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Ab-initio Coarse-Graining of Entangled Polymer Systems

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1 Introduction

1.1 Viscoelasticity of Polymer Systems

Ever since Richard Kuhn’s description of a polymer as a coiling flexible thread [1], polymer systems have received continuous interest from both theorists and experimentalists. In semi-dilute and concentrated polymer solutions each polymer chain interacts with many other chains. The effect of these intermolecular interactions is revealed by the peculiar flow behaviour of these materials: they are very viscous and have surprising elastic properties. In uncrosslinked polymers these elastic properties manifest themselves temporarily, but still sometimes on time scales as long as seconds or hours.

This peculiar viscoelastic behaviour is often rationalized by viewing polymer systems as temporary rubbery networks. Such a network arises as a result of mutual uncrossability of the polymer chains - they are entangled. Many attempts have already been made to fundamentally explain the entanglement phenomenon. The usual procedure is to propose a microscopic model, calculate the consequences for various dynamic properties, and compare the outcome with experiment, if available. Theoretical treatments of this sort include cooperative motion models, where the focus is on the increased friction experienced by a test chain because it drags other chains with it over finite distances [2]. A major difficulty in such an approach is the specification of the location and duration of entanglements, because the exact nature of an entanglement is not known.

With the advent of the reptation theory of Doi, Edwards, and de Gennes [3], a new concept was introduced in the theory of polymer dynamics. In reptation theory each polymer is supposed to move in a tube around a Gaussian path in space. The tube only serves one purpose, namely to roughly represent the uncrossability of the surrounding chains and to turn a difficult multichain problem into a one-chain problem. The tube is clearly a mean field concept, and to this day it is debated how much validity should be ascribed to it [2, 4].
Recent years have witnessed the rapid growth of another technique to gain fundamental understanding of the dynamics of polymer systems: computer simulations. By use of computers, a range of increasingly complex models can be solved.

1.2 Detailed Computer Simulations

At a very detailed level, molecular dynamics (MD) simulations can be performed, in which each atom of a polymer chain is represented separately, see Fig. 1a. The atoms are modelled as interacting particles and they move according to Newton’s laws. Accurate force fields have been constructed to cater for anyone’s research interests, provided they exclude chemical reactions and other phenomena of a quantum mechanical nature. Bulk behaviour is simulated by applying periodic boundary conditions to the simulation box. Typical
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MD simulations cover the motion of a few tens of thousands of atoms over a period of a few nanoseconds; on current computers such a run would take a week to complete.

There are limitations, however, to the length of polymers that can be simulated this way, for two reasons. First, the typical size of the polymer typically grows as $\sqrt{n}$, where $n$ is the number of monomers in a chain. A polymer should not interact with itself via the periodic boundaries, which means that the volume of the box, and hence the number of particles, should scale as $n^{3/2}$. Second, the longest relaxation time of a polymer chain scales very fast, usually as $n^2$ or $n^3$. To obtain a well-equilibrated system, and also to measure certain long-time correlation functions, the simulation must be performed for at least as long as this time scale. It should come as no surprise that atomistically detailed MD simulations have only been performed for relatively short chains of up to 100 monomers or, if longer chains were studied, only for relatively short times.

1.3 Coarse-Grained Simulations

In order to increase the time and length scales accessible in the simulation of polymers, detailed atomistic models are replaced by coarse-grained (CG) models in which each particle represents a collection of atomic particles. The coarse-graining and subsequent analysis of the dynamic data can be performed in two ways: bottom-up (ab-initio) or top-down.

In the top-down approach a certain model for the polymer interactions is chosen beforehand. Examples include simulations on a lattice, see Fig. 1c, and simulations of chains of (relatively) hard beads, see Fig. 1d. These models are also referred to as generic models because they are thought to reproduce generic polymer behaviour. Usually the magnitude of the interactions are chosen such that bond crossings will be forbidden or at least energetically unfavourable. A well-studied example is the polymer model of Kremer, Grest and co-workers [6, 7], in which the polymer segments are modelled as relatively hard beads connected by finitely extensible non-linear springs. The simulations are performed in reduced units, i.e. length, mass, and energies are related to the size $\sigma$, mass $m$, and interaction energy $\epsilon$ of the beads. There exists a possibility to estimate the time and length scales occurring in the simulation $a$ posteriori. However, when more than one length scale is relevant, the proportionalities between different length scales may not be the same as those that occur in real polymer systems. Specifically, chemically realistic polymers are flexible only at large length scales. At these length scales the beads will be almost empty and consequently very soft. Treating a polymer as a flexible string of hard beads may therefore not give quantitative or even realistic results for (certain aspects of) the dynamics and rheology.

In this chapter we will focus on the bottom-up (ab initio) approach where the interactions between the CG particles are derived from the underlying
atomistic interactions by suitable averaging techniques [8–11]. The theory underlying this kind of coarse-graining is treated in Sect. 2. Although the dynamics of the atomistic model is deterministic and conservative, the dynamics of the resulting coarse-grained model is stochastic and includes dissipation and possibly memory effects. If the theory is followed to the rule, a correct description of the structure and dynamics follows automatically. One should be careful, however. For practical and computational reasons the effective potentials, as well as frictions and random forces, are usually represented by single or pair and sometimes triplet terms (Sect. 3). The general observation is that when the degree of coarse-graining is sufficiently large the effective potentials become very soft, as represented in Fig. 1b. Employing a single or pair friction approximation, this usually means that the bonds between the CG particles can easily cross each other, leading to very unrealistic dynamics. Luckily this can be cured. In Sect. 4 we will introduce a constraint which, when introduced in a coarse-grained simulation, can re-establish the uncrossability of chains. At the end of this chapter we will give two examples of simulations of entangled polyethylene melts and entangled wormlike micelles.

2 Theory

2.1 Coarse-Grained and Bath Variables

Coarse-graining is the process of removing those degrees of freedom that one is not going to use or measure in the final analysis. An example will make things clear. Suppose that a full description of the system being studied needs \( N + B \) degrees of freedom

\[ R_1, R_2, \ldots, R_N, q_1, q_2, \ldots q_B, \]  

and that one is only interested in the behaviour of \( R_1, R_2, \ldots R_N \). The latter may for example be coordinates describing the positions of \( N/3 \) colloidal particles while the \( q \)'s describe the configuration of a solvent in which the colloids are dissolved. Usually in a situation like this, one is only interested in the dynamics and thermodynamics of the colloids. Another example more appropriate to this chapter is where the \( R \)'s provide a rough description of the configurations of polymers in a polymer melt, while the \( q \)'s are the remaining internal coordinates describing the details of the configurations. For instance, one may subdivide each of the chains in the melt into a number of subchains, and use \( R_1, \ldots, R_{N/3} \) to describe the centres of mass of these subchains.

Obviously, in order to describe the dynamics and thermodynamics of the \( R \)'s one cannot just ignore the \( q \)'s, but rather one has to perform a statistical average over all their possible values. We shall explain how this averaging should be done in case one wants to derive the appropriate equations of motion of the \( R \)'s [12–14]. We then automatically find the appropriate averages needed to describe the thermodynamics of the \( R \)'s.
So, suppose we are given an initial box described by the coordinates of (1) and the corresponding momenta
\[ P_1, \ldots, P_N, p_1, \ldots, p_B. \] (2)

In general the momenta are defined in terms of all coordinates and the corresponding velocities, i.e. time derivatives. For our purposes it is sufficiently general if we assume \( P_i = M \dot{R}_i \), where \( M \) is the mass of \( R_i \), and \( p_i \) is some function of the \( q \)'s and their time derivatives. Now, given the initial conditions, we may solve the equations of motion and calculate \( R_1(t), \ldots, R_N(t) \) at all times of interest. Together these functions yield the path of the system in \( R \)-space. This path depends on the initial coordinates and momenta. If we keep the initial \( R \)'s and \( P \)'s constant, but vary the \( q \)'s and \( p \)'s, we get an ensemble of paths all starting at \( R = \{ R_1, \ldots, R_N \} \) with velocities \( \dot{R} = \{ \dot{R}_1, \ldots, \dot{R}_N \} \), gradually spreading with time as in Fig. 2. In this figure \( P(R,t) \) is the probability distribution of \( R(t) \), i.e. \( P(R,t) dR \) is the probability of finding \( R(t) \) in the interval \([R, R + dR]\). The aim of coarse-graining is to provide an equation of motion for the \( R \)'s, yielding the same ensemble of paths with the same distribution \( P(R,t) \), but without recourse to the ‘bath’ variables \( q \) and \( p \). The generalised Langevin equation does exactly this.

### 2.2 An Exact Equation of Motion

We will now give a derivation of the exact equation of motion for the \( R \) coordinates [12–14]. With some approximations this leads to the generalised Langevin equation.

The dynamics of the full system is governed by the Hamiltonian

\[ H(P, R, p, q) = T(P) + T_B(p, q) + \Phi(R, q), \] (3)
where $T(P)$ is the kinetic energy of the $R$-coordinates and $T_B(p, q)$ that of the $q$-coordinates; $\Phi(R, q)$ is the potential energy of the full system. The time derivative of any function $F = F(P(t), R(t), p(t), q(t))$ is found according to

$$\frac{dF}{dt} = \frac{dP}{dt} \frac{\partial F}{\partial P} + \frac{dR}{dt} \frac{\partial F}{\partial R} + \frac{dp}{dt} \frac{\partial F}{\partial p} + \frac{dq}{dt} \frac{\partial F}{\partial q} = -\frac{\partial H}{\partial R} \frac{\partial F}{\partial P} + \frac{\partial H}{\partial P} \frac{\partial F}{\partial R} - \frac{\partial H}{\partial q} \frac{\partial F}{\partial p} + \frac{\partial H}{\partial p} \frac{\partial F}{\partial q} \equiv iL_R F + iL_q F = i\mathcal{L}F. \quad (4)$$

In the second line we have used Hamilton’s equations. In the last line we have defined the Liouville operator $\mathcal{L}$. For ease of notation we have omitted indices with all variables; absence of indices at coordinates and momenta indicates that they should be dressed with dummy indices which should then be summed over the appropriate ranges. Now let us make a Taylor expansion in time of the momentum of coordinate $n$,

$$P_n(t) = \sum_{k=0}^{\infty} \frac{t^k}{k!} \frac{d^k}{dt^k} P_n\bigg|_{t=0} = \sum_{k=0}^{\infty} \frac{t^k}{k!} (i\mathcal{L})^k P_n \equiv \exp\{i\mathcal{L}t\} P_n. \quad (5)$$

The last equality defines the exponential of an operator. Note that here and in the following all operators operate on a phase function $F(P, R, p, q)$, which is a function of the phase point $(P, R, p, q)$. The phase point should always be evaluated at the original time $t = 0$, i.e. we operate on $F(P(0), R(0), p(0), q(0))$, unless the phase function is explicitly followed by $(t)$, in which case we operate on $F(P(t), R(t), p(t), q(t))$. For example, in the last equation $\exp\{i\mathcal{L}t\}$ operates on the momentum $P_n$ at the original time $t = 0$. With this definition the equation of motion that we are seeking reads

$$\frac{dP_n}{dt}(t) = e^{i\mathcal{L}t} i\mathcal{L}P_n. \quad (6)$$

Obviously $i\mathcal{L}P_n$ is the force that initially acts on coordinate $R_n$:

$$i\mathcal{L}P_n = -\frac{\partial \Phi}{\partial R_n}. \quad (7)$$

The ‘propagator’ $\exp\{i\mathcal{L}t\}$ turns this into the force at time $t$. Concomitantly with our wish to get rid of the $q$’s, we would like to replace the force $-\partial \Phi/\partial R_n$ with its average over the $q$’s and the $p$’s. Therefore we introduce with each function $F(R, P, q, p)$ its partial average

$$\mathcal{P}F(R, P) = \frac{1}{Q_B} \int dp dq \ e^{-\beta H_B(p, q; R)} F(R, P, q, p) \equiv \langle F \rangle_B, \quad (8)$$

$$H_B(p, q; R) = T_B(p, q) + \Phi(R, q), \quad (9)$$

$$Q_B(R) = \int dp dq \ e^{-\beta H_B(p, q; R)}. \quad (10)$$
Here $\beta = 1/(k_B T)$ and $\mathcal{P}$ is a projection operator, with the property $\mathcal{P}^2 F = \mathcal{P} F$.

Equation (8) is appropriate in those cases where the $q$’s are internal coordinates. In the colloidal example, i.e. in the case when $\Phi(R,q)$ remains finite when the $q$’s go to infinity, it is often more useful to work in the semigrand ensemble, where the number of coarse-grained particles and the chemical potential of the $q$’s are fixed [15].

We now rewrite (6):

$$\frac{dP_n}{dt}(t) = e^{i\mathcal{L}t}(\mathcal{P} + (1 - \mathcal{P}))i\mathcal{L}P_n$$

$$= e^{i\mathcal{L}t}\mathcal{P}i\mathcal{L}P_n + e^{i\mathcal{L}t}(1 - \mathcal{P})i\mathcal{L}P_n. \quad (11)$$

In the first term we recognise the force on particle $n$ averaged over the bath variables:

$$\mathcal{P}i\mathcal{L}P_n = \left\langle -\frac{\partial \Phi}{\partial R_n} \right\rangle_B = -\frac{\partial A}{\partial R_n}, \quad (12)$$

$$A(R) = -k_B T \ln Q_B(R). \quad (13)$$

Here $A(R)$ is the free energy of the $q$’s at fixed values of the $R$’s. On the basis of the second equality in (12) it is also called the potential of mean force.

Again, note that $Q_B(R)$ denotes the semigrand partition function in case of diffusive $q$’s. The first term of (11) now reads

$$e^{i\mathcal{L}t}\mathcal{P}i\mathcal{L}P_n = -\frac{\partial A}{\partial R_n}(t), \quad (14)$$

which is the mean force on coordinate $R_n$ at time $t$ obtained as the negative gradient of the potential of mean force when the $R$’s have values $R_1(t), \ldots, R_M(t)$.

The remaining term in (11) represents friction and random forces. We extract the latter by writing

$$e^{i\mathcal{L}t}(1 - \mathcal{P})i\mathcal{L}P_n = e^{(1-\mathcal{P})i\mathcal{L}t}(1 - \mathcal{P})i\mathcal{L}P_n$$

$$+ \int_0^t d\tau \ e^{i\mathcal{L}(t-\tau)}\mathcal{P}i\mathcal{L}e^{(1-\mathcal{P})i\mathcal{L}\tau}(1 - \mathcal{P})i\mathcal{L}P_n. \quad (15)$$

This looks rather formidable, so let’s give the first term in (15) a simple name:

$$e^{(1-\mathcal{P})i\mathcal{L}}(1 - \mathcal{P})i\mathcal{L}P_n \equiv F_n^R, \quad (16)$$

$$e^{(1-\mathcal{P})i\mathcal{L}t}(1 - \mathcal{P})i\mathcal{L}P_n \equiv F_{n,t}^R. \quad (17)$$

Equation (15) follows from the following identity valid for any operator $A$ and $B$:

$$e^{(A+B)t} = e^{At} + \int_0^t d\tau \ e^{(A+B)(t-\tau)} Be^{A\tau}.$$  

Substitute $A = (1 - \mathcal{P})i\mathcal{L}$ and $B = \mathcal{P}i\mathcal{L}$. 

\( F_{n,t}^R \) is a random force because, when averaged over the bath variables, it yields zero:

\[
\langle F_{n,t}^R \rangle_B = \mathcal{P} e^{(1-\mathcal{P})i\mathcal{L}_t}(1-\mathcal{P})i\mathcal{L}P_n = 0. \tag{18}
\]

The reader should beware that, contrary to the previous state functions, the random force \( F_{n,t}^R \) is not simply the function \( F_R^p \) evaluated at the phase point at time \( t \). Rather, \( F_{n,t}^R \) depends on the initial state point, which is propagated by the operator \( \exp\{ (1-\mathcal{P})i\mathcal{L}_t \} \). Since this is not the usual \( \exp\{ i\mathcal{L}_t \} \) operator, \( t \) now merely acts as a parameter. To avoid confusion we have purposely denoted the random force as \( F_{n,t}^R \), not as \( F_{n,t}^R(t) \).

In the second term of (15) we recognise the same random force again, now with \( \tau \) instead of \( t \). The second term is simplified further by realising that

\[
2 \mathcal{P} i\mathcal{L}F_{n,t}^R = \mathcal{P} (i\mathcal{L}_R + i\mathcal{L}_q) F_{n,t}^R = \mathcal{P} i\mathcal{L}_R F_{n,t}^R. \tag{19}
\]

This may be worked out further using the definition of the Liouville operator:

\[
\mathcal{P} i\mathcal{L}_R F_{n,t}^R = \left\langle \sum_m \left\{ \frac{P_m}{M} \frac{\partial}{\partial R_m} - \frac{\partial H}{\partial R_m} \frac{\partial}{\partial P_m} \right\} F_{n,t}^R \right\rangle_B = \sum_m \left\langle \frac{P_m}{M} \frac{\partial F_{n,t}^R}{\partial R_m} \right\rangle_B - \frac{\partial}{\partial P_m} \left\langle \frac{\partial \Phi}{\partial R_m} F_{n,t}^R \right\rangle_B. \tag{20}
\]

The first average can also be expressed as

\[
\left\langle \frac{\partial F_{n,t}^R}{\partial R_m} \right\rangle_B = \frac{1}{\mathcal{Q}_B} \int dp dq \ e^{-\beta H_B} \frac{\partial F_{n,t}^R}{\partial R_m}
\]

\[
= \frac{1}{\mathcal{Q}_B} \frac{\partial}{\partial R_m} \int dp dq \ e^{-\beta H_B} F_{n,t}^R + \frac{\beta}{\mathcal{Q}_B} \int dp dq \ \frac{\partial \Phi}{\partial R_m} F_{n,t}^R
\]

\[
= \beta \left\langle \frac{\partial \Phi}{\partial R_m} F_{n,t}^R \right\rangle_B. \tag{21}
\]

So for both averages in (20) we need to evaluate

\[
\left\langle \frac{\partial \Phi}{\partial R_m} F_{n,t}^R \right\rangle_B = - \left\langle (i\mathcal{L}_m) F_{n,t}^R \right\rangle_B
\]

\[
= - \left\langle (\mathcal{P} i\mathcal{L}_m) F_{n,t}^R \right\rangle_B - \left\langle [(1-\mathcal{P})i\mathcal{L}_m] F_{n,t}^R \right\rangle_B
\]

\[
= - \left\langle (i\mathcal{L}_m) F_{n,t}^R \right\rangle_B - \left\langle F_{n,t}^R \right\rangle_B. \tag{22}
\]

\[2\] This is true for any \( F(P(t), R(t), p(t), q(t)) \) because

\[
\mathcal{P} i\mathcal{L}_q F = \frac{1}{\mathcal{Q}_B} \int dp dq \ e^{-\beta H_B} \left( - \frac{\partial H_B}{\partial q} \frac{\partial}{\partial p} + \frac{\partial H_B}{\partial p} \frac{\partial}{\partial q} \right) F
\]

\[
= \frac{1}{\mathcal{Q}_B} \int dp dq \ \left( - \frac{\partial H_B}{\partial q} \frac{\partial}{\partial p} + \frac{\partial H_B}{\partial p} \frac{\partial}{\partial q} \right) \left[ e^{-\beta H_B} F \right] = 0,
\]

where we have used that \( H_B \to \infty \) as \( p \to \infty \) or \( q \to \infty \).
Because $\langle F_{R,m}^R \rangle_B = 0$, the equation of motion now reads
\[
\frac{dP_n}{dt}(t) = -\frac{\partial A}{\partial R_n}(t) + F_{n,t}^R - \sum_m \int_0^t d\tau \, e^{iL(t-\tau)} \left\{ \frac{\beta P_n}{M} - \frac{\partial}{\partial P_m} \right\} \langle F_{m,R}^R F_{n,R}^R \rangle_B (t-\tau).
\]
(23)

Note that this is still an exact equation of motion for $P_n(t)$. $\langle F_{m,R}^R F_{n,R}^R \rangle_B$ is a function of $\tau$ for each point in phase space $(R,P)$. Sampling the random forces is terribly expensive, so this is just as difficult as running the full system.

2.3 Generalized Langevin Equation

Let us gradually simplify (23). First we assume that $\langle F_{m,R}^R F_{n,R}^R \rangle_B$ is independent of the initial momenta $P$. Then get rid of the $\partial/\partial P_m$ term. The time propagator propagates the phase point to time $t - \tau$:
\[
\frac{dP_n}{dt}(t) = -\frac{\partial A}{\partial R_n}(t) + F_{n,t}^R - \sum_m \int_0^t d\tau \, P_m(t-\tau) \frac{\beta}{M} \langle F_{m,R}^R F_{n,R}^R \rangle_B (t-\tau). \quad (24)
\]
This is the generalized Langevin equation alluded to before. Equation (24) should be interpreted with care. In particular, $\exp\{iL(t-\tau)\} \langle F_{m,R}^R F_{n,R}^R \rangle_B = \langle F_{m,R}^R F_{n,R}^R \rangle_B (t-\tau)$ is the same function of $\tau$ as $\langle F_{m,R}^R F_{n,R}^R \rangle_B$ but now evaluated at the point $R(t-\tau)$ in configuration space. This is still very difficult, so usually approximations are made for the $\tau$-dependence of the correlation.

The simplest approximation is to assume that the random force correlation differs from zero only for very small values of $\tau$, short enough for $P_m$ to change only very little. In practice, such a complete separation of time scales is often hard to achieve, but can be approached if the mass of the CG particle is much larger than that of a bath particle. We can then bring the momenta outside the integral,
\[
\frac{dP_n}{dt} = -\frac{\partial A}{\partial R_n}(t) + F_{n,t}^R - \sum_m P_m(t) \int_0^t d\tau \, \frac{\beta}{M} \langle F_{m,R}^R F_{n,R}^R \rangle_B (t-\tau). \quad (25)
\]
We next assume that the coordinates $R$ hardly change while the random forces decorrelate. We may then evaluate the random force correlation at the point $R(t)$ instead of $R(t-\tau)$:
\[
\frac{dP_n}{dt} = -\frac{\partial A}{\partial R_n}(t) + F_{n,t}^R - \sum_m P_m(t) \int_0^t d\tau \, \frac{\beta}{M} \langle F_{m,R}^R F_{n,R}^R \rangle_B (t-\tau). \quad (26)
\]
\[
\equiv -\frac{\partial A}{\partial R_n}(t) + F_{n,t}^R - \sum_m P_m(t) \xi_{mn}(R(t)). \quad (27)
\]
This is called the Langevin equation. In the last line we have defined the friction $\xi_{mn}(R(t))$, which must be evaluated at the point $R(t)$ in configuration space. More precisely, we can interpret each term $P_m(t)\xi_{mn}(R(t))$ in
(27) as the friction force on coordinate \( n \) caused by the momentum \( P_m(t) \) of coordinate \( m \). As is obvious from these equations, the friction forces are not independent of the random forces. In fact, if we write the \( \tau \)-dependence of the random force correlation as a delta function, we find\(^3\)

\[
\langle F^R_{m} F^R_{n,\tau} \rangle_B(t) = 2Mk_B T \xi_{mn}(R(t)) \delta(\tau) .
\]  

This is a clear example of the so-called fluctuation-dissipation theorem, which states that the random forces and friction forces are related.

In summary, we have shown how to systematically coarse-grain a system by “projecting out” all irrelevant variables. This procedure is optimal if the memory of the random force correlation can be assumed to be short, that is if some separation of scales exists between the coarse-grained and bath variables.

3 Coarse-Graining in Practice

3.1 Representation of the Potential of Mean Force

The obvious question now is: how does one coarse-grain a polymer system in practice? Unfortunately, there is no unique answer; the method of choice is often based on physical intuition. As suggested we may subdivide each polymer chain into subchains, partitioning the degrees of freedom into two sets: the coarse-grained coordinates \( R \), which are the centres of mass of the subchains, and the coordinates \( q \), which are the remaining internal coordinates describing the details of the configurations. If we now simulate a system that contains only CG particles, using the potential of mean force \( A(R) \) in (13) will ensure the correct distribution of \( R \) coordinates. However, the potential of mean force is generally a complicated function of all coordinates \( R \), and possibly includes complicated multi-body interactions. For practical and computational reasons it is impossible to calculate and store the potential of mean force for all possible multibody configurations. Some approximations will need to be made. The most widely used approximation is that the potential of mean force can be assumed to be pairwise additive. For polymers a distinction may be made between nonbonded and bonded particles, with possibly an angular term for bonded triplets to account for chain stiffness. Schematically, the potential of mean force is expressed as

\[
A(R) = \sum_{i<j} \varphi^{nb}(R_{i,j}) + \sum_i \varphi^b(R_{i,i+1}) + \sum_i \varphi^\theta(\theta_i) .
\]  

The first sum is over all non-bonded pairs at distance \( R_{i,j} \), the second sum over all bonded particles at distance \( R_{i,i+1} \), and the third sum over all groups

\(^3\) The factor 2 in (28) arises because the integral in (26) is taken over half a delta peak.
of three consecutive bonded particles with internal angle $\theta_i$. The form and magnitude of the effective potentials $\varphi^{nb}$ and $\varphi^b$ may be found by matching the structure at the pair-level in coarse-grained simulations with the structure measured in microscopic simulations [16], and similarly for $\varphi^\theta$.

### 3.2 Polyethylene

As an example, we will investigate polyethylene melts. To determine the target distribution functions, atomistically detailed simulations of $C_{120}H_{242}$ chains were performed at $T = 450$ K [17,18], which is about the limit of what current-day computers can do for sufficiently long time scales. There is much freedom to choose the number of monomers $\lambda$ per CG particle. In our previous work, the following considerations were taken into account: (1) $\lambda$ should be large enough to allow for a significant increase in the time and length scales accessible to simulation, and (2) $\lambda$ should not be so large that the "size" of a CG particle exceeds the typical diameter of the tube in the reptation picture, in other words the entanglement length. A suitable choice was $\lambda = 20$ CH$_2$ units, which is still roughly one third of the smallest entanglement length reported in the literature [19]. With this choice each polyethylene chain of 120 CH$_2$ units was represented by 6 CG particles. The structure could be matched reasonably well by expressing the nonbonded interaction as a Gaussian pair potential, and the bonded interactions as a sum of a repulsive interactions, described by two Gaussians, and an attractive term, described by a single power law. In formula:

\begin{align}
\varphi^{nb}(R) &= c_0 e^{-\left(R/b_0\right)^2}, \\ 
\varphi^b(R) &= \varphi^{rep}(R) + \varphi^{att}(R), \\ 
\varphi^{rep}(R) &= c_1 e^{-\left(R/b_1\right)^2} + c_2 e^{-\left(R/b_2\right)^2}, \\ 
\varphi^{att}(R) &= c_3 R^\mu.
\end{align}

The resulting interactions are shown in Fig. 3. Because the degree of coarse-graining is so high, the CG particles are rather empty and the interactions between the CG particles are very soft. By this we mean that there is a finite possibility that CG particles end up on top of each other. This is not an artefact. The centres-of-mass of two different pieces of polymer may actually be at the same coordinates, without any of their constituent atoms overlapping.

### 3.3 Thermodynamic and Dynamic Consistency of the Potential of Mean Force

At this point we would like to issue a warning. In the ideal case we would have available the exact potential of mean force $A$ for all possible CG coordinates $R$, as well as all possible system densities $\rho$ and temperatures $T$. This would guarantee a perfect description of the thermodynamic properties of our system. However, as explained before, for practical and computational reasons i
Fig. 3. The potential of mean force between bonded (circles) and nonbonded (squares) coarse-grained pieces of polyethylene, each piece representing the centre-of-mass of 20 carbon groups. These potentials were obtained from distribution functions measured in atomistically detailed molecular dynamics simulations of C$_{120}$H$_{242}$. The solid lines are fits with simple analytical functions (see text). Note that $kT = 3.74$ kJ/mol.

is impossible to calculate and store the potential of mean force for all possible configurations, so approximations will need to be made.

The use of spatial correlations to construct the potentials is as arbitrary as any other object function, like for instance the compressibility of the system. From a thermodynamic point of view, the free energy may be a good starting point to judge the effectiveness of a model. In particular, a coarse-grained model that has minimal free energy is believed to be the best representation of the fine-grained, microscopic level [20].

Whatever choice is made for the object function, the reader should beware that this choice determines the applicability and non-applicability of the model for certain thermodynamic and dynamic properties. In practice it is only possible to correctly represent a few, but not all properties of the system. For example, in the previous subsection we have made the choice to approximate the free energy by effective pair interactions which reproduce the bonded and nonbonded pair correlation functions as closely as possible. Often the thermodynamics of such a CG system will not correspond to the thermodynamics of the microscopic system. Indeed, it is intuitively clear that the softness of the interactions leads to a pressure which is generally too small and a system which is too compressible. This thermodynamic inconsistency
is often worsened by ignoring the state point dependence of the potential of mean force. For a discussion on these matters, the reader is referred to [21–23].

3.4 Representation of the Friction

Once a choice is made for the representation of the potential of mean force, the dynamics of the CG coordinates can be optimized by a careful choice of the friction, which by the fluctuation-dissipation theorem automatically determines the random forces. Note that the thermodynamics of the CG system is not influenced by the frictional and random forces, and is therefore already fixed by our choice of the potential of mean force.

As with the potential of mean force, the friction is generally a complicated function of all coordinates $R$, and possibly includes complicated memory and multi-body terms. Fortunately, if the degree of coarse-graining is very large and hydrodynamic retardation effects may be neglected, the friction memory is short relative to the velocity decorrelation time of the CG particles. In that case, the Langevin equation (27) applies. As a further approximation we may assume that the friction $\xi_{mn}$ depends only on the distance $R_{mn}$ between particles $m$ and $n$. Doing so, we arrive at the so-called dissipative particle dynamics method [24]. Although costly this method is rather popular since it conserves momentum, which is a prerequisite for hydrodynamic behaviour, and it is easy to use in non-equilibrium simulations. In the case of polymer melts, it is often even admissible to use a scalar friction with a static background, because the friction may be thought of as being caused by the motion of a (a part of a) chain relative to the rest of the material, which to a first approximation may be taken to be at rest. Propagation of a velocity field as in a normal liquid is highly improbable, meaning that hydrodynamic interactions are screened [3].

4 Twentanglement

4.1 Uncrossability of Chains

The softness of the interactions between the CG particles poses another problem. At some point one may have found a realistic friction for the CG particles, a friction which correctly predicts the relaxation of a time correlation function sensitive to the dynamics at the scale of a few CG particles. One then usually finds the dynamics at the scale of an entire polymer chain is too fast. The reason, of course, is that the bonds are able to cross each other [18]. The entanglement effect, leading to altered and much slower dynamics, is usually lost.

In this section we will describe an algorithm designed to prevent unphysical bond crossings in simulations of polymer systems [18]. Employing this so-called Twentanglement algorithm to a simulation of highly coarse-grained polymer chains will reintroduce the entanglement effect. The principle of the
algorithm is depicted in Fig. 4. The bonds are considered to be elastic bands between the bonded particles. As soon as two of these elastic bands make contact, an ‘entanglement’ is created which prevents the elastic bands from crossing. To avoid any confusion, in the algorithm ‘entanglements’ are defined as objects which prevent the crossing of chains. Usually only a few of these contribute to entanglements in the usual sense of longlasting obstacles, slowing down the chain movement. For instance, a C_{60}H_{122} chain is generally considered not to be entangled, yet many ‘entanglements’ occur in a coarse-grained simulation.

4.2 Algorithm

At each simulation step, after updating the positions of the CG particles, the Twentanglement algorithm is called. It consists of three parts:

1. Given the new positions of the CG particles and the topology (order of CG particles and entanglements within each chain), move the entanglements to their new positions and calculate the resulting forces on the CG particles.
2. Detect new entanglements and disentanglements caused by movements of the CG particles and entanglements.
3. If possible, let entanglements slip across a CG particle or each other (topology-altering moves).

Moving Entanglements

Suppose entanglements already exist. In the algorithm entanglements have no volume and are fully characterised by their positions X. Each bond behaves as an elastic band with respect to the entanglements. This is accomplished as follows. The attractive potential \( \varphi^{\text{att}} \) between bonded CG particles (33) is no longer a function of the direct distance \( R_{i,i+1} \), but of the path length \( L_{i,i+1} \) from CG particle \( i \), via the entanglements, to CG particle \( i + 1 \). If there are \( p \) entanglements along its path, the path length is defined as (Fig. 5)
Fig. 5. Definition of the pathlength $L_{i,i+1}$ between bonded coarse-grained entities at $\mathbf{R}_i$ and $\mathbf{R}_{i+1}$. Reprinted with permission from [18]. Copyright (2001) American Institute of Physics.

$$L_{i,i+1} = |\mathbf{R}_i - \mathbf{X}_1| + |\mathbf{X}_1 - \mathbf{X}_2| + \ldots + |\mathbf{X}_p - \mathbf{R}_{i+1}|.$$  

Since each CG particle represents a large collection of monomers, the heavy backbone of the polymer chain will generally move very sluggishly. This in contrast to an entanglement which at the atomic level includes only a few monomer units. Consequently, the time scale with which the entanglement position adjusts itself is much shorter than the time scale with which the polymer backbone is moving. Effectively, on the coarse-grained time scale, there will be an equilibrium of forces at each entanglement. Such an equilibrium of forces is achieved by the following minimization:

$$\min_X \sum_i \varphi^{att}(L_{i,i+1}(\mathbf{R}, X)),$$

i.e. the entanglement positions $X$ are determined by the requirement that the total attractive part of the energy is at its minimum. During this minimization the CG particles are kept at their respective positions $\mathbf{R}$. Note that all other energy terms are still determined by the CG particle positions only.

**Detecting New (Dis)Entanglements**

In the algorithm, a polymer chain is viewed as a succession of objects, either coarse-grained particles or entanglements, connected by line segments. During the simulation the algorithm keeps track of all (unattached) pairs of line segments which are close together. For each pair of line segments and at each instant of time the following triple product is calculated:

$$V_{ij} = (\mathbf{r}_i - \mathbf{r}_j) \cdot [(\mathbf{r}_{i+1} - \mathbf{r}_i) \times (\mathbf{r}_{j+1} - \mathbf{r}_j)],$$

where we have used Fig. 4 as a reference for the indices. The absolute value of (36) is the volume of the parallelepiped defined by the vectors $\mathbf{r}_{i+1,i}$, $\mathbf{r}_{j+1,j}$, and $\mathbf{r}_{i,j}$. Aside from some pathological cases [18], if $V_{ij}$ changes sign from one time step to the next, a bond crossing may have occurred. Additional checks are made to ensure that the crossing takes place along the physical part of the line segments (the above equation checks if two infinite lines have...
crossed). If a real bond crossing has occurred, an entanglement is created at the crossing point. Subsequently, the associated volume $V_{ij}$ will serve to detect future disentanglements. If the volume $V_{ij}$ of the four objects surrounding an entanglement changes sign, a possible disentanglement has occurred, i.e. Fig. 4 may also be read backwards.

**Topology-Altering Moves**

While searching for its equilibrium position, an entanglement can move freely along the chain between two adjacent objects. In some cases, however, the attractive part of the energy might be lower if the entanglement could slip past a CG particle, or to the other side of another entanglement, or, in other words, if the topology would be altered. The algorithm detects if an entanglement has a tendency to get close to either one of its adjacent objects. If the distance is smaller than some prescribed value $\epsilon$, where $\epsilon$ is sufficiently small compared to the average bond length, a subalgorithm will check topology-altering moves. The list of possible moves is quite extensive. The reader is referred to [18] for a complete treatment. Two examples are given in Fig. 6: (a) If an entanglement slips past the last CG particle of a chain, the entanglement is lost, and (b) if a chain is entangled with itself, forming a loop, the loop will disappear if it shrinks far enough.

We will now treat two applications of the above algorithm: polymