



# LUND UNIVERSITY

## A Many-Body Hamiltonian for Nanoparticles Immersed in a Polymer Solution

Woodward, Clifford E.; Forsman, Jan

*Published in:*  
Langmuir

*DOI:*  
[10.1021/la5037184](https://doi.org/10.1021/la5037184)

2015

[Link to publication](#)

*Citation for published version (APA):*

Woodward, C. E., & Forsman, J. (2015). A Many-Body Hamiltonian for Nanoparticles Immersed in a Polymer Solution. *Langmuir*, 31(1), 22-26. <https://doi.org/10.1021/la5037184>

*Total number of authors:*  
2

### General rights

Unless other specific re-use rights are stated the following general rights apply:

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

Read more about Creative commons licenses: <https://creativecommons.org/licenses/>

### Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

LUND UNIVERSITY

PO Box 117  
221 00 Lund  
+46 46-222 00 00

# A Many-Body Hamiltonian for Nanoparticles Immersed in a Polymer Solution

Clifford E. Woodward<sup>†</sup>, and Jan Forsman<sup>††\*</sup>

<sup>†</sup>*University of New South Wales, Canberra Canberra ACT 2600, Australia*

<sup>††</sup>*Theoretical Chemistry, P.O.Box 124, S-221 00 Lund, Sweden*

E-mail: jan.forsman@teokem.lu.se

## Abstract

We develop an analytical theory for the many-body potential of mean force (POMF) between  $N$  spheres immersed in a continuum chain fluid. The theory is almost exact for a  $\Theta$  polymer solution in the protein limit (small particles, long polymers), where  $N$ -body effects are important. Polydispersity in polymer length according to a Schulz-Flory distribution emerges naturally from our analysis, as does the transition to the monodisperse limit. The analytical expression for the POMF allows for computer simulations employing the *complete*  $N$ -body potential (i.e., without  $n$ -body truncation;  $n < N$ ). These are compared with simulations of an explicit particle/polymer mixture. We show that the theory produces fluid structure in excellent agreement with the explicit model simulations even when the system is strongly fluctuating, e.g., at or near the spinodal region. We also demonstrate that other commonly used theoretical approaches, such as truncation of the POMF at the pair level or the Asakura Oosawa model, are extremely inaccurate for these systems.

---

\*To whom correspondence should be addressed

## Introduction

The addition of non-adsorbing polymers to particle dispersions can lead to destabilization.<sup>1-4</sup> This phenomenon is driven by the net attraction that results when polymers are depleted from the regions between particles. While the physics is well understood, a proper theoretical treatment of such systems is very challenging, due mainly to the multi-dimensional configuration space explored by the polymer chains in the complex shaped interstitial regions between particle surfaces. Even for theta ( $\Theta$ ) solvents, where the polymers can be approximated as being ideal, the major part of the complexity remains. The direct simulation of explicit particle/polymer mixtures is computationally expensive and other ways of modelling this system are desirable. One such approach was suggested by Asakura and Oosawa (AO)<sup>5</sup> as well as Vrij.<sup>6</sup> Here polymer molecules in a  $\Theta$  solvent are implicitly treated as mutually penetrable spheres with radius  $R_g$  (polymer radius of gyration). The particles are hard spheres with radius  $R_s$  and cross-interactions are also hard-sphere like.<sup>1,2,7-10</sup> As it does not account for polymer deformation, the AO model is limited to cases where the asymmetry parameter,  $q(\equiv R_g/R_s)$  is small, which corresponds to the colloidal regime. The nanoparticle or protein regime is given by  $q > 1$ .<sup>11,12</sup> Recent work by Lu and Denton<sup>13</sup> has sought to extend the applicability of the AO model to higher  $q$ .

An alternative way of treating particle/polymer mixtures is to use an effective Hamiltonian strategy. Here one defines a potential of mean force (POMF), which is a *free energy*, obtained by carrying out a partial trace over polymer degrees of freedom in the field of the fixed particles. This POMF is an  $N$ -body potential (where  $N$  is the number of particles in the volume). The effective Hamiltonian approach has been used in the colloidal limit, where it suffices to truncate the many-body interactions to just 1- and 2-body terms.<sup>14</sup> This has allowed a great deal of theoretical progress in colloidal systems, as the machinery of fluid state theory (developed primarily for pairwise additive potentials) can be brought to bear on the effective particle fluid. Unfortunately, for large  $q$ , polymer molecules may influence many particles simultaneously, giving rise to significant many-body effects and this has hindered similar progress in the protein regime for decades. There are two major challenges summarized by the following questions:

- *What is the mathematical structure of the many-body POMF in the protein regime?*
- *How can thermodynamic properties be efficiently calculated using the many-body POMF?*

So far these questions have remained largely unanswered (even for  $\Theta$  solvents). Chervanyov and Heinrich,<sup>15</sup> recently revisited the effective Hamiltonian approach and presented a 3-body term for spheres in a polymer fluid under  $\Theta$  conditions. While a valuable contribution to the field, 3-body terms are computationally expensive to evaluate in simulations. Furthermore, it is not clear that truncation at 3-body terms will necessarily provide a good description of the thermodynamics in any case, especially at large  $q$ .

The purpose of this letter is to introduce a new many-body POMF theory for particle/polymer mixtures, which is valid in the protein regime. This work is based on an earlier approach used by us to describe many-body interactions in *equilibrium* polymers.<sup>16,17</sup> It generalizes recent work by us on pair interactions between particles in a polydisperse polymer fluid to many-body interactions for a collection of spheres.<sup>18</sup> Here, we will obtain new compact expressions to describe the full  $N$ -body POMF for a polymer fluid with a general Schulz-Flory polydispersity. We are able to demonstrate that this  $N$ -body interaction is extremely accurate, as the full POMF (i.e., *all* the  $n$ -body terms;  $n \leq N$ ) can be evaluated as easily as for pairwise additive potentials. For the first time the results of our theory are compared with (computationally intensive) structural information obtained from simulations of the mixture containing an explicit model for polymer molecules.

## Model and theory

We consider  $N$  spherical particles immersed in a  $\Theta$  polymer within a volume  $V$  defined by a semi-permeable membrane, which allows the passage of polymer but not of the particles. The system is in chemical equilibrium with a large reservoir of *polydispersed* polymer molecules, whose molecular weight profile is given by the following  $n$ -order Schulz-Flory (S-F) distribution,<sup>19</sup>

$$F^{(n)}(\kappa, s) = \frac{\kappa^{n+1}}{\Gamma(n+1)} \frac{s^n}{\bar{s}^{n+1}} \exp(-\kappa s/\bar{s}) \quad (1)$$

Here,  $\Gamma(n)$  is the Gamma function and  $\kappa$  is treated as an independent variable. When  $\kappa = n + 1$ ,  $\bar{s}$  is the average polymer length. The distribution becomes more monodisperse as  $n$  increases. The full POMF between the particles is the free energy of the polymer molecules in the field determined by the particles with fixed positions  $\{\mathbf{R}_i; i = 1, N\}$ . In a  $\Theta$  solvent, the polymer behaves as an ideal fluid, hence the POMF is proportional to the excess polymer adsorption within the volume  $V$ . Specifically,

$$\beta\Delta\omega^{(n)}(\kappa) = -\Phi_p \int_V d\mathbf{r} \{\hat{g}^{(n)}(\mathbf{r}) - 1\} \quad (2)$$

where  $\Delta\omega^{(n)}(\kappa)$  denotes the POMF in the  $n$ -order polydisperse polymer,  $\beta = 1/k_B T$ , is the inverse thermal energy and  $\Phi_p$  is the average polymer density in the reservoir. The function  $\hat{g}^{(n)}(\mathbf{r})$  is the total probability distribution of polymer ends (which is normalized to unity in the bulk reservoir). We shall treat the polymer as a continuous chain, which is described by Edward's diffusion equation for the monodisperse polymer fluid. The quantity,  $\hat{g}^{(n)}(\mathbf{r})$ , is the density of ends averaged over the S-F distribution, Eq.(1). This introduces the explicit  $\kappa$  dependence to the POMF. Using the fact that  $\kappa$  is an independent variable, one obtains the following recursion formula for the POMF,

$$\Delta\omega^{(n)}(\kappa) = \sum_{m=0}^n \frac{(-\kappa)^m}{m!} \frac{\partial^m}{\partial \kappa^m} \Delta\omega^{(0)}(\kappa) \quad (3)$$

which follows from the form of the distribution in Eq.(1). Thus,  $\Delta\omega^{(0)}(\kappa)$  is a generating function for the family of effective potentials corresponding to the  $n$ -order S-F distributions. The actual POMF is obtained by substituting  $\kappa = n + 1$  on the RHS of Eq.(3).

The solution for  $\Delta\omega^{(0)}(\kappa)$  is rather long and complex. We also use a limited number of approximations, appropriate to the protein regime, so as to obtain a relatively simple closed expression for the POMF. These include a *spherical approximation*, which assumes that the environment about particles in the liquid is to good approximation spherically symmetric. Consistent with this is the assumption that the environments are essentially identical, i.e, translationally invariant. The derivation is presented in the Supporting Information (SI). The final result, after subtracting the

(uninteresting) 1-particle contribution, is

$$\beta\Delta\omega^{(0)}(\kappa) = -4\pi\Phi_p R_g^3 \kappa^{-3/2} \sum_{i=1}^N \frac{\varepsilon^2 \sum_{j \neq i} k_0(\lambda R_{ij})}{\mathcal{H}_0(\sigma)^2 + \mathcal{H}_0(\sigma) \mathcal{J}_0(\sigma) \sum_{j \neq i} k_0(\lambda R_{ij})} \quad (4)$$

where  $\lambda^2 = \kappa/R_g^2$ , and  $\sigma = \lambda R_s$ . The quantities  $\mathcal{H}_0(\sigma)$  and  $\mathcal{J}_0(\sigma)$  are analytic functions (see SI) and  $k_0(x) = e^{-x}/x$ . The parameter  $\varepsilon$  measures the depletion region of the polymer proximal to the particle surfaces and is determined so as to make the continuous chain model more consistent with the discrete model used in our explicit simulations.

To test our POMF, we carried out Canonical Ensemble Monte Carlo (MC) simulations. We used both a mixture model and a system of just particles, interacting with our POMF. In the mixture model, the particles were treated as hard spheres with radius  $R_s$  and the polymer chains were modelled as monodispersed discrete chains. The monomers were point particles with freely rotating bonds of length,  $b$ . Four different polymer + particle systems were investigated:

1. 1863 polymers, with 601 monomers/chain ( $R_g/b = 10$ ), and spheres, with  $R_s/b = 5$ , in a simulation box with side length  $L/b = 150$ . This defines our  $q2$  system.
2. 1680 polymers, with 150 monomers/chain ( $R_g/b = 5$ ), and spheres, with  $R_s/b = 5$ , in a simulation box with  $L/b = 100$ . This defines our  $q1(low)$  (low polymer concentration) system.
3. 3360 polymers, with 150 monomers/chain, and spheres, with  $R_s/b = 5$ , in a simulation box with  $L/b = 100$ . This defines our  $q1(high)$  system.
4. 1104 polymers, with 601 monomers/chain, and spheres, with  $R_s/b = 2.5$ , in a simulation box with  $L/b = 100$ . This defines our  $q4$  system.

For all of the systems above, a number of different particle concentrations were investigated, spanning from (particle) dilute to concentrated, across a demixing regime. Standard cubic periodic boundary conditions were applied in all cases. In the POMF simulations the particles were treated as hard spheres. The addition of the POMF then modelled the effect of the polymers. We note that the POMF only requires summations over particle pairs in order to evaluate the free energy

of a particular particle configuration, see Eq.(4). Thus, implementing our POMF in a simulation is as straightforward (and efficient) as for pair-additive potentials. In the POMF simulations the polymers are assumed polydisperse, while those of the mixture are monodisperse. Using Eq(3) we are able to generate the POMF for progressively more monodisperse polymer, though the monodisperse limit is clearly unobtainable via this method. However, previous work<sup>20</sup> suggests, that for polymers in  $\Theta$  solvents and in a depleting environment, surface forces do not appear to be particularly sensitive to the degree of polydispersity for  $n \geq 1$ , especially if the average radius of gyration ( $R_g$ ) is large, which is consistent with the protein regime. Hence we used the  $n = 1$ , S-F distribution to generate the POMF. That is, the many-body potential  $\Delta\omega^{(1)}$ , was used in our simulations.

When determining the value of  $\varepsilon$ , we noted that the depletion region around spheres occurs at a scale where the discrete chain model will lead to results slightly different to a continuous chain model. This will affect the ability of the many-body POMF to mimic the effects of the discrete chain model. By considering the exact interaction between just two particles immersed in a discrete chain fluid, we are able to determine an optimal value for  $\varepsilon$ , by matching the 2-body component of the many-body POMF with the exact discrete chain system. Essentially exact agreement can be obtained by this process, which validates the functional form of the POMF and guarantees its accuracy at the 2-particle level. This is described in the SI. However, as we shall show below, accuracy at the 2-particle level is far from sufficient to give a good description of the full many-body system. In the explicit model, Canonical Ensemble simulations were used. On the other hand, our POMF model is developed in a semi-Grand Ensemble (polymer chemical potential fixed). Hence, we need to estimate an appropriate value for the reservoir polymer density,  $\Phi_p$ . We used two different approaches, depending upon the total particle concentration,  $N/V$ . These are also outlined in the SI.

## Results

A range of particle concentrations were investigated in each of the systems for both the *explicit* mixture and the POMF (*implicit*) simulations. At each particle concentration, the particle-particle radial distribution function,  $g(r)$ , was evaluated. This function is a good indicator of the accuracy of our POMF, as  $g(r)$  is sensitive to both strength and range of interactions, and will also reflect many-body effects, if they are present. In Figure 1 we compare the distributions obtained from explicit and implicit simulations of the  $q2$  system. There is quantitative agreement over the full

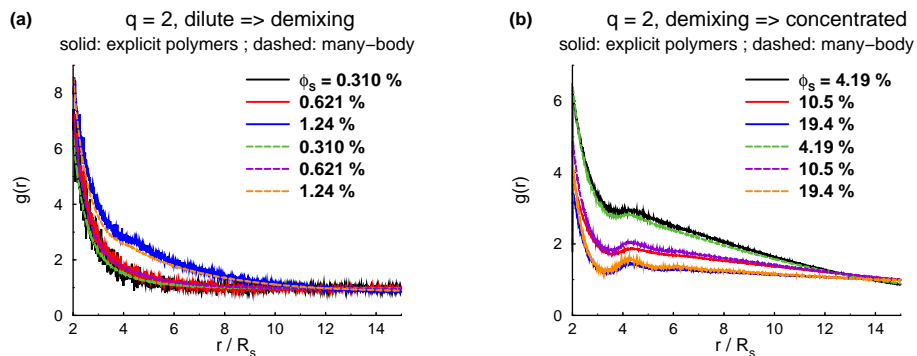


Figure 1: Particle-particle radial distribution functions at  $q = 2$ , obtained from simulations of particles and explicit polymers and simulations utilizing the many-body potential. The simulation volume is constant, while the particle volume fraction,  $\phi_s$ , is varied by two orders of magnitude ( $\phi_s \approx 0.3\% - 20\%$ ). At intermediate concentrations, the average concentration lies within a demixing regime (see main text).

(a) Dilute phase => demixing regime

(b) Demixing regime => concentrated phase

range of particle densities. We should note that the explicit mixture simulations use several hundred thousand monomers, making them computationally extremely expensive. On the other hand, the corresponding implicit simulations are finished within a minute or two on a standard laptop.

It is interesting to determine the significance of many-body effects in this system. To test this, we performed an *implicit* simulation of the  $q2$  at  $\phi_s \approx 1.2\%$ , but using only the 2-body interaction term as the POMF. The results are shown in Figure 2. It is clear that the 2-body potential severely overestimates the depletion attraction. We also used the AO model to treat the  $q2$  system with  $N_s = 6$ . The AO theory also overestimates the depletion forces considerably (at least for this case),



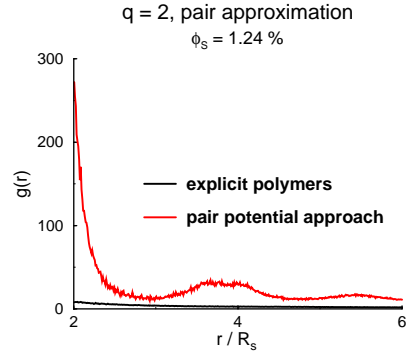


Figure 2: Structural comparisons between the explicit polymer system, with  $\phi_s \approx 1.24\%$  and  $q = 2$  and predictions resulting from the pair interaction part of the many-body Hamiltonian.

as shown in Figure 3.

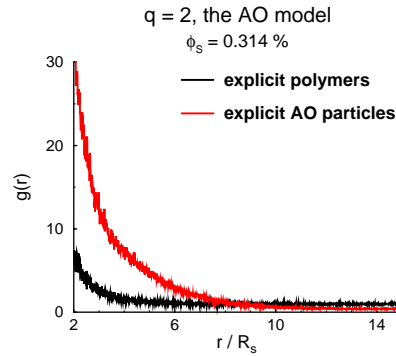


Figure 3: Structural comparison between the explicit polymer system, with  $\phi_s \approx 0.3\%$ ,  $q = 2$ , and the corresponding system using the AO model.

Figure 4 summarizes structural comparisons for the  $q1(low)$  system. Again, there is almost quantitative agreement throughout the entire range of particle concentrations, as was observed with longer chains.

For both the  $q1(low)$  and  $q2$  systems, there is an intermediate particle concentration regime wherein  $g(r)$  displays a slowly decaying tail. This behaviour is indicative of the spinodal region wherein long-wavelength correlations are manifested in  $g(r)$ . In the SI, we demonstrate that the phase separation is accommodated by a divergence of the structure factor in the low- $k$  regime, as expected. Spinodal fluctuations in particle/polymer mixtures have been experimentally observed

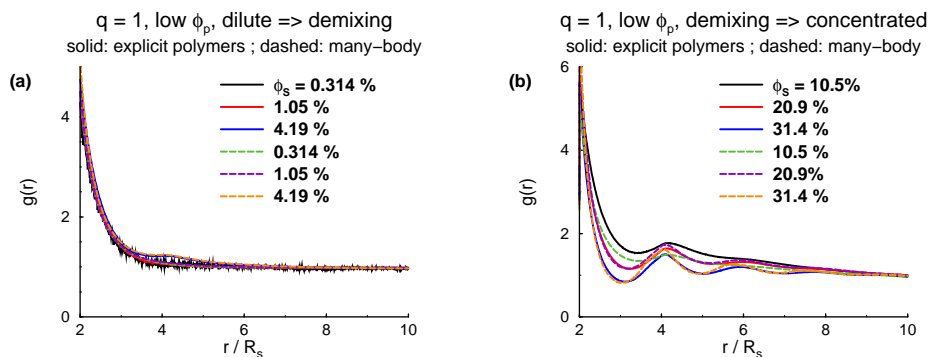


Figure 4: Particle-particle radial distribution functions, as obtained from simulations of particles with explicit polymers, with  $q = 1$ , as well as those provided by simulations utilizing the many-body potential. The polymer concentration is “low” (see main text).

(a) Dilute phase => demixing regime

(b) Demixing regime => concentrated phase

under microgravity.<sup>21</sup> They are more likely to be seen within the protein regime, whereas crystalline, rather than liquid-like, condensed phases tend to form in the colloid regime.<sup>22</sup> Remarkably, the many-body POMF also predicts this behaviour. Large wavelength fluctuations in the particle density, characteristic of spinodal decomposition, would be accompanied by anti-correlated long-wavelength fluctuations in the polymer concentration. Such an effect is captured by the many-body POMF, but is completely absent in the simple 2-body approximation. We note that predictions for  $g(r)$  by the many-body POMF model is least accurate in these strongly fluctuating systems, where the simple cell model that we used to estimate the polymer reservoir chemical potential, becomes inaccurate.

As mentioned earlier, the polymer concentration is increased in the  $q1(\text{high})$  system, relative to  $q1(\text{low})$ , and we therefore anticipate phase separation across a broader range of particle concentration. This is confirmed by the data displayed in Figure 5, where we again observe an essentially quantitative agreement between the many-body simulations and those with explicit polymers.

