Consistent and transferable coarse-grained model for semidilute polymer solutions in good solvent

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Consistent and transferrable coarse-grained model for semidilute polymer solutions in good solvent

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We present a coarse-grained model for linear polymers with a tunable number of effective atoms (blobs) per chain interacting by intra- and inter-molecular potentials obtained at zero density. We show how this model is able to accurately reproduce the universal properties of the underlying solution of athermal linear chains at various level of coarse-graining and in a range of chain densities which can be widened by increasing the spatial resolution of the multiblob representation, i.e., the number of blobs per chain. The present model is unique in its ability to quantitatively predict thermodynamic and structural properties of polymer solutions deep in the semidilute regime with a very limited computational effort, overcoming most of the problems related to the simulations of semidilute polymer solutions in good solvent conditions.

The last decade has witnessed a considerable effort in developing coarse-grained (CG) models to bridge the length-scale gap between the microscopic scale and the meso(macro)-scopic scale typical of soft-matter and biological systems. Two general strategies have been attempted: the structure-based route in which CG models are tuned to reproduce some structural properties at the local scale and the thermodynamic-based route in which the models are required to reproduce solvation free energies. Also mixed strategies have been developed and applied to a large variety of physical systems. An overview of methods and recent applications can be found in refs. [1–4].

The structure-based route groups a number of atoms into effective "particles" and assumes state-dependent pair interactions between them. These potentials are derived from the local structure of the atomic-level system, using the Iterative Boltzmann Inversion (IBI) [5–7], the Inverse Monte Carlo (IMC) [8] or by liquid-state theory techniques [9, 10]. The state dependence of the effective pair potentials hides the underlying many-body character and entropic content of the effective interactions and poses the question of their transferability. Indeed, if the effective potentials are not transferrable, setting up the CG model requires deriving the effective interactions for all thermodynamic states of interest, seriously limiting the benefits of the coarse-graining strategy. Generally speaking, the problem of transferability remains unsolved.

In this letter we present a CG model for homopolymers in good-solvent conditions (athermal solvent) which is fully transferrable both with the number of effective monomers per chain and with the density of chains. The model is set up at zero density (isolated chain) by mapping a single long chain onto a short linear molecule of n effective monomers (blobs). The effective intramolecular n-body potential is represented by a sum of two-body, three-body (bending) and four-body (torsional angle) potentials [11]. The potentials are first obtained for $n = 4$ (tetramer model) and then transferred to longer chains (multiblob model) by simply rescaling the length scale of the pair potentials. Angular interactions are assumed to be independent of the model resolution. Intermolecular pair potentials between blobs of different chains are also obtained at zero density for two isolated tetramers. The same rescaling of the central potentials, together with the corresponding increase in the number of blobs per chain, ensures the transferability of the zero-density CG model to any finite density, allowing us to explore polymer solutions deep in the semidilute regime with a limited computational effort.

Structure-based single-blob CG models for polymer solutions have been introduced some time ago [12–17]. For two isolated coils in athermal solvent the effective interaction between the centers of mass of the coils is roughly Gaussian, of the order of $2k_BT$ at overlap, and with a range of the order of the coil radius of gyration. This single-blob model is only accurate in the dilute regime, in which chain overlaps can be neglected. In a semidilute solution of N linear chains of L monomers in a volume V, chain density, $c = N/V$, is larger than the overlap density $c^* = 3/4\pi \hat{R}_g^3$ ($\hat{R}_g = bL^\nu$ is the isolated coil radius of gyration, b the monomer size and ν the scaling exponent) while the monomer density is still very small, a condition that can always be satisfied if chains are long enough [18]. An accurate description of the thermodynamic and

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structural behavior of polymers in these conditions can be obtained by using CG chains, in which a number m of the original monomers are grouped in one effective monomer (blob) to map the original chain of $L = nm$ monomers onto a chain of n effective blobs (multiblob model). If the level of coarse graining, i.e. the number n of blobs per chain, is such that the blob density $c_b = nc$ is below the overlap blob density $c_b^* = 3/4\pi\hat{r}_g^3$ ($\hat{r}_g \sim m^\nu$ is the zero-density radius of gyration of the blob), then pairwise, zero-density intermolecular potentials between blobs can be safely used. These ideas were discussed in Refs. [19, 20] and recently reviewed in Ref. [11]. Although in principle very appealing, the problem with this approach is how to obtain the intramolecular potential. Indeed, this inherently many-body potential is in principle of increasing complexity when increasing the number of blobs per chain, and since blobs are tethered together in some fixed topology, a zero-density expansion cannot be invoked to decompose it into a sum of two-body, three-body, etc. terms. We will show in the following that a careful parametrization of n-body terms up to $n = 4$ is enough to obtain a very accurate and transferrable CG potential field.

A crucial requirement of any accurate multiblob representation of the underlying full-monomer (FM) chain model is to preserve the value of the radius of gyration for all values of n. Let us consider a chain of L monomers mapped onto a chain of n blobs each representing the center of mass of a subchain of m monomers. The fundamental relation $R_g^2 = R_{g,b}^2(n) + r_g^2(n)$, among the chain radius of gyration R_g, the radius of gyration $R_{g,b}(n)$ of the chain of n blobs, and the blob radius of gyration $r_g(n)$, holds for any single configuration and therefore on average. In the scaling limit, it has been found that [11]

$$\hat{R}_{g,b}^2(n)/\hat{R}_g^2 = (1 - k^2/n^{2\nu}), \qquad (1)$$

$$k^2 = \hat{r}_g^2(n)n^{2\nu}/\hat{R}_g^2 = (1.03 - 0.04/n)^2, \qquad (2)$$

where $\nu = 0.587597(7)$ [21]. Here and in the following we will use a hat to indicate zero-density averages. A consistent multiblob model must obey these relations when varying n. For $n \gg 1$, $\hat{R}_{g,b}(n) \simeq \hat{R}_g$ and $\hat{R}_{g,b}^2(n)/\hat{r}_g^2(n) = 0.94n^{2\nu}$. A proper definition of $\hat{R}_g$, independent on n, including the prefactor, is crucial since chain structural properties are universal only if distances are expressed in terms of $\rho = r/\hat{R}_g$. Moreover, at finite density results from different values of n, should be compared at the same value of the polymer volume fraction $\Phi = c/c^* = 3c/(4\pi\hat{R}_g^3)$. Changing the definition of $\hat{R}_g$ with n, changes the definition of both ρ and Φ and the comparison among models with different n becomes meaningless.

In Ref. [11] a CG model with four blobs per chain (tetramer) was developed and throughly studied. Central potentials between first, second and third neighbors along the chain, as well as a bending and torsional an-

TABLE I: $\hat{R}_{g,b}(n)/\hat{R}_g$ and universal ratio $A_2 = B_2/\hat{R}_g^3$ (B_2 is the second virial coefficient) as a function of n for polymers obtained by FM simulations (FM), and for the original and modified 4MB models. The universal value for polymers of the second virial coefficient is $A_2 = 5.500(3)$ [23].

	$\hat{R}_{g,b}(n)/\hat{R}_g$			$A_2 = B_2\,\hat{R}_g^3$	
n	FM	4MB-1	4MB-2	A_2(4MB-1)	A_2(4MB-2)
4	0.8921	0.8933(3)	0.8903(2)	5.600(2)	5.596(3)
10	0.9642	0.9812(3)	0.9638(7)	5.676(2)	5.619(2)
20	0.9842	1.0060(6)	0.983(3)	5.714(2)	5.614(3)
30	0.9902	1.0131(8)	0.990(3)	5.734(3)	5.618(6)

gle potentials were determined by IBI to reproduce the pair distances and angular distributions of a FM chain in the scaling limit, mapped onto four blobs [11]. Moreover, an intermolecular Gaussian potential between any pair of blobs of different tetramers was assumed and optimized to reproduce the radial distribution function between the centers of mass of two chains in the scaling limit [17]. The model perfectly reproduces the structure of the isolated chain, and provides accurate results for the thermodynamics of the solution up to $\Phi \simeq 2$. The (universal) angular distributions of the tetramer are induced by the the specific mapping of subchains onto their centers of mass, a procedure which introduces an explicit angular correlation along the chain even for ideal chains [22]. Failure in reproducing the correct angular distributions is at the basis of the inconsistent behavior observed for simpler multiblob models [11, 19, 20]. Note that while central potentials are two-body interactions, bending and torsional angle potentials represent genuine three- and four-body interactions, respectively. Interestingly [11], a hierarchical order in the intensity of the various potential was observed, the strongest and most relevant being the central first-neighbor interaction (bonding), followed by the second and third neighbor central interactions, and finally by the bending and the torsional angle potentials. Therefore, correlations along the chain decrease with the chemical distance and many-body effects are smaller than two-body ones, although of different nature. This observation suggests to use tetramers as building blocks of a resolution-invariant multiblob model.

