Coarse-grained models for semi-dilute polymer solutions under good-solvent conditions

Coarse-grained models for semi-dilute polymer solutions under good-solvent conditions

Andrea Pelissetto

Dipartimento di Fisica, Università degli Studi di Roma 'La Sapienza', Piazzale Aldo Moro 2,
I-00185 Roma, Italy
and
INFN–Sezione di Roma I, Piazzale A Moro 2, I-00185 Roma, Italy

E-mail: Andrea.Pelissetto@roma1.infn.it

Abstract
We determine coarse-grained models with a relatively small number of units which reproduce the universal behavior of polymer solutions in the semi-dilute regime under good-solvent conditions. We check both the thermodynamical behavior (osmotic pressure and chemical potential) and structural properties (polymer size).

1. Introduction

Polymer solutions have been extensively studied by theorists and experimentalists for many years, because of their interesting physical and chemical properties and for their many technological applications. When the degree of polymerization N is large and the solution is under good-solvent conditions, the behavior is now well understood. In this regime several properties are universal, that is independent of chemical details, and obey general scaling laws which can be derived by using the renormalization group (RG) [1–4]. A quantitative determination of polymer universal properties is often obtained by means of Monte Carlo (MC) or molecular dynamics (MD) methods, even though, in some cases, perturbative field theory [4, 5] or integral-equation approaches [6] also give quite accurate predictions. In MC or MD studies, one investigates the behavior of systems of polymers of fixed length N; then, one can extrapolate to the infinite-length limit, in order to determine the universal behavior. Because of the presence of strong scaling corrections, a reliable extrapolation requires data for several large values of N, which is a computationally very demanding task. Of course, how large scaling corrections are and how large N should be in order to be close to the asymptotic regime—otherwise, no extrapolation is possible—depends on the model one is considering: while the large-N limit is universal, corrections depend on the model.

Over the years two different strategies have been put forward to determine models with 'small' scaling corrections, which allow one to compute universal polymer properties with a relatively limited computational effort. One of these approaches starts from the general principles of the RG. Consider a generic Hamiltonian $\mathcal{H}$. One can write $\mathcal{H}$ in terms of the RG fixed-point Hamiltonian $\mathcal{H}^*$ and of the RG perturbations $\mathcal{O}_i$ of the fixed point [7]:

$$\mathcal{H} = \mathcal{H}^* + \sum_i \alpha_i \mathcal{O}_i, \qquad (1)$$

where α_i are model- and N-dependent coefficients. In the polymer case there are two relevant operators (we do not consider the identity operator that does not play any role here) and thus two quantities should be tuned in order to observe the universal behavior: the polymer length N should go to infinity and the monomer density c_m to zero. The other operators are *irrelevant* perturbations, since their RG dimensions y_i are negative, and give rise to the corrections to scaling. For instance, the leading irrelevant operator (the one with the smallest $|y_i|$) gives corrections proportional to $\alpha_\Delta \sim v_\Delta N^{-\Delta}$, $\Delta = -|y_i|\nu = 0.515 \pm 0.017$ [8]. Note that the correction in any quantity is always proportional to the coupling v_Δ. Thus, in a model which is such that $v_\Delta = 0$, the leading scaling correction vanishes for any quantity. In these optimal models the convergence is faster and thus the asymptotic behavior is observed for smaller values of N. An example of an optimal model is the lattice Domb–Joyce model [9] for a particular value of the coupling w; it shows a faster convergence to the infinite-N limit than the more common self-avoiding walk model (see, e.g., [8, 10] and references therein).
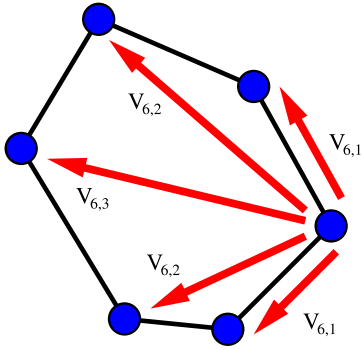
Figure 1. A coarse-grained model of a ring polymer with $n = 6$ units. Beside the intermolecular potential $W_6(r)$, three different intramolecular potentials $V_{6,k}(r)$, $k = 1, 2, 3$ must be defined. $V_{6,1}(r)$ gives the interaction between two neighbors along the chain, $V_{6,2}(r)$ between two next-to-nearest neighbors, $V_{6,3}(r)$ between two atoms which have two atoms in between (the chemical distance is three).

(This figure is in colour only in the electronic version)

A different approach is based on coarse-grained models in which the polymer solution is replaced by a fluid of simple molecules which interact by means of effective potentials which are such as to reproduce, for instance, polymer center-of-mass correlation functions [11–16]. The main difficulty of this approach is that the exact coarse-graining procedure generates many-body interactions [17]. If all of them are taken into account, the coarse-grained model is exactly equivalent to the original one. However, in practice only two-body interactions can be considered and this limits the usefulness of the model to the dilute regime defined by $\Phi = c/c^* \lesssim 1$, where c is the polymer number density ($c = c_{\rm m}/N$, where $c_{\rm m}$ is the monomer number density) and c^* is the overlap density conventionally defined as

$$\frac{1}{c^*} = \frac{4\pi}{3}\hat{R}_{\rm g}^3, \tag{2}$$

where $\hat{R}_{\rm g}$ is the zero-density radius of gyration. In order to be accurate in the semi-dilute regime, coarse-grained models with pairwise interactions require density-dependent pair potentials [14]. They, however, spoil the simplicity of the coarse-graining procedure and introduce some theoretical difficulties related to the fact that interactions are now state-dependent [18]. As suggested in [19], these shortcomings can be overcome by switching to a multi-blob representation. In the spirit of the de Gennes–Pincus blob picture [1], one replaces a polymer of length N by a polyatomic molecule made up by n effective units; each unit effectively represents a blob of N/n monomers. A simple argument indicates that this model might be accurate up to packing fractions $\Phi \lesssim n^{3\nu-1}$, where $\nu \approx 0.5876$ is the Flory exponent[1]. Thus, by increasing n one obtains a model which is also accurate in the semi-dilute region. However, this remarkable improvement has a cost. To understand the problem, let us

---

[1] At present the most accurate estimates of ν are $\nu = 0.587\,58 \pm 0.000\,07$ [8], $\nu = 0.5874 \pm 0.0002$ [20], $\nu = 0.587\,65 \pm 0.000\,20$ [21], $\nu = 0.5876 \pm 0.0002$ [22] and $\nu = 0.5876 \pm 0.0002$ [23] (assuming $0.50 \leqslant \theta \leqslant 0.53$). For an extensive list of results, see [24].

imagine we are dealing with ring polymers so that there are no end effects. Disregarding many-body interactions, in order to specify the model we must define an intermolecular potential $W_n(r)$ and $\lfloor n/2 \rfloor$ intramolecular potentials $V_{n,k}(r)$, where k gives the chemical distance (shortest-path distance) of two atoms along the molecule, see figure 1. Note that we have added a suffix n to the potentials, to make it clear that they depend on the number n of units. In the linear-polymer case, since there is no translation invariance along the chain, there are several intermolecular potentials and a larger numbers of intramolecular potentials. Thus, the complexity of determining many-body interactions is replaced in the multi-blob approach by the difficulty of determining a relatively large number of effective potentials from suitably defined polymer correlation functions. In practice, this approach can be implemented exactly only for $n = 2$ [25].

In order to go beyond the diatomic model, [19] made the approximation that the potentials are essentially independent of n and on the position of the blobs in the chain, i.e. made the transferability approximation

$$W_n(r) = W_1(r),$$
$$V_{n,k}(r) = W_1(r) \qquad \text{for } k > 1, \tag{3}$$
$$V_{n,1}(r) = V_{2,1}(r).$$

In this paper we show that this approximation is not accurate unless n is quite large ($n \gtrsim 1000$); for $n = 26$ (this would be the appropriate number of units to investigate solutions with polymer packing fraction $\Phi \lesssim 10$) the model significantly overestimates the osmotic pressure. We will propose a different strategy which will provide us with models which reproduce with good accuracy the thermodynamic behavior up to $\Phi \approx 10$.

The paper is organized as follows. In section 2 we define the Hamiltonian of the model and the quantities we compute. In section 3 we discuss the multi-blob model introduced in [19], while in section 4 we discuss a different, more phenomenological approach. Finally, in section 5 we draw our conclusions. In the appendix, we compute the chemical potential for the optimal coarse-grained models.

