Do effective interactions depend on the choice of coordinates?

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(Received 2 August 2001; published 25 January 2002)

A common approach to complex systems such as colloidal suspensions or polymer solutions describes the mesoscopic behavior using effective interactions. These potentials act between the macromolecular entities and can be derived by integrating out the microscopic degrees of freedom. The remaining macroparticle coordinates need to be chosen *a priori*. Two obvious choices are (i) the centers of mass and (ii) distinct microscopic entities, such as special "tagged" monomers. Here we compare both in the framework of the Asakura-Oosawa colloid-ideal polymer mixture. Using computer simulations, we find that although the effective pair interaction between colloid and polymer differ markedly, correlation functions are in fair agreement.

Choosing optimal coordinates is often the first step to solve a physical problem. Optimal coordinates are such that they exploit the simplifying physical properties, e.g., symmetries, of a system, and help to find the relevant degrees of freedom that are responsible for the physical effect under consideration. As concerns any exact treatment, changing coordinates is an exact mathematical transformation that preserves all properties of a model. Approximations, however, usually depend on the variables used. Different results may be obtained if the same approximation is done in different coordinates. Approximations are usually necessary if one is dealing with complex systems. In soft matter systems there is a hierarchy of relevant variables on different length scales. While basical microscopic degrees of freedom, namely, the positions of the atoms, are responsible for the behavior on all length scales, there exist variables that especially govern the interesting mesoscopic regime. Colloidal particles have the positions of their atoms as basic position coordinates; an obvious choice for the (mesoscopic) degree of freedom of the colloid is its center of mass. The concept, however, to derive effective interactions between mesoscopic objects from an averaging over the microscopic degrees of freedom extends far beyond colloids and has been applied to systems like star polymers [1] or linear polymers [2–6], and mixtures of colloids and star polymers [7]. The choice of meaningful position coordinates for such macromolecular entities is not in all cases as straightforward as it may seem at first glance. In the case of star polymers, the position of the central molecule to which the polymeric arms are attached was used to derive an effective interaction [8,9]. In the context of linear polymer coils, one can think of tagged monomers (segments) that are visible in a scattering experiment. Both are, in general, different from the position of the center of mass of the whole object. The question arises: what is the superior variable? Is it the center of mass or the position of the special microscopic object?

In this paper, we study this question in the context of the Asakura-Oosawa (AO) colloid-ideal polymer mixture [10,11] that consists of a hard-sphere model for the colloids, and a hard-core exclusion between a colloid and a spherical polymer coil. The polymers do not interact with themselves; they are assumed to be ideal. Recently the phase diagram and structure [12,13], and the interface between demixed phases [14] were studied. An effective Hamiltonian was derived [15], and a density-functional theory [16] was proposed and entropic wetting investigated [17].

Here we supplement this model with a simple prescription for the behavior of a tagged monomer on each polymeric chain: The monomer is allowed to move freely inside the sphere that represents the polymer. It is, however, not allowed to leave the sphere, and hence is bound to its chain [18]. Although both the AO model and the tagged monomer prescription are highly approximative as concerns the real world, there is one feature that makes the model suitable for the present investigation: The position of the polymer center of mass differs strongly from that of the tagged monomer. Hence going from one to the other is not a small change, and we expect insight into the question raised above.

We treat this *full model* two ways: First by integrating out the positions of the tagged monomers. This leads to the usual AO model with colloid positions and polymer center of mass position, and constitutes our *reference* system. The second treatment is by integrating out the polymer centers. This is done exactly in the limit of vanishing colloid density and leads to an effective pair potential between a colloid and a tagged monomer. We neglect all higher-body interactions between colloids and tagged monomers, as is usually done. This constitutes the *effective model* with colloid and monomer position coordinates. The comparison of the reference model with the effective model is the purpose of this paper. As expected, the effective interactions between tagged monomer and colloid as well as polymer center and colloid are markedly different. Also, a comparison of the appropriate correlation functions shows differences. However, only small deviations exist, as we show by simulations. This leads to the conclusion that the choice of coordinates matters if high accuracy is reached for, but not if one aims at the gross physical features of the system.