Finally, we extend our comparisons further into the protein limit. In principle, we expect that the many-body potential itself becomes more accurate in this regime. On the other hand, this might be offset by an increasing difficulty for accurate estimates of the free volume fraction. Still, the

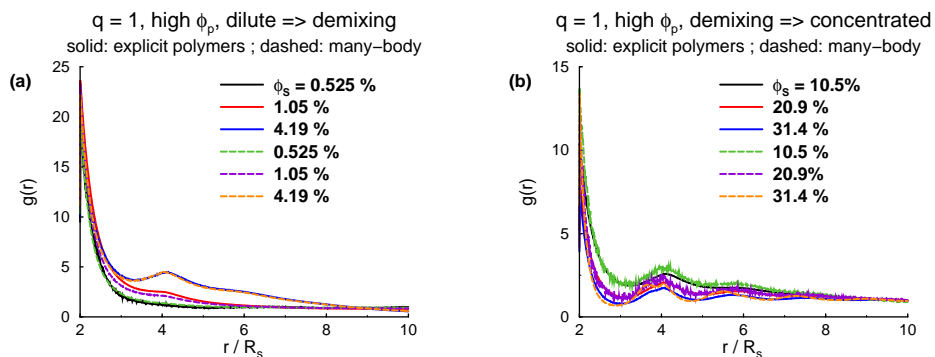


Figure 5: Particle-particle radial distribution functions, as obtained from simulations of particles with explicit polymers, with  $q = 1$ , as well as those provided by simulations utilizing the many-body potential.  
 (a) Dilute phase => demixing regime  
 (b) Demixing regime => concentrated phase

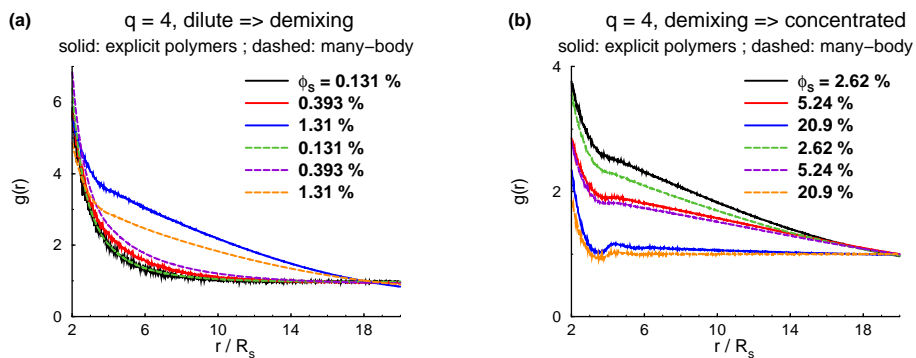


Figure 6: Particle-particle radial distribution functions, as obtained from simulations of particles with explicit polymers, with  $q = 4$ , as well as those provided by simulations utilizing the many-body potential.  
 (a) Dilute phase => demixing regime  
 (b) Demixing regime => concentrated phase

comparisons shown in Figure 6 suggest that the structural predictions are satisfactory also for such high  $q$ -values.

## Conclusions

In summary, we have evaluated structural properties using a many-body potential for particle/polymers mixtures under theta solvent conditions. This potential is particularly useful in the protein regime,

wherein the polymer radius of gyration is large compared to the particles. Comparisons with simulations of a mixture model, in which the polymers are treated explicitly, show the theory to give remarkably accurate results, which are far superior to approaches that use a 2-particle approximation or the AO model. The present approach should admit a more extensive exploration of particle/polymer mixtures in the protein regime. In future work, we plan to use a similar methodology to treat good solvent systems, as well as those with adsorbing particles, or grafted chains.

## Acknowledgement

JF acknowledges financial support by the Swedish Research Council.

## Supporting Information Available

### References

1. Lekkerkerker, H. N. W.; Poon, W. C.-K.; Pusey, P. N.; Stroobants, A.; Warren, P. B. Phase Behaviour of Colloid + Polymer Mixtures. *EPL (Europhysics Letters)* **1992**, *20*, 559 – 564.
2. Lekkerkerker, H.; Stroobants, A. On the spinodal instability of highly asymmetric hard sphere suspensions. *Physica A: Statistical Mechanics and its Applications* **1993**, *195*, 387 – 397.
3. Ilett, S. M.; Orrock, A.; Poon, W. C. K.; Pusey, P. N. Phase behavior of a model colloid-polymer mixture. *Phys. Rev. E* **1995**, *51*, 1344 – 1352.
4. Lekkerkerker, H. N. W.; Tuinier, R. *Colloids and the depletion interaction*; Springer: Heidelberg, 2011.
5. Asakura, S.; Oosawa, F. Interaction between particles suspended in solutions of macromolecules. *Journal of Polymer Science* **1958**, *33*, 183–192.
6. Vrij, A. Polymer at interfaces and the interactions in colloidal dispersions. *Pure Appl. Chem.* **1976**, *48*, 471–483.
7. Dijkstra, M.; van Roij, R.; Evans, R. Phase diagram of highly asymmetric binary hard-sphere mixtures. *Phys. Rev. E* **1999**, *59*, 5744–5771.

8. Sear, R. P. Phase Separation in Mixtures of Colloids and Long Ideal Polymer Coils. *Phys. Rev. Lett.* **2001**, *86*, 4696 – 4699.
9. Tuinier, R.; Rieger, J.; de Kruijff, C. Depletion-induced phase separation in colloid - polymer mixtures. *Advances in Colloid and Interface Science* **2003**, *103*, 1 – 31.
10. Dijkstra, M.; van Roij, R.; Roth, R.; Fortini, A. Effect of many-body interactions on the bulk and interfacial phase behavior of a model colloid-polymer mixture. *Phys. Rev. E* **2006**, *73*, 041404 – 041413.
11. Mutch, K. J.; van Duijvelde, J. S.; Eastoe, J.; Grillo, I.; Heesan, R. K. Scaling the structure factors of protein limit colloid-polymer mixtures. *Langmuir* **2009**, *26*, 1630 – 1634.
12. Mahynski, N. A.; Lafitte, T.; Panagiotopoulos, A. Z. Pressure and density scaling for colloid-polymer systems in the protein limit. *Phys. Rev. E* **2012**, *85*, 051402 – 051410.
13. Lu, B.; Denton, A. R. Crowding of polymer coils and demixing in nanoparticle–polymer mixtures. *Journal of Physics: Condensed Matter* **2011**, *23*, 285102.
14. Meijer, E. J.; Frenkel, D. Colloids dispersed in polymer solutions. A computer simulation study. *J. Chem. Phys.* **1994**, *100*, 6873 – 6887.
15. Chervanyov, A. I.; Heinrich, G. Potential theory of the depletion interaction in the colloid-polymer mixtures. *The Journal of Chemical Physics* **2009**, *131*, 234907.
16. Forsman, J.; Woodward, C. A simple many-body Hamiltonian for polymer-colloid mixtures: simulations and mean-field theory. *Soft Matter* **2012**, *8*, 2121 – 2130.
17. Woodward, C. E.; Forsman, J. Many-body interactions between particles in a polydisperse polymer fluid. *J. Chem. Phys.* **2012**, *136*, 084903.
18. Wang, H.; Woodward, C. E.; Forsman, J. Exact evaluation of the depletion force between nanospheres in a polydisperse polymer fluid under theta conditions. *J. Chem. Phys.* **2014**, *140*, 194903.
19. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953.
20. Forsman, J.; Woodward, C. E. Colloidal interactions in thermal and athermal polymer solutions: the Derjaguin approximation, and exact results for mono- and polydisperse ideal chains. *J. Chem. Phys.* **2009**, *131*, 044903.

21. Bailey, A. E.; Poon, W. C. K.; Christianson, R. J.; Schofield, A. B.; Gasser, U.; Prasad, V.; Manley, S.; Segre, P. N.; Cipelletti, L.; Meyer, W. V. et al. Spinodal Decomposition in a Model Colloid-Polymer Mixture in Microgravity. *Phys. Rev. Lett.* **2007**, *99*, 205701 – 205704.
22. Min, Y.; Akbulut, M.; Kristiansen, K.; Golan, Y.; Israelachvili, J. The role of interparticle and external forces in nanoparticle assembly. *Nat. Mater.* **2008**, *7*, 527–538.

# Table of contents graph

Particles ( $R_s$ ) + non-adsorbing polymers ( $R_g = 2R_s$ )

solid: explicit polymers; dashed: many-body potential