2. Definitions

As in [19] a polymer is modeled by a polyatomic molecule with n atoms, each of them corresponding to a polymer blob. Atoms belonging to different molecules interact by means of an intermolecular potential $W(r)$. The potential between atoms belonging to the same molecule is also given by $W(r)$, if the two atoms are not nearest neighbors along the molecule (the chemical, or shortest-path, distance is larger than one); otherwise, the corresponding potential is $W(r) + w_{nn}(r)$. Thus, the Hamiltonian for a polymer solution made up by L polymer chains is

$$\mathcal{H} = \sum_{i=1}^{L} \sum_{\alpha=1}^{n-1} w_{nn}(\mathbf{r}_\alpha^{(i)} - \mathbf{r}_{\alpha+1}^{(i)}) + \sum_{i=1}^{L} \sum_{1 \leqslant \alpha < \beta \leqslant n} W(\mathbf{r}_\alpha^{(i)} - \mathbf{r}_\beta^{(i)})$$
$$+ \sum_{1 \leqslant i < j \leqslant L} \sum_{\alpha,\beta=1}^{n} W(\mathbf{r}_\alpha^{(i)} - \mathbf{r}_\beta^{(j)}), \tag{4}$$

where $\mathbf{r}_\alpha^{(i)}$ is the position of atom α belonging to molecule i.

In order to understand the accuracy of this model, we shall compare the results for the osmotic pressure Π with high-precision results recently obtained from monomer-level simulations [10]. For $N \to \infty$ the osmotic pressure Π satisfies the general scaling law

$$Z \equiv \frac{\Pi}{k_{\mathrm{B}}Tc} \approx f_Z(\Phi), \tag{5}$$

where c is the polymer number density and Φ is the polymer packing fraction

$$\Phi = \frac{4\pi \hat{R}_{\mathrm{g}}^3 c}{3}. \tag{6}$$

The function $f_Z(\Phi)$ is universal and given by [10]

$$f_Z(\Phi) = \frac{(1 + 2.503\,42\Phi + 2.5454\Phi^2 + 1.029\,75\Phi^3)^{0.6555}}{(1 + 0.500\,318\Phi)^{0.6555}}. \tag{7}$$

For $\Phi \lesssim 10$, this expression is quite accurate, the error being less than 1–2%. For small Φ we have $Z = 1 + a_2\Phi + O(\Phi^2)$. The coefficient a_2 is directly related to the second virial coefficient and to the so-called interpenetration ratio[2]

$$\Psi = \frac{a_2}{3\sqrt{\pi}}. \tag{8}$$

For $N \to \infty$, Ψ converges to a universal constant Ψ^* which is known quite accurately [26]:

$$\Psi^* = 0.246\,93 \pm 0.000\,13. \tag{9}$$

Other estimates of Ψ^* are reported in [26].

The determination of the second virial coefficient for polymeric systems is quite easy; efficient algorithms are discussed in [26, 27]. The direct determination of the osmotic pressure instead is not an easy task: one might use the repulsive-wall thermodynamic integration method [28–30], look at the sedimentation equilibrium in an external constant force field [30, 31], or compute it from measurements of the chemical potential [30, 32]. Here we shall compute the derivative

$$K \equiv \frac{1}{k_{\mathrm{B}}T}\frac{\partial \Pi}{\partial c}. \tag{10}$$

The determination of K is much simpler. By using the compressibility rule [33], it can be derived from the total structure factor, which can be easily measured in simulations. Some technical details are reported in [10].

3. A first multi-blob model

In [19] the interaction potentials $w_{nn}(r)$ and $W(r)$ are defined as those appropriate for the coarse-grained model with $n = 1, 2$, i.e.

$$\begin{aligned} W(r) &= B\exp[-\alpha(r/\hat{r}_{\mathrm{g}})], \\ w_{nn}(r) &= A(r/\hat{r}_{\mathrm{g}} - a_0)^2, \end{aligned} \tag{11}$$

---

[2] If we write $Z = 1 + B_2 c + O(c^2)$, where B_2 is the second virial coefficient, we have $a_2 = 3B_2/(4\pi \hat{R}_{\mathrm{g}}^3)$ and $\Psi \equiv \frac{1}{4}\pi^{-3/2}B_2\hat{R}_{\mathrm{g}}^{-3}$.

where $\hat{r}_{\mathrm{g}}$ is the zero-density radius of gyration of the blob. By comparing with MC results for self-avoiding walks with $L = 2000$, one obtains [19]

$$\begin{aligned} \alpha &= 0.80, & B &= 1.92, \\ A &= 0.534, & a_0 &= 0.730. \end{aligned} \tag{12}$$

It is convenient to introduce an adimensional scale

$$\rho = \sqrt{\alpha}r/\hat{r}_{\mathrm{g}}, \tag{13}$$

so that

$$W(\rho) = B\mathrm{e}^{-\rho^2} \qquad w_{nn}(\rho) = a(\rho - \rho_0)^2. \tag{14}$$

Parameters (12) correspond to

$$B = 1.92 \qquad a = 0.668 \qquad \rho_0 = 0.653. \tag{15}$$

In the multi-segment philosophy of [19], one must also relate the radius of gyration $\hat{R}_{\mathrm{g}}$ of the polymer to the radius of gyration $\hat{R}_{c,\mathrm{g}}$ of the coarse-grained molecule. A simple relation can be derived by assuming factorization of the polymer form factor:

$$\hat{R}_{\mathrm{g}}^2 = \hat{R}_{c,\mathrm{g}}^2 + \hat{r}_{\mathrm{g}}^2 = \frac{\hat{r}_{\mathrm{g}}^2}{\alpha}\left(\frac{\alpha \hat{R}_{c,\mathrm{g}}^2}{\hat{r}_{\mathrm{g}}^2} + \alpha\right). \tag{16}$$

The correction due to $\hat{r}_{\mathrm{g}}^2$ (in the units we use, see (13), it amounts to adding $\alpha = 0.8$ to the estimated $\hat{R}_{c,\mathrm{g}}^2$) is essential for small values of n, but becomes a tiny correction for $n \gtrsim 25$.

We determine the interpenetration ratio Ψ for several values of n; the results are shown in figure 2. For $n = 1$ the result $\Psi = 0.2576$ is close to the asymptotic one (9). The small difference is due to the fact that the parameters (12) are slightly different from those that are appropriate for the asymptotic pair potential reported in [16]. As n increases, the interpenetration ratio Ψ increases too, and becomes significantly larger than the correct result: only for large values of n does it decrease again and converge to the asymptotic value (9). For small values of n, say $n \approx 2$–10, there may be two reasons for the discrepancy. First, relation (16) may not provide the correct radius of gyration of the polymer. Second, the transferability approximation may not be appropriate. On the other hand, for $n \gtrsim 25$ we do not expect $\hat{R}_{\mathrm{g}}$ to differ significantly from $\hat{R}_{c,\mathrm{g}}$, so that the observed deviations are most probably a consequence of the failure of the approximation (3). To verify this statement, for $n = 26$ we compute the ratio $\hat{R}_{\mathrm{g}}^2/\hat{R}_{c,\mathrm{g}}^2$ (note that this quantity is universal and depends only on n) by direct monomer-level simulations. We use Domb–Joyce walks with 5200 monomers at $w^* = 0.505\,838$, a value which is close to the optimal one (see [26] for details on the model). We obtain $\hat{R}_{\mathrm{g}}^2/\hat{R}_{c,\mathrm{g}}^2 \approx 1.069$. Since the blobs have 200 monomers each, we expect this estimate to be close to the asymptotic ($N \to \infty$) value. Equation (16) gives instead $\hat{R}_{\mathrm{g}}^2/\hat{R}_{c,\mathrm{g}}^2 \approx 1.029$. If we use the MC estimate of $\hat{R}_{\mathrm{g}}^2/\hat{R}_{c,\mathrm{g}}^2$, we obtain $\Psi \approx 0.3133$ instead of the result $\Psi \approx 0.3317$ reported in figure 2. The difference is tiny and the new estimate is only slightly better than the previous one.
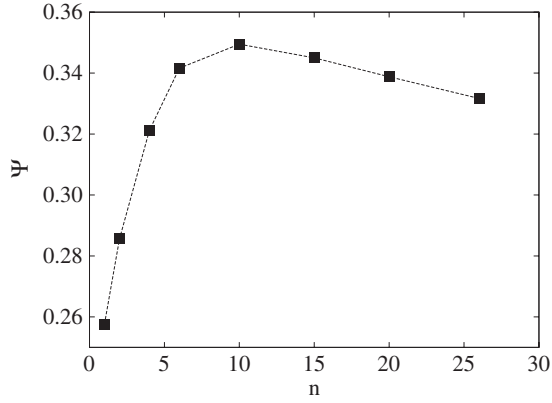
Figure 2. Estimates of the interpenetration ratio Ψ for $n \leqslant 26$. We use potentials (14), fixing the parameters as in (15). The radius of gyration is computed by using (16). The asymptotic universal value for polymer solutions is $\Psi^* = 0.24693 \pm 0.00013$ [26]. For $n = 100$ and 1000, we obtain $\Psi \approx 0.2957$ and 0.264, respectively.

For $n = 26$ we also compute the inverse compressibility K for two different values of the polymer packing fraction, $\Phi \approx 1$ and 10. More precisely, we perform two MC runs at $\Phi_c = 1$ and 10, where

$$\Phi_c \equiv \frac{4\pi R_{c,\mathrm{g}}^3 c}{3}. \qquad (17)$$

We obtain

$$\begin{aligned} \Phi_c = 1 \qquad & K = 7.71(4), \\ \Phi_c = 10 \qquad & K = 115.7(5). \end{aligned} \qquad (18)$$

If we use (16), these two values of Φ_c correspond to $\Phi = 1.04$ and 10.44; the asymptotic expression (7) then predicts $K = 5.1$ and 82. If instead we use the MC determined ratio $\hat{R}_\mathrm{g}^2/\hat{R}_{c,\mathrm{g}}^2 \approx 1.069$, we obtain $\Phi = 1.14$ and $\Phi = 11.42$ and $K = 5.6$ and $K = 92$, respectively. In both cases, we observe a significant difference between the estimates (18) and the asymptotic prediction (7).

These results allow us to conclude that the transferability hypothesis does not provide a model which reproduces the polymer thermodynamics with good accuracy. Therefore, we must somehow take into account the n dependence of the potentials. An exact treatment is technically impossible. A phenomenological approach will be discussed in section 4.

4. A different parametrization of the coarse-grained model

In the previous section we have shown that the transferability approximation fails. Here we use a more phenomenological approach and determine a different set of parameters which provide coarse-grained models whose thermodynamical behavior is very close to that of large-N polymer systems. We do not consider small values of n, since we would like to apply the model in the semi-dilute region $\Phi \lesssim 5$–10 and to investigate the behavior of binary mixtures of polymers and small colloids (in this case, it is natural to have a blob size comparable to the dimension of the colloids). Since the relation

between $\hat{R}_\mathrm{g}$ and $\hat{R}_{c,\mathrm{g}}$ is not easily defined, we simply set $\hat{R}_\mathrm{g} = \hat{R}_{c,\mathrm{g}}$. This definition does not allow us to consider very small values of n and makes the interpretation of the model as the result of a coarse-graining procedure less clear. It is, however, very convenient in practice since, at the end, we only want a model which shows the correct universal behavior and which can be simulated with a limited computational effort. We use the same Hamiltonian (4) as before, with $w_{nn}(r)$ and $W(r)$ defined in (14). The parameters a, ρ_0, and B are assumed to depend on n and, for each n, are determined as follows.

(a) We choose arbitrarily ρ_0. This parameter is kept fixed in the procedure.

(b) We perform zero-density simulations for several values of a and B. By using data reweighting methods, this allows us to determine the interpenetration ratio as a function of these two parameters, i.e. to obtain the function $\Psi(a, B)$. Then, for each value of a we determine $B_{\mathrm{opt}}(a)$, which is such that $\Psi(a, B_{\mathrm{opt}}) = \Psi^*$, where Ψ^* is the asymptotic value (9).

(c) We perform MC simulations at $\Phi = 10$ for several values of a, fixing each time $B = B_{\mathrm{opt}}(a)$. We measure the inverse compressibility K and then select the value of a such that $K \approx 77$, which is the asymptotic value obtained by using (7).

We apply this procedure to two values of ρ_0, $\rho_0 = 0.653$ as in (12), and $\rho_0 = 0$. The results of the simulations are reported in table 1. By requiring $K(\Phi = 10)$ to give the asymptotic result $K \approx 77$, we can select the optimal values of the parameters:

$$\begin{aligned} n = 26 \qquad & a = 0.15 \qquad & B = 8.28 \qquad & \rho_0 = 0.653, \\ n = 26 \qquad & a = 0.125 \qquad & B = 8.86 \qquad & \rho_0 = 0, \\ n = 51 \qquad & a = 0.12 \qquad & B = 9.178 \qquad & \rho_0 = 0, \\ n = 101 \qquad & a = 0.12 \qquad & B = 8.50 \qquad & \rho_0 = 0. \end{aligned} \qquad (19)$$

Note that ρ_0 does not play a great role and the values of a and B corresponding to $\rho_0 = 0.653$ and 0 are close. Moreover, at fixed ρ_0, the n dependence of the coefficients is tiny.

Since, by construction, these models give the correct interpenetration ratio Ψ, and therefore the correct thermodynamical behavior in the dilute regime, and the correct inverse compressibility K for $\Phi = 10$, we expect them to reproduce quite accurately the thermodynamical behavior of polymer solutions for any $\Phi \lesssim 10$. In order to check the behavior for intermediate values of the concentration, we consider the model with $n = 26$, $a = 0.125$, $B = 8.86$, and $\rho_0 = 0$, and compute K for some intermediate values of Φ. We obtain

$$\Phi = 4 \qquad K = 23.3 \pm 0.2 \qquad K_{\mathrm{asympt}} \approx 24.1, \qquad (20)$$

$$\Phi = 6 \qquad K = 39.3 \pm 0.5 \qquad K_{\mathrm{asympt}} \approx 40.2, \qquad (21)$$

$$\Phi = 8 \qquad K = 58.6 \pm 0.5 \qquad K_{\mathrm{asympt}} \approx 58.0. \qquad (22)$$

Here K_{asympt} is the asymptotic value obtained by using (7). Results are quite close, indicating that the thermodynamical behavior is correctly reproduced in the whole interval $\Phi \lesssim 10$.

Table 1. Estimates of the inverse compressibility $K(\Phi)$ and of the size ratio $S_g(\Phi)$ (see (23) for the definition) for polymer packing fractions $\Phi = 1, 10$ for several values of n, a, B, ρ_0. The results corresponding to $n = \infty$ are obtained by using (7) and (24).

n	a	B_{opt}	ρ_0	$K(\Phi = 1)$	$K(\Phi = 10)$	$S_g(\Phi = 1)$	$S_g(\Phi = 10)$
26	0.6	0.542	0.653	4.64(3)	47.8(1)	0.9374(9)	0.805(1)
26	0.2	4.0	0.653	4.76(2)	65.9(3)	0.9322(6)	0.772(2)
26	0.175	5.507	0.653	4.79(2)	70.7(7)	0.9335(6)	0.771(3)
26	0.15	8.28	0.653	4.78(2)	77.3(5)	0.9334(6)	0.772(2)
26	0.15	5.058	0	4.81(2)	69.4(7)	0.9340(7)	0.773(4)
26	0.125	8.86	0	4.89(3)	78.4(6)	0.9286(6)	0.761(2)
51	0.125	8.075	0	4.84(2)	74.2(6)	0.9296(5)	0.738(2)
51	0.12	9.178	0	4.80(3)	75.6(6)	0.9301(5)	0.745(3)
101	0.125	7.60	0	4.89(3)	73.2(2.5)	0.9302(8)	0.703(6)
101	0.12	8.50	0	4.87(7)	75.4(1.8)	0.9293(8)	0.709(4)
∞				4.90	77.4	0.9287	0.689

In the appendix we present another test, computing the chemical potential μ as a function of Φ. The results are consistent with what is expected on the basis of (7).

It is also interesting to verify the accuracy of the coarse-grained models for the calculation of structural properties. For this purpose, we consider the ratio

$$S_g(\Phi) \equiv \frac{R_g^2(\Phi)}{\hat{R}_g^2}. \qquad (23)$$

Such a quantity converges to a universal function $f_g(\Phi)$ as the polymer length goes to infinity. This function has been estimated quite accurately in [10]:

$$S_g(\Phi) \approx f_g(\Phi)$$
$$= \frac{(1 + 0.332\,72\Phi)^{0.115}}{(1 + 0.986\,633\Phi + 0.499\,436\Phi^2 + 0.049\,5970\Phi^3)^{0.115}}. \qquad (24)$$

Estimates of $S_g(\Phi)$ are reported in table 1. For $\Phi = 1$, there is perfect agreement in all cases, and therefore, in the dilute regime the models are also appropriate for the study of structural properties. For $\Phi = 10$ we instead observe quite large differences. For instance, for $n = 26$ all models overestimate the ratio by 10%. However, note that the discrepancy rapidly decreases with increasing n, and for $n = 101$, the ratio $S_g(\Phi = 10)$ is quite close to the asymptotic value.

The results for $S_g(\Phi)$ allow us to reinterpret the coarse-grained model as an optimal model in the RG sense, as we have discussed in the Introduction. Indeed, at fixed Φ we expect

$$S_g(\Phi, N) = f_g(\Phi) + \frac{\alpha_1(\Phi)}{n^\Delta} + \frac{\alpha_2(\Phi)}{n^{\Delta_2}} + \cdots \qquad (25)$$

where $\Delta \approx 0.5$, $\Delta_2 \approx 1$. The coefficients $\alpha_1(\Phi)$ and $\alpha_2(\Phi)$ depend on the Hamiltonian parameters. However, for the models (19) with $\rho_0 = 0$, a and B vary only slightly and thus we expect this dependence to be tiny. If we neglect it, all results are consistent with $\alpha_1(\Phi) \approx 0$ and $\alpha_2(\Phi) \approx 2$. In other words, our phenomenological approach naturally provides an approximately optimal model in the RG sense.

5. Conclusions

In this paper we discuss coarse-grained models which provide an effective accurate description of polymer solutions in the semi-dilute regime. We start from the multi-blob model of [19] and discuss two different strategies one can use to determine the coefficients that parametrize the interaction potentials.

We first consider the method of [19], which is essentially based on the transferability hypothesis (3), and show that the resulting model is not very accurate: both in the dilute and in the semi-dilute regime the osmotic pressure is significantly overestimated. Next, we consider a different, more phenomenological approach which, by its very definition, gives models which reproduce the thermodynamical behavior of polymer solutions in the semi-dilute regime. With $n = 26$ units, the osmotic pressure determined in the coarse-grained model is very close to that of large-N polymer solutions up to $\Phi \approx 10$, with differences of a few per cent. These models are also reasonably accurate for structural properties, although in this case somewhat larger values of n, $n = 100$ say, must be considered.

It is interesting to note that the interaction potentials we obtain for $n \gtrsim 26$ are quite different from those appropriate for effective models with $n = 1, 2$. Indeed, in all cases the constant B that parametrizes the intermolecular potential (11) is quite large ($B \approx 8$–9), so that the blobs are not soft particles. Second, the spring constant A is significantly smaller ($A \approx 0.1$) than that obtained for $n = 2$, see (12). This means that the blob–blob distance has a very broad distribution. *A posteriori*, it is possible to justify both results physically. Consider a real polymer of length L, with hard-core monomers, and a coarse-grained model with n units. If n is small, L/n is relatively large. Hence, each blob contains many monomers and therefore it is relatively easy for the blobs to overlap. If, instead, n is large, each blob contains a small number of monomers. In this case, the repulsion of the monomers makes it difficult for the blobs to overlap. In the limiting case, $n = L$, no overlap is possible. Thus, as n increases we expect the soft-core potentials to turn into strongly repulsive ones. Also, the decrease in A has an analogous interpretation. If n is small, the blob size has a narrow distribution since it is obtained by averaging over a large number of monomers. The blob–blob distance should be determined by the blob size, hence it should

also have a narrow distribution. On the other hand, if n is large, we expect a broader distribution both for the blob size and for the blob–blob distance, because of the small number of monomers in each blob.

The coarse-grained model we have considered is defined off the lattice. However, it is probably of interest to check whether a similar model can be defined on the lattice, since lattice models are particularly convenient from a computational point of view. One possibility would be to start from the Domb–Joyce model (the parameter w, see [10] for a precise definition, is essentially equivalent to B), giving up the condition that two successive monomers belong to nearest-neighbor lattice sites. One could thus allow arbitrary bond lengths controlled by an additional tethering potential depending on a parameter a. Tuning a and w, one might obtain a lattice course-grained model appropriate for the study of thermodynamic and structural properties of polymer solutions under good-solvent conditions in the semi-dilute regime.

Acknowledgments

Appendix. Computation of the chemical potential

In this appendix we report another test of the coarse-grained models (19), by computing the relation between the chemical potential μ and Φ. For this purpose we perform grand-canonical simulations using the configurational-bias method [34]. In these simulations we fix the fugacity $z = e^{\beta\mu}$ and compute the density, or equivalently Φ. Some of the results are reported in table A.1. The results should be compared with the general thermodynamic relation

$$\beta\mu(\Phi) = \ln\Phi + \mu_0 + \int_0^\Phi \frac{K(\varphi) - 1}{\varphi}\,\mathrm{d}\varphi, \qquad (A.1)$$

where μ_0 is a model-dependent constant and K the inverse compressibility. In order to determine μ_0, for each model we have performed a simulation with a large negative values of μ, so that $\Phi \lesssim 0.01$ and we have required $\beta\mu = \ln\Phi + \mu_0 + 3\sqrt{\pi}\Psi^*\Phi$, which is the low-density expansion of (A.1). If

the coarse-grained models provide good approximations of the universal behavior, (A.1) should be satisfied for all Φ, once we compute $K(\Phi)$ by using (7). The results reported in the Table show that this relation is well satisfied. In the dilute regime differences are less than 1%, while in the semi-dilute regime ($\Phi \approx 6$) it rises to 3%.

References

[1] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
[2] de Gennes P G 1972 *Phys. Lett.* A **38** 339
[3] Freed K F 1987 *Renormalization Group Theory of Macromolecules* (New York: Wiley)
[4] Schäfer L 1999 *Excluded Volume Effects in Polymer Solutions* (Berlin: Springer)
[5] des Cloizeaux J and Jannink G 1990 *Polymers in Solution, Their Modelling and Structure* (Oxford: Oxford University Press)
[6] Schweizer K S and Curro J G 1997 *Adv. Chem. Phys.* **98** 1
[7] Wegner F J 1976 *Phase Transitions and Critical Phenomena* vol 6 , ed C Domb and M S Green (New York: Academic)
[8] Belohorec P and Nickel B G 1997 Accurate universal and two-parameter model resultsfrom a Monte Carlo renormalization group study *Guelph University Report* unpublished
[9] Domb C and Joyce G S 1972 *J. Physique* C **5** 956
[10] Pelissetto A 2008 *J. Chem. Phys.* **129** 044901
[11] Flory P J and Krigbaum W R 1950 *J. Chem. Phys.* **18** 1086
[12] Grosberg A V, Khalatur P G and Khoklov A R 1982 *Mater. Chem. Phys.* **3** 709
[13] Dutenhahn J and Hall C K 1994 *Macromolecules* **27** 5399
[14] Bolhuis P G, Louis A A, Hansen J P and Meyer E J 2001 *J. Chem. Phys.* **114** 4296
[15] Likos C N 2001 *Phys. Rep.* **348** 267
[16] Pelissetto A and Hansen J P 2005 *J. Chem. Phys.* **122** 134904
[17] Bolhuis P G, Louis A A and Hansen J P 2001 *Phys. Rev.* E **64** 021801
[18] Louis A A 2002 *J. Phys.: Condens. Matter* **14** 9187
[19] Pierleoni C, Capone B and Hansen J P 2007 *J. Chem. Phys.* **127** 171102
[20] Prellberg T 2001 *J. Phys. A: Math. Gen.* **34** L599
[21] Hsu H-P, Nadler W and Grassberger P 2004 *Macromolecules* **37** 4658
[22] Pelissetto A and Vicari E 2007 *J. Phys. A: Math. Theor.* **40** F539
[23] Clisby N, Liang R and Slade G 2007 *J. Phys. A: Math. Theor.* **40** 10973
[24] Pelissetto A and Vicari E 2002 *Phys. Rep.* **368** 549
[25] Pierleoni C, Addison C I, Hansen J P and Krakoviack V 2006 *Phys. Rev. Lett.* **96** 128302
[26] Caracciolo S, Mognetti B M and Pelissetto A 2006 *J. Chem. Phys.* **125** 094903
[27] Li B, Madras N and Sokal A D 1995 *J. Stat. Phys.* **80** 661
[28] Dickman R 1987 *J. Chem. Phys.* **87** 2246
[29] Addison C I, Louis A A and Hansen J P 2004 *J. Chem. Phys.* **121** 612
[30] Ivanov V A, An E A, Spirin L A, Stukan M R, Müller M, Paul W and Binder K 2007 *Phys. Rev.* E **76** 026702
[31] Addison C I, Hansen J P and Louis A A 2005 *ChemPhysChem* **6** 1760
[32] Müller M and Paul W 1994 *J. Chem. Phys.* **100** 719
[33] Hansen J-P and McDonald I R 2006 *Theory of Simple Liquids* 3rd edn (New York: Academic)
[34] Frenkel D and Smit B 1996 *Understanding Molecular Simulation* (San Diego, CA: Academic)

Table A.1. Estimates of the polymer packing fraction $\Phi(\mu)$ for several values of n and $\beta\mu$ such that $\Phi \approx 0.1, 1, 6$. Here $\beta\mu_{\mathrm{pred}}$ is the prediction (A.1) with $K(\Phi)$ computed by using (7). The results refer to the optimal models (19) with $\rho_0 = 0$.

n	$\beta\mu$	Φ	$\beta\mu_{\mathrm{pred}}$
26	$-7.824\,05$	0.0993(1)	-7.823
	$-2.407\,95$	1.0164(2)	-2.382
	26.025 8	6.0167(5)	26.64
51	$-6.502\,29$	0.1022(3)	-6.498
	$-1.203\,97$	0.9974(7)	-1.187
	27.230 5	6.046(1)	28.13
101	$-2.673\,65$	0.1023(3)	-2.668
	2.674 15	1.0089(7)	2.698
	31.638 4	6.143(2)	32.61