The model we consider consists of N^c colloids with coordinates $\mathbf{r}_i^c$ and N^p polymers with centers of mass $\mathbf{r}_j^p$ and N^p tagged monomers (segments) with positions $\mathbf{r}_j^m$ in a volume V_0. The interaction between colloids is

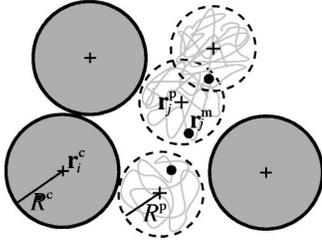$$V^{cc}(r) = \begin{cases} \infty & \text{if } r \leq 2R^c, \\ 0 & \text{else.} \end{cases} \tag{1}$$

FIG. 1. Sketch of the Asakura-Oosawa model. Gray spheres are colloids with radii R^c and positions $\mathbf{r}_i^c$, dashed spheres are ideal polymers with radii R^p and centers of mass $\mathbf{r}_j^p$, dots are tagged monomers with positions $\mathbf{r}_j^m$.

The interaction between a colloid and a polymer center is

$$V^{cp}(r) = \begin{cases} \infty & \text{if } r \leq R^c + R^p, \\ 0 & \text{else,} \end{cases} \qquad (2)$$

while a tagged monomer interacts with (its) polymer through

$$V^{mp}(r) = \begin{cases} 0 & \text{if } r \leq R^p, \\ \infty & \text{else.} \end{cases} \qquad (3)$$

The total potential energy is given by

$$V^{\text{total}}(r) = \sum_{i<j} V^{cc}(|\mathbf{r}_i^c - \mathbf{r}_j^c|) + \sum_{i,j} V^{cp}(|\mathbf{r}_i^c - \mathbf{r}_j^p|)$$
$$+ \sum_i V^{mp}(|\mathbf{r}_i^p - \mathbf{r}_i^m|). \qquad (4)$$

Note that the last summation only includes contributions from pairs of polymer centers and tagged monomers with *equal* indices. This ensures that each tagged monomer i is uniquely bound to its polymer i. See Fig. 1 for a sketch of the model. As thermodynamical variables, we use the packing fractions of colloids, $\eta^c = 4\pi N^c (R^c)^3/(3V_0)$, and of polymers $\eta^p = 4\pi N^p (R^p)^3/(3V_0)$, and the size ratio $q = R^p/R^c$. The diameters are denoted by $\sigma^c = 2R^c$ and $\sigma^p = 2R^p$.

To derive effective interactions, we keep the hard-core colloid-colloid interaction, and integrate out either the tagged monomers or the polymer centers. Effective binary models result that differ in the cross interaction between unlike species. In both cases, the polymeric degrees of freedom remain ideal. The first case, integrating out the monomer positions $\mathbf{r}_i^m$, is especially simple, as each monomer is homogeneously distributed inside its polymeric sphere. Note that no overlap between colloid and monomer can occur due to V^{cp} and V^{mp}. We end up with a model containing $\mathbf{r}_i^p$ and $\mathbf{r}_j^c$. The "effective" interaction between a polymer center and a colloid is the same as the pure interaction $V^{cp}(r)$. In the second case, we intend to derive an effective interaction V_{eff}^{cm} between a tagged monomer and a colloid. This is done in the limit $\eta^c \to 0$, so that no colloid-colloid interactions need to be taken into account. Due to the ideality of the polymeric degrees of freedom, whether center or monomer, of *different* chains, only a single polymer needs to be considered. Naturally a *pair* potential $V_{\text{eff}}^{cm}(r)$ arises. It is given by
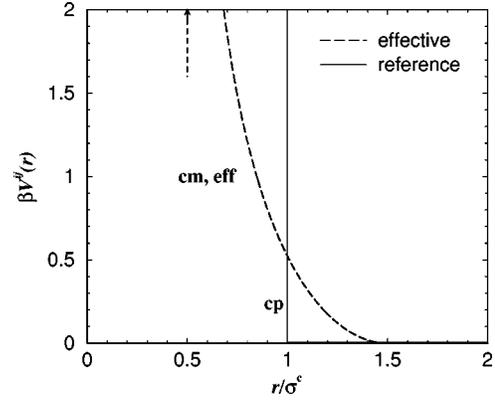

FIG. 2. Comparison of two cross potentials $V^{cp}(r)$ (reference) and $V_{\text{eff}}^{cm}(r)$ (effective) for size ratio $q=1$. The arrow denotes the hard core of $\mathbf{V}_{\text{eff}}^{cm}(r)$.

