] purports that polymer mediated interactions are *always attractive*. We have previously demonstrated that deGennes' theorem is not universally valid[2], and that repulsions can be induced by non-grafted polymers, for certain systems, some examples of which will be considered below.

An interesting study, of particular relevance to these considerations, was recently published by Feng et al.[3] They investigated polymer-colloid dispersions at various temperatures, and with a rather high polymer concentration. At low temperatures, i.e., under good solvent conditions, the systems formed colloidal crystals, under the action of polymer-induced depletion. However, upon raising the temperature, the crystals melted and homogeneous dispersions were formed. Surprisingly, a further increase in temperature caused the particles to flocculate! To explain their results, Feng et al. constructed an effective temperature-dependent polymer/particle interaction, which switched from non-adsorbing (at low temperatures) to adsorbing (at high temperatures). In the cross-over regime their model predicts a weak interaction and with the inclusion of electrostatic repulsions between particles, the net interaction could become repulsive. In their model the polymers were crudely treated as hard spheres and a linear relation was assumed between polymer adsorption strength and temperature. The effective adsorption potential of Feng et al. is thus a *free energy*, which was arrived at by using a phenomenological approach, matched to experiment. While such modelling certainly can be useful, there is some value to be gained from explaining this phenomenon using a fundamental Hamiltonian, free from temperature-dependent interactions, in combination with a theoretical treatment in which all polymer configurations are accounted for (subject to a mean-field Boltzmann weight). That is the aim of this work. We will furthermore show that polymer-induced equilibrium surface interactions mediated by non-grafted neutral polymers can give rise to a net repulsion between particles at separations beyond a few monomer diameters (which is the relevant range in a coarse-grained polymer model). Hence, in the absence of additional DLVO interactions, our model predicts that polymer mediated interactions *alone* are able to explain the re-entrant behavior observed by Feng et al.

The particles in the systems studied by Feng et al.[3] were at least an order of magnitude larger than the radius of gyration of the polymers. This will allow us to simplify the modeling by considering the interaction between two infinitely large planar surfaces immersed in a polymer solution. The latter is characterized by its chemical potential. The interaction between spheres can then be obtained by using the Derjaguin Approximation[4]. We stress that while we are guided by the experimental systems studied by Feng et al., we will not attempt to model a *specific* experimental system. Instead we will pursue a more generic approach, which will focus on qualitative behavior, driven by plausible underlying mechanisms. Exactly the same polymer solution model was previously used by us in a study on induced capillary phase transitions in polymer solutions[5]. We provide a brief recapitulation here. With $\mathbf{R} = (\mathbf{r}_1, ..., \mathbf{r}_r)$ representing a configuration of a polymer composed of r connected monomers, we let $N(\mathbf{R})d\mathbf{R}$ denote the number of polymer molecules having configurations between $\mathbf{R}$ and $\mathbf{R} + d\mathbf{R}$. The monomers are held together by a bonding potential, $V_b(\mathbf{R})$, which allows total orientational freedom of bonds which have a fixed length, b. That is, $e^{-\beta V_b(\mathbf{R})} \propto \prod \delta(|\mathbf{r}_{i+1} - \mathbf{r}_i| - b)$. where, $\delta(x)$ is the Dirac delta function and $\beta = 1/(k_B T)$ is the inverse thermal energy. The monomers can be in either of two states, labelled as "A" or "B", with degeneracies g_A and g_B. The A monomers are solvophilic, while the B monomers are solvophobic. The entropy of the solvophobic state is larger than that of the solvophilic state ($g_A < g_B$), which implies the latter dominates at lower temperature. Raising the temperature causes demixing, as the solvophobic states will become more probable. This model gives a simple generalized representation of the generally complex interactions between monomer units and the solvent. It was first proposed by Karlström[6], to explain the lower critical solution temperature (LCST) of an aqueous PEO solution. In the specific case of PEO, the A state presumably corresponds to monomer configurations with a net dipole moment. In a recent study we showed, using this generic model, that such systems might display capillary wetting, well below the LCST[5]. We will assume that the polymer solution is incompressible. This is ensured by constraining the total density of monomers+solvent particles (assumed to have equal size) to a fixed value, n_t. That is, we have $n_t = n_m(\mathbf{r}) + n_s(\mathbf{r})$, i.e. n_t is given by the sum of monomer and solvent densities. We used such a model in earlier work[7], which can be viewed as a continuum space version of the Scheutjens-Fleer theory[8]. Introducing the monomer state probabilities P_A and P_B, we write the free energy functional of the solution, $\mathscr{F}$, as:

$$\begin{aligned}
\beta\mathscr{F} \quad = \quad & \int N(\mathbf{R})\left(\ln[N(\mathbf{R})] - 1\right) d\mathbf{R} + \beta \int N(\mathbf{R}) V_b(\mathbf{R}) d\mathbf{R} + \\
& \int (n_t - n_m(\mathbf{r})) \ln\left[n_t - n_m(\mathbf{r})\right] + n_m(\mathbf{r}) d\mathbf{r} + \beta \mathscr{U}[n_m(\mathbf{r}), P_A(\mathbf{r})] + \\
& \int n_m(\mathbf{r})(1 - P_A(\mathbf{r})) \ln\left[\frac{1 - P_A(\mathbf{r})}{g_B}\right] d\mathbf{r} + \int n_m(\mathbf{r}) P_A(\mathbf{r}) \ln\left[\frac{P_A(\mathbf{r})}{g_A}\right] d\mathbf{r} + \\
& \beta \int (n_m(\mathbf{r}) P_A(\mathbf{r}) V_{ex}^{(A)}(\mathbf{r}) + n_m(\mathbf{r})(1 - P_A((\mathbf{r})) V_{ex}^{(B)}(\mathbf{r}) + \\
& (n_t - n_m(\mathbf{r})) V_{ex}^{(s)}(\mathbf{r})) d\mathbf{r}
\end{aligned} \tag{1}$$

where $V_{ex}^{\alpha}(\mathbf{r}))$ is the external (surface) potential acting on α particles ($\alpha = A, B$ or s). The first two terms in eq.(1) represents the configurational free energy of an ideal bulk polymer solution, whereas the third integral is the ideal entropy of the solvent, taking into account that its density is constrained by the monomer density, and the incompressibility relation. Attractive interparticle interactions are collected in $\mathscr{U}[n_m(\mathbf{r}), P_A(\mathbf{r})]$:

$$\mathscr{U}[n_m(\mathbf{r}), P_A(\mathbf{r})] = \frac{1}{2} \sum_{\alpha,\beta} \int \int n_\alpha(\mathbf{r}) n_\beta(\mathbf{r}') \phi_{\alpha\beta}^{(a)}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' d\mathbf{r} \tag{2}$$

where we have defined $n_A(\mathbf{r}) \equiv n_m(\mathbf{r}) P_A(\mathbf{r})$ and $n_B(\mathbf{r}) \equiv n_m(\mathbf{r})(1 - P_A(\mathbf{r}))$. More specifically, all particles, i.e. monomers and solvent particles interact via Lennard-Jones (L-J) potentials, sharing a common size parameter σ:

$$\phi_{\alpha\beta}^{(a)}(r) = 4\varepsilon_{\alpha\beta}\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right), \qquad r > \sigma \tag{3}$$

Using ε_{AA} as a reference,we define a reduced temperature $T^* = kT/\varepsilon_{AA}$, and reduced L-J parameters $\varepsilon^*_{\alpha\beta} \equiv \varepsilon_{\alpha\beta}/\varepsilon_{AA}$. The two integrals that follow immediately after $\mathscr{U}[n_m(\mathbf{r}), P_A(\mathbf{r})]$ in eq. (1) account for the entropy associated with state degeneracies. Finally, the last three terms of eq.(1) represent the surface interactions of state A monomers, state B monomers, and solvent particles, respectively.

In principle, we are now left with an unfortunately wide range of adjustable parameters. However, we reduce this number, and simplify the model, by constraining several parameters to have the same value. Specifically, we shall adopt exactly the same bulk fluid energy parameters as were used in a previous work, where capillary induced phase separations were studied, at temperatures below the bulk LCST[5] [*]: $\varepsilon^*_{AA} = \varepsilon^*_{SS} = \varepsilon^*_{AS} = 1$, $\varepsilon^*_{BB} = \varepsilon^*_{SB} = 0.3$, and $\varepsilon^*_{AB} = \sqrt{0.3} \approx 0.45$. These values are certainly to some extent ambiguous, and they are not "optimized" to model a specific system. However, they are physically reasonable, and have been shown (cf. reference[5]) to generate a polymer solution model that displays an LCST, for long enough chain lengths. Our generic approach is partly motivated by the fact that experiments suggest that the observed behaviours are rather general and non-specific, these motivations should suffice for the present work and scope. We simplify things even further by assuming inert hard walls, which act identically on *all* species. These walls are located at $z = 0$ and $z = h$. In other words, V_{ex}, which is common to solvent particles and monomers, vanishes for $0 < z < h$, and is infinite elsewhere. We will only consider separations for which $h > 4\sigma$. Note that σ reflects the size of a solvent molecule, and with an aqueous solvent, we expect that $\sigma \approx 3.1$ Å. Thus $h < 4\sigma$ would typically correspond to less than about 1.2 nm in experiential scenarios. A coarse-grained model, such as ours, is not well suited to describe interactions at such short length scales (where solvent molecular packing, hydration forces etc. come into play).

The number of monomers in each polymer, r, is 1600 [†]. Inspired by recent DFT modelling of PEG in water at low temperatures (good solvent conditions)[9], where an optimized bond length (chosen to reproduce experimentally observed radii of gyrations) typically is 2-3 times the monomer bead diameter, we have set $b = 2\sigma$. We will consider two different choices for the ratio between monomer state degeneracies. Quantum chemical calculations[10] have identified 27 monomer rotational conformations, two of which are sterically prevented. Two out of the remaining 25 possess a strong dipole moment, presumably resulting in a strong interaction with a polar solvent. The remaining 23 conformations are less well solvated [‡]. This would imply a monomer degeneracy ratio $g_B/g_A = 11.5$[6]. In our previous study, we were guided by these arguments, and set $g_B/g_A = 12$. This value is used in the present work as well. It should be noted that the demixing loop diminishes for short polymers, and vanishes below some threshold chain length, r_c. For our set of energy parameters, and with $g_B/g_A = 12$, r_C is about 80-90. However, while experimental phase diagrams follows the same qualitative trend, the LCST persists (barely) down to PEG2000, i.e. the experimental "r_c" is slightly below 45[12]. We can achieve similar results with our model system if we set $g_B/g_A = 13$, so this option will also be explored. In the Electronic Supporting Information (ESI), we provide details on how the LCST varies with polymer length, for $g_B/g_A = 12, 13$. The idea of more polar "A states" being replaced by less polar (but more abundant) "B states" at higher temperatures find some experimental support by NMR studies of dimethoxyethane, dissolved in (highly polar) dimethylformamide[13]. According to those studies (see table 6 of ref.[13]), the relative population of the more polar *gauche* states decreases with increasing temperature.

The functional was minimized with respect to $n_m(\mathbf{r})$ as well as $P_\alpha(\mathbf{r})$. A mean-field assumption was invoked, allowing us to integrate away all dependencies in the x, y plane parallel with the confining walls. This is convenient, but the simplification does result in a loss of proper intra- and intermolecular chain correlations. The potential $\omega = \mathscr{F}/A - \int_0^h \mu_p n_m(z) dz$ where μ_p is the polymer chemical potential and A is the surface area, allows a grand canonical formulation. We also introduce $g_s(h) = \omega - \Pi h$ with Π denoting the bulk osmotic pressure. We can interpret g_s as the total (including bulk) Gibbs free energy change per unit surface area[14]. Finally, we define $\Delta g_s(h) \equiv g_s(h) - g_s(h->\infty)$ as the net interaction free energy per area.

Before we highlight the results obtained with this model, we summarize the general response of polymer mediated surface interactions to a progressively increasing adsorption. These results are interesting in their own right, and have not (to the best of our knowledge) been presented before. In order to save space, details of models and calculations are provided in the ESI. The main overall result is that there is in general a "window" regime of intermediate adsorption potentials, for which the polymer mediated surface interaction is either *repulsive*, or essentially vanishing. For stronger (more attractive) adsorption potentials, there is a net attraction, due to bridging, whereas depletion attraction dominates for weak adsorption potentials. In the ESI, we illustrate this for ideal chains (theta solvent model), in which case the results are *exact*, but also for excluded volume polymers (good solvent model). In the latter case, we have included predictions for infinitely long chains, displaying the same qualitative response. One could argue that the "window regime" is of limited practical importance, but it is actually quite relevant to the kind of colloidal systems that we aim to investigate[3], since an increase in temperature will effectively push the system from the depletion regime into the intermediate adsorption regime, and finally into the bridging dominated adsorption regime. Note that this result is *not* achieved by the use of temperature-dependent interactions. Instead the adsorption increase that results from a raised temperature, stems from a higher population of B-state monomers, which effectively have a higher surface affinity.

We now switch focus, back to our main models of this study. We

---

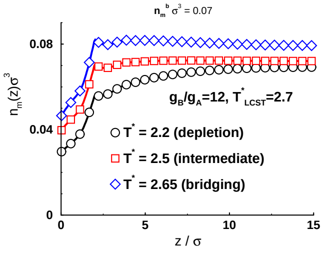
[*] A computational benefit results from shifting the reduced energy levels by one unit, since all *AA*, *AS* and *SS* interactions then vanish. Since all relative energy differences are maintained by such a global energy shift, it will have no influence upon the results.

[†] A case with $r = 400$ is given in the Electronic Supporting Information as a comparison.

[‡] One could also use hydrogen bonding ability, rather than overall dipole moment, as a measure of the monomer-solvent interactions, with a qualitatively similar result[11].

will start by investigating the model with $g_B/g_A = 12$. The bulk solution of this system displays a demixing regime, with a reduced lower critical temperature T^*_{LCST} at just above 2.7 (for $r = 1600$). In Figure 1 (a), we illustrate how the monomer density profile changes with temperature, at a single surface (for $g_B/g_A = 12$). The increased surface affinity at higher temperatures is accompanied by a higher population of B monomers (see graph (b) of Figure 1). Note that these effectively have a stronger surface affinity than the A state monomers, despite the fact that both are confined by simple hard walls. This is because the B monomers suffer a smaller energetic penalty at the surfaces, than the A monomers or the solvent particles do.

(a) monomer density distributions



(b) monomer state distributions

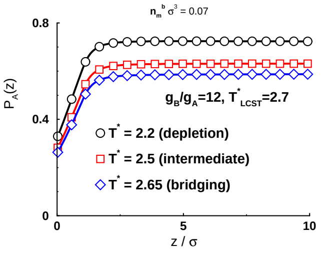
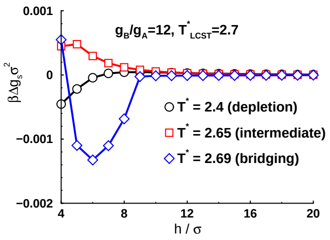


Fig. 1 Calculated equilibrium profiles at a single surface, as obtained for various temperatures, using our model with $g_B/g_A = 12$.
(a) Total monomer density profiles, $n_m(z)$.
(b) The A-state probability profile, $P_A(z)$.

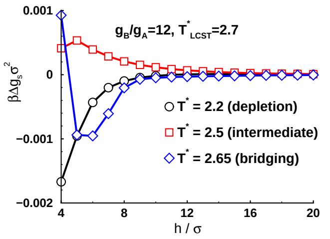
In Figure 2, we see how a gradual temperature increase will lead to attraction => repulsion => attraction, where the first regime is depletion dominated, while the attraction at high temperature is generated by bridging. This behaviour is common to all three investigated polymer concentrations. We see that the temperature regime across which the transition occurs, increases with the bulk density, n_m^b. All these findings, including the fact that the transition from depletion attraction across repulsion to bridging attraction occurs below the LCST, is in agreement with experimental findings by Feng et al. In principle, the free energy minimum found for bridging systems might indicate that the equilibrium separation in condensed phases at high temperatures would be larger than in those brought about by depletion, i.e. at low temperatures. This is also in line with observations by Feng et al, but given the crudeness of our model this could be a fortuitous coincidence.

We emphasize that while these results were obtained for 1600-mers, the polymer length dependence is small, at least for $r > 100$ or so. We provide an explicit comparison in the ESI, with corresponding results for 400-mers. The dominance of solvophilic A state monomers at low temperatures renders the surfaces non-adsorbing, with a concomitant depletion attraction. At high temperatures, on the other hand, B state monomers are prevalent. These are effectively adsorbed at the surfaces, resulting in attractive bridging interactions. Armed with the results established in the ESI, for "intermediate" adsorptions, we anticipate a temperature regime between these extremes where the polymer induced interaction is either repulsive or essentially vanishing. The former is obviously true in the investigated cases.

(a) $n_m^b\,\sigma^3 = 0.05$



(b) $n_m^b\,\sigma^3 = 0.07$



(c) $n_m^b\,\sigma^3 = 0.1$

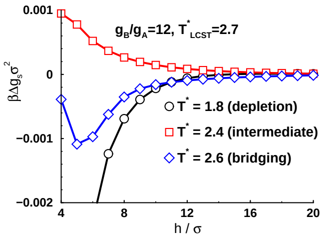


Fig. 2 Net interaction free energies versus surface separation (h), at various temperatures, for three different bulk monomer concentrations. The LCST, T^*_{LCST}, is slightly above 2.7 for this model system ($g_B/g_A = 12$).
(a) $n_m^b\sigma^3 = 0.05$, with n_m^b denoting the bulk monomer density.
(b) $n_m^b\sigma^3 = 0.07$
(c) $n_m^b\sigma^3 = 0.1$

For completeness, we will also include predictions for $g_B/g_A = 13$, where the LCST for 1600-mers is shifted from $T^*_{LCST} \approx 2.7$ (for $g_B/g_A = 12$) to $T^*_{LCST} \approx 2.44$ (slightly above each value). This will allow us to determine if the relation to the LCST is essentially universal. The results are summarized in Figure 3. We indeed find an overall response to temperature increase, in a regime below the LCST, that agrees with that found for our previous model, i.e. this seems to be a general behaviour. In all of the cases reported here, the polymer density exceeds the overlap concentration. However, we have checked that the same overall behaviour can be found

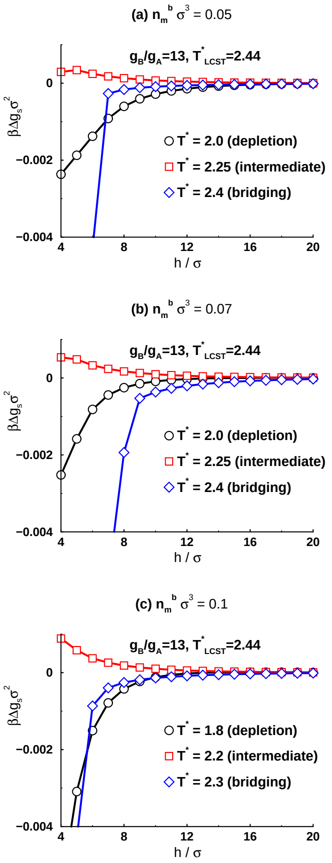


Fig. 3 Net interaction free energies, at various temperatures, for three different bulk monomer concentrations. The LCST, T^*_{LCST}, is slightly above 2.44 for this model system ($g_B/g_A = 13$).
(a) $n_m^b\sigma^3 = 0.05$, with n_m^b denoting the bulk monomer density.
(b) $n_m^b\sigma^3 = 0.07$
(c) $n_m^b\sigma^3 = 0.1$

also in cases where this is not true, i.e. below the overlap concentration (not shown). In a previous work[5], we showed that polymer solutions displaying an LCST might undergo a capillary-induced phase separation (CIPS) in narrow geometries, such as the confined space between two approaching (large) colloidal particles. Furthermore, CIPS can occur even at temperatures below the LCST, i.e. even in cases where there is only a single fluid phase in the bulk. Although this is not central to our previous work, we do observe similar behaviours close to (but still below) the LCST, for some of the systems displayed in Figure 3. The CIPS generates a sudden and strong attractive interaction. This is studied in some detail in the ESI. Note that the free energy minimum that was observed for $g_B/g_A = 12$ is absent in this case. This is probably due to the occurrence of CIPS, i.e. at separations below a CIPS transition, the free energy tends to vary linearly (and attractively) with separation. The absence of an LCST for $g_B/g_A = 12$ means that there is no CIPS, and hence no such linear free energy regime.

As mentioned earlier, Feng et al. showed that many colloid + polymer systems "melt" from a condensed state at low temperatures, but re-flocculates again upon further heating. The particles used in their study typically had diameters of 1-2 μm. This is considerably larger than the size of the polymers, allowing us to make use of Derjaguin's Approximation[4] (DA) to evaluate corresponding predictions by our model. In other words, the potential of mean force (PMF) acting between particles of radius R_c can be obtained from the interaction free energy per unit area, between planar surfaces: $W(D) = -\pi R_c \int_D^\infty dx g_s(x)$, where D measures the separation between the particle *surfaces*, while $g_s(x)$ is the the corresponding interaction free energy per unit area in a planar geometry. Using this relation, and assuming a particle diameter of 1 μm, we arrive at the PMF:s (W) shown in graph (a) of Figure 4. We have then made the simplifying assumption that Δg_s is constant for $h < 4\sigma$. With $\sigma \approx 3.1$ Å, this implies that the PMF:s below about 12 Å should be regarded as highly approximate. As mentioned earlier, a proper treatment this regime would require an explicit solvent model. In Figure 4 (b), we show structure factors, as obtained from canonical Metropolis Monte Carlo (MC) simulations of particles interacting with the PMF:s presented in Figure 4 (a). In addition to these PMF:s, the simulated particles had a hard-sphere diameter of 1 μm, and the overall particle volume fraction was 0.2 %. Both of these parameters were typical to the systems studied by Feng et al. The simulations furthermore utilized standard cubic periodic boundary conditions. In order to facilitate efficient free energy barrier crossings, a mixture of two different kinds of single particle MC moves were used: standard

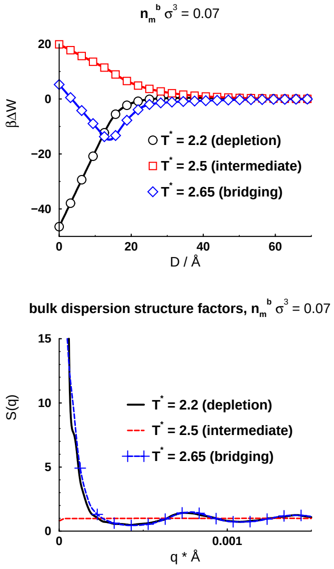


Fig. 4 (a) Predicted potentials of mean force (PMF) between particles of diameter $1\mu m$, at three different temperatures, with $n_m^b\sigma^3 = 0.07$ ($g_B/g_A = 12$). The Derjaguin Approximation has been used to generate these potentials, from the corresponding predictions of the interaction free energies per unit area in a planar geometry - cf. Figure 2. Note that D measures the separation between particle surfaces.
(b) Simulated structure factors in colloidal suspensions of average volume fraction 0.2 %, where the particle-particle PMF:s are shown in (a). The particles also carry a hard sphere diameter of 1 μm.

displacements, centred at the current position of a particle, and translocation to a random position in the simulation box, respectively.

The simulated large values of $S(q)$ at low q values for high and low temperatures, are indicative of aggregated particles. Although not shown, the radial distribution functions of these systems display very strong peaks at separations just above a hard sphere diameter. In other words, in qualitative agreement with experiment, the particle + polymer system changes from aggregated to homogeneously dispersed, and finally a re-entrant flocculation, as the temperature is increased. Note that the entire investigated temperature regime is below the LCST of the system.

In summary, we have firstly established that polymer mediated surface interactions are in general either repulsive, or negligible, for "intermediate" surface affinities, i.e. in a regime between adsorbing and non-adsorbing. We have also constructed a polymer+ particle dispersion model which displays a temperature response that is in qualitative agreement with recent findings by Feng et al..[3], i.e. flocculated - homogeneous dispersion - flocculated, upon increasing the temperature. This is achieved without any assumptions of temperature-dependent interactions.

References

1 P. G. deGennes, *Macromol.*, 1982, **15**, 492.
2 C. E. Woodward and J. Forsman, *Phys. Rev. E*, 2006, **74**, 010801.
3 L. Feng, B. Laderman, S. Sacanna and P. Chaikin, *Nat Mater*, 2015, **14**, 61.
4 B. V. Derjaguin, *Kolloid Zeits.*, 1934, **69**, 155.
5 F. Xie, C. E. Woodward and J. Forsman, *Langmuir*, 2013, **29**, 2659–2666.
6 G. Karlström, *The Journal of Physical Chemistry*, 1985, **89**, 4962–4964.
7 J. Forsman and C. E. Woodward, *Macromol.*, 2006, **39**, 1269.
8 J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.*, 1979, **83**, 1619–1635.
9 F. Xie, K. van Gruithuisen, P. Schurtenberger, A. Stradner, M. Turesson and J. Forsman, *Manuscript, in preparation*, 2015.
10 M. Andersson and G. Karlstrom, *The Journal of Physical Chemistry*, 1985, **89**, 4957–4962.
11 R. E. Goldstein, *The Journal of Chemical Physics*, 1984, **80**, year.
12 S. Saeki, N. Kuwahara, M. Nakata and M. Kaneko, *Polymer*, 1976, **17**, 685 – 689.
13 V. Viti, P. L. Indovina, F. Podo, L. Radics and G. NÃľmethy, *Molecular Physics*, 1974, **27**, 541–559.
14 B. C. Freasier and S. Nordholm, *J. Chem. Phys.*, 1983, **79**, 4431.