A first tetramer-based multiblob model (4MB-1) is obtained by using the tetramer potentials of Ref. [11] (see supplementary material). The length scale of the central potentials ($V_{i,i+1}, V_{i,i+2}, V_{i,i+3}$ and W) is set by the blob radius of gyration $\hat{r}_g$. In practice this means that in changing the number of blobs from n to n', the length scale is multiplied by $(n/n')^\nu$ (see supplemental material). The angular potentials are instead invariant under this scale transformation. This model, however, is not found to be fully satisfactory as illustrated in Table I, where we report results for the zero-density chain radius of gyration and the second dimensionless virial coefficient
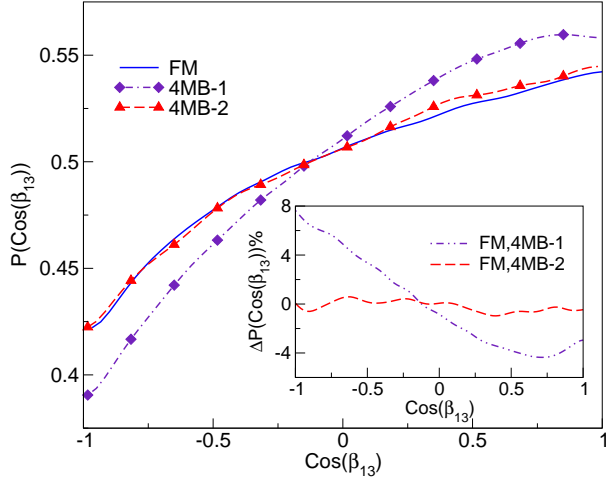
FIG. 1: Probability distribution of $\cos\beta_{13}$ in the original tetramer model (4MB-1) and in the modified tetramer model (4MB-2). The distribution for a FM chain with four blobs is also reported for comparison (FM). The inset displays the relative difference of the two models with the FM prediction.

FIG. 2: Intramolecular radial distribution function $\rho^2 g_{intra}(\rho)$ versus the reduced blob distance $\rho = r/\hat{R}_g$ for model 4MB-2 with $n = 20$ and for the FM chain with 20 blobs (FM). Four values of the reduced density are reported: $\Phi = 0, 1.09, 4.36, 8.72$. For sake of clarity, results at different densities are shifted upward according to the legend.

for increasing n for polymer chains in the scaling limit (FM)[25], the multiblob model (4MB-1), and the modified multiblob model (4MB-2) still to be discussed. In particular, in model 4MB-1, $\hat{R}_{g,b}(n)/\hat{R}_g$ becomes greater than 1 for increasing n, a fact clearly incompatible with the multiblob procedure [see Eq. (1)]. Also a systematic increase with n in the second virial coefficient of 4MB-1 is observed which witnesses the inability of such model to be fully consistent at all resolutions. The origin of such inconsistency can be ascribed to a residual inaccuracy of the original tetramer model to reproduce four-body correlations. In Fig 1 we show, for $n = 4$, the probability distribution of $\cos\beta_{13} = (\mathbf{b_1} \cdot \mathbf{b_3})/(|\mathbf{b_1}||\mathbf{b_3}|)$ where $\mathbf{b}_i$ is the bond vector between blobs i ad $i + 1$. Data of the 4MB-1 model are compared with FM results. Despite the explicit presence of the angular potential which reproduces very accurately the torsional angle distribution [11], $P(cos\beta_{13})$ is not well reproduced in the 4MB-1 model—more elongated configurations are apparently enhanced. This inaccuracy, irrelevant for the properties of the multiblob model at the tetramer level ($n = 4$), accumulates when transferring the tetramer potentials to longer chains, producing the observed increase of $\hat{R}_{g,b}(n)/\hat{R}_g$ and A_2 with n. We propose here a modified tetramer model in which a new potential on $\cos\beta_{13}$ is added to reproduce the FM behavior. As for the other potentials, also in this case the IBI procedure is applied to extract the optimal potential. At the same time the dihedral angle potential is re-optimized to keep the level of accuracy of the original tetramer model. Explicit expressions for the potentials are provided in the supplementary material. The good accuracy of the new model is illustrated in Fig. 1. The modified tetramer model can now be
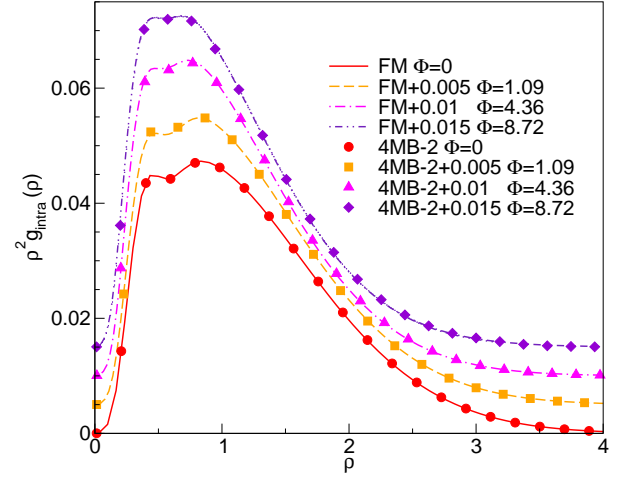
safely used as building block of a fully consistent model (4MB-2) which puts in action the ideas of the multiblob approach. As illustrated in Table I, at zero density the agreement with the FM predictions for the rescaled radius of gyration is excellent for all n values investigated. Also the virial coefficient is independent on n and in good agreement with the FM prediction $A_2 = 5.500(3)$ [24]. This is the first requirement of transferability with n at zero density. We have also checked that genuine five-body correlations, as represented by the two-dimensional correlation function between two subsequent dihedral angles along the chain, are well reproduced by the 4MB-2 model, the relative deviation from the FM results being $\lesssim 6\%$ (see supplementary material). This observation supports our implicit assumption that irreducible n-body terms in the intramolecular potential for $n \geq 5$ are negligible.

The second and more difficult requirement for a transferable CG model is the ability to reproduce FM predictions at any finite chain density by increasing the number of blobs n. To illustrate the ability of our multiblob model to match this second requirement we compare single-chain properties and the Equation of State (EOS) with FM predictions in the reduced density range $\Phi = c/c^* \lesssim 9$. Note that a unique definition of Φ for increasing n is only possible for a resolution-invariant model at zero density, as the one proposed here. In Fig. 2 we compare FM and 4MB-2 predictions for the intramolecular radial distribution function $\rho^2 g_{intra}(\rho)$, which is universal in terms of the reduced intra-blob distance $\rho = r/\hat{R}_g$, for a chain of $n = 20$ blobs and for increasing density. The observed agreement is remarkable in particular at the highest density investi-
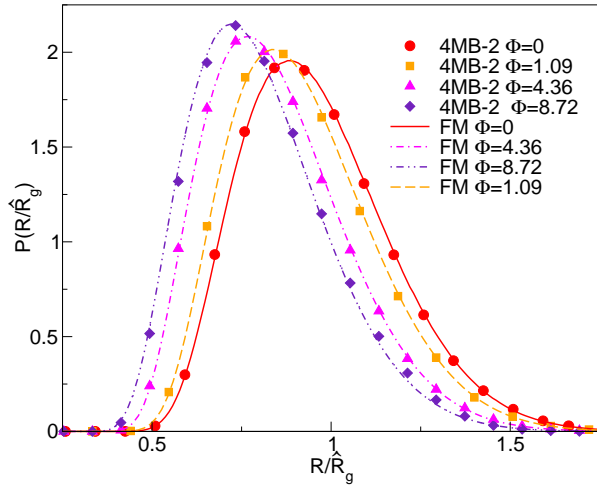
FIG. 3: Chain radius of gyration probability distribution function $P(R/\hat{R}_g)$ (R is the radius of gyration of a single chain and $\hat{R}_g$ its zero-density average) at $\Phi = 0, 1.09, 4.36, 8.72$ for a chain of $n = 20$ blobs. Comparison between the 4MB-2 model and the FM predictions.

TABLE II: Compressibility factor Z for the 4MB-2 model for several values of n and for polymers in the scaling limit [23], at various reduced densities Φ from the dilute to the semidilute regime.

Φ	$n = 10$	$n = 20$	$n = 30$	FM
0.54	1.875(1)	1.874(2)	1.870(2)	1.8535
1.09	2.9760(4)	2.9784(6)	2.9819(1)	2.9586
2.18	5.6004(7)	5.708(1)	5.729(3)	5.63297
4.36	11.4541(5)	12.058(1)	12.269(3)	12.2585
6.54	17.532(2)	18.931(4)	19.515(5)	20.0486
8.72	23.751(1)	25.592(4)	26.989(8)	28.7032

gated, $\Phi = 8.72$, deep inside the semidilute regime. The same kind of agreement is observed for the distribution of the radius of gyration $P(R/\hat{R}_g)$ shown in Fig. 3. The agreement will worsen at the highest densities for shorter chains, but it remains very good for $n \geq 20$. We would like to emphasize the nontrivial nature of the observed agreement. Indeed, $\rho^2 g_{intra}(\rho)$ is a weighted average of the length distribution over all pairs of blobs, so the agreement for this quantity demonstrates the accuracy of the 4MB-2 model to reproduce pair distances well beyond four neighbors. $P(R/\hat{R}_g)$ includes information on pair distances but also on all possible cross-terms between different pairs, so the observed agreement for this quantity is even less obvious.

Finally, we have computed the EOS, using the standard molecular virial route to the pressure for several values of n. In Table II we report the compressibility factor $Z = \beta\Pi/c$, where $\beta = 1/k_BT$ and Π is the osmotic pressure of the solution.

Up to density $\Phi \simeq 2$, for all values of n studied re-

sults differ by less than 1% from the asymptotic polymer value. However, as expected from the multiblob heuristic argument, when density increases longer chains are systematically more accurate. At $\Phi = 4.36$ the relative deviation in Z is $\sim 5\%$ for $n = 10$, but $\lesssim 1\%$ for both $n = 20$ and $n = 30$. At $\Phi = 8.72$, the deviation is $\sim 15\%$ for $n = 10$, and decreases to $\simeq 10\%$ for $n = 20$ and $\simeq 6\%$ for $n = 30$.

In conclusion, we have developed a fully consistent, scale preserving, multiblob CG model for linear polymers in good solvent. The model is built by transferring to smaller length scales a tetramer model parametrized to reproduce a number of scalar correlations of the FM chain at zero density. We have shown that this model is fully consistent when varying the number of blobs at zero density, and more relevant, it is able to reproduce the universal EOS for athermal semidilute polymer solutions at high chain concentrations if a sufficiently large numbers of blobs per chain is chosen. In particular, the present multiblob model with only 30 blobs provides an accuracy of $\sim 5\%$ on the compressibility factor at $\Phi \sim 9$, a level of accuracy which would require the use of the order of thousand monomers even with the most efficient lattice model, namely the Domb-Joyce model tuned in such a way to cancel the leading-order corrections to scaling [23]. The present model opens the way to a quantitative study of semidilute polymer solutions in situations where local structure is important like, for instance, polymer brushes, colloid-polymer mixtures or polymer-decorated colloidal systems. It would also be extremely interesting to develop an analogous multiblob strategy for θ solvent conditions and finally to extend this approach to diblock copolymer solutions. Work in these directions is in progress. As a final remark it is interesting to observe that our model represents, to a very good approximation, the first example of a truly "fixed-point" model in the renormalization-group language, the elusive model which reproduces the scaling behavior at any level of coarse-graining. Previous work focused on defining models in which the leading scaling corrections were zero within errors. Here, instead, we obtain a model in which *all* scaling corrections are apparently small, and which is thus able to predict the scaling behavior for any $n \geq 4$. Of course, there is a price to pay: for any n, we do not have access to all possible observables, but only to the large-scale properties that can be modelled by the chosen CG model.

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