$$V_{\text{eff}}^{cm}(r) = -k_B T \ln \Xi, \qquad (5)$$

$$\Xi = \int d^3x \exp\left[-\frac{V^{mp}(|\mathbf{r} - \mathbf{x}|) + V^{cp}(\mathbf{x})}{k_B T} \right], \qquad (6)$$

where $r = |\mathbf{r}|$. The integration variable $\mathbf{x}$ is the polymer center of mass, $\mathbf{r}$ is the position of the tagged monomer, and the colloid sits at the origin. For small distances $r < R^c$, all configurations are forbidden due to overlap of the colloid and the polymer, $V^{cp} = \infty$, hence $\Xi = 0$. For large distances, $r > R^c + 2R^p$ no overlap with the colloid occurs and we obtain $\Xi = 4\pi(R^p)^3/3$. The contribution for $R^c \leq r \leq R^c + 2R^p$ is given by the overlap volume of two spheres with radii $R^c + R^p$ and R^p, which is

$$I(r) = \frac{\pi}{12r}(R^c + 2R^p - r)^2[r^2 - 3(R^c)^2 + 2r(R^c + 2R^p)], \qquad (7)$$

and $\Xi = 4\pi(R^p)^3/3 - I(r)$ is obtained. In summary, the effective interaction potential is

$$V_{\text{eff}}^{cm}(r) = \begin{cases} \infty & \text{if } r \leq R^c, \\ -\ln\left[1 - \dfrac{3I(r)}{4\pi(R^p)^3} \right] & \text{if } R^c \leq r \leq R^c + 2R^p, \\ 0 & \text{else,} \end{cases} \qquad (8)$$

where we have shifted the potential by an irrelevant constant of $\ln[4\pi(R^p)^3/3]$, so that it is vanishes for large separations. This has no effect on observable quantities. In Fig. 2 we compare both cross potentials V^{cp} and V_{eff}^{cm} as a function of r. Both differ considerably.

The full model has three components: colloids, polymer centers, and tagged monomers; hence one can investigate six different pair correlation functions $g^{ij}(r)$. Both the effective as well as the reference model have two components, of which only the colloid-colloid pair distribution function $g^{cc}(r)$ can be compared directly. The other two involve polymeric degrees of freedom, whether the polymer center or the tagged monomer, and cannot be compared directly. However,
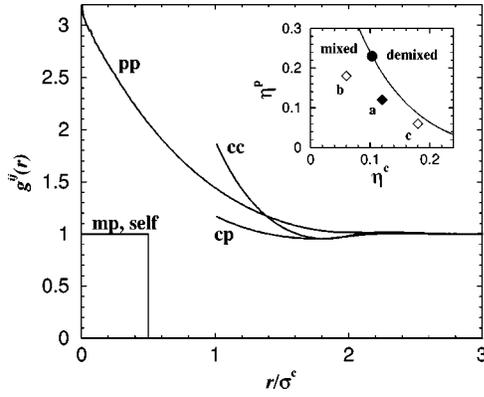
FIG. 3. Full model. Pair-distribution functions $g^{ij}(r)$ for pairs of colloids (cc), polymer centers (pp), colloids and polymer centers (cp), and monomers and polymer centers (mp, self-part) for $q=1$, $\eta^c = \eta^p = 0.12$ [statepoint (a)]. The inset shows the phase diagram from free volume theory [19] with a critical point (dot), and three statepoints [(a), (b), (c), see Table I] marked.

we can compare $g^{mp}_{\text{self}}*g^{cp}$ with g^{mc}, and $g^{mp}_{\text{self}}*g^{pp}*g^{mp}_{\text{self}}$ with g^{mm}, where the star denotes convolution. This is equivalent to multiplying the corresponding structure factors in Fourier space, where the Fourier transform of g^{mp}_{self} plays the role of the polymer form factor. In order to obtain the pair distribution functions, we have carried out Monte Carlo (MC) computer simulations with 512 particles and 10^6 Monte Carlo moves per particle. To obtain the correlation functions involving monomers for the reference system, instead of calculating the convolutions explicitly, a simulation of the full model was done. MC moves for the monomers are particularly simple. Any random vector $\mathbf{r}^m_i$ within a sphere with radius R^p around $\mathbf{r}^p_i$ is a valid monomer position.

As an illustration, we first show pair-correlation functions for the full model in Fig. 3 for equal sizes, $q=1$, and equal densities, $\eta^c = \eta^p = 0.12$. Both, $g^{cc}(r)$ and $g^{cp}(r)$ show hard-sphere-like behavior. They vanish inside the core, $r < \sigma^c$ and $r < R^c + R^p$, respectively, and have oscillations outside. The behavior of $g^{pp}(r)$ is different; polymers tend to form clusters, as can be seen from the rise for small separations. Also plotted is $g^{mp}_{\text{self}}(r)$, which is unity for $r < R^p$, and zero outside. The inset shows the phase diagram from free volume theory [19] for $q=1$. We pick three statepoints in the mixed phase, at equal total density $\eta^c + \eta^p = 0.24$. Statepoint (c) has higher colloid density, and statepoint (b) has lower colloid density compared to (a), see Table I. In Fig. 4 we compare results from the effective model to those from the reference model. See Fig. 4 for results at statepoint (a). The results for the reference model are obtained by appropriate

TABLE I. Summary of statepoints where pair distribution functions are considered.

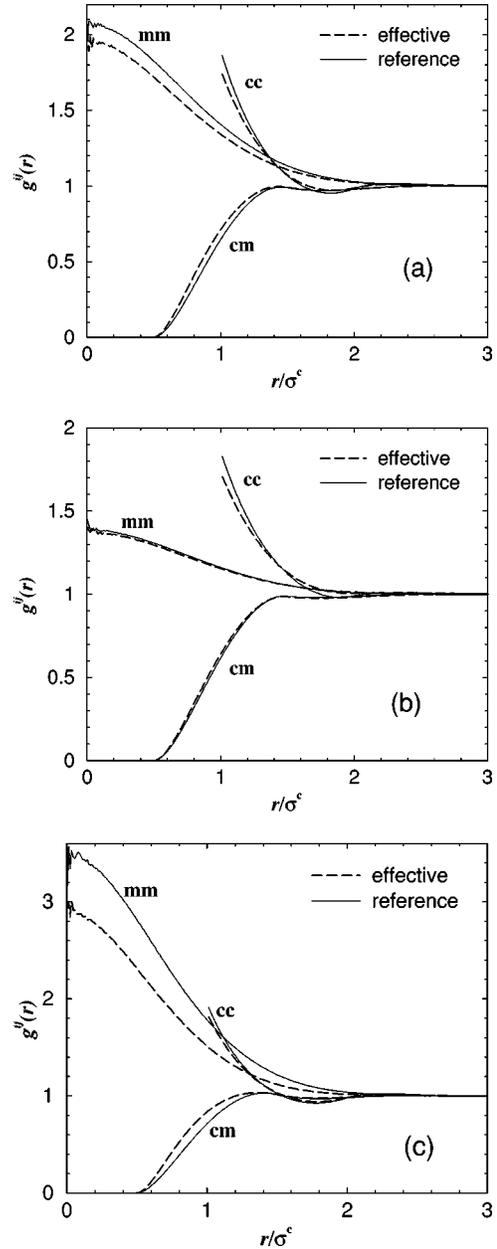| Statepoint	η^c	η^p
(a)	0.12	0.12
(b)	0.06	0.18
(c)	0.18	0.06

FIG. 4. Comparison of an effective and reference model. Pair-distribution functions $g^{ij}(r)$ for pairs of colloids (cc), tagged monomers (mm), as well as colloids and monomers (cm) for $q=1$ at statepoints $\eta^c = \eta^p = 0.12$ (a); $\eta^p = 0.18$, $\eta^c = 0.06$ (b); and $\eta^p = 0.06$, $\eta^c = 0.18$ (c).

convolutions with g^{mp}_{self}. This implies that g^{cc} is identical to Fig. 3. A single convolution turns the jump in g^{cp} to the gradual decrease to zero of g^{mp}. Via two convolutions the cusp at $r=0$ of g^{pp} becomes flat in g^{mm}. The corresponding results for the effective model are close to those for the reference model, except for slightly less structured behavior. Increasing the polymer concentration [statepoint (b)] reduces the overall structure and reduces the differences between results for the effective and reference model. As expected, as in the limit $\eta^c \to 0$, the effective model becomes exact by con-

struction. If we increase η^c [statepoint (c)], stronger deviations occur. The strong clustering of g^{mm} is especially underestimated by the effective model. The colloid-colloid structure, however, is affected only a little.

Coming back to the question, whether effective interactions depend on the choice of coordinates, the answer is certainly yes. However, the more relevant question is: to what extent does the choice of coordinates affect the structural properties calculated from the effective interactions? There the answer is only a little. A few cautionary remarks are in order. First, it is unclear whether the robustness of correlation functions is also present in more realistic models than the highly simplified AO colloid-ideal polymer mixture. In particular, long-ranged forces could lead to different behavior. Second, the present paper covers only bulk fluid states. In crystals or inhomogeneities caused by external influence, the situation may also be different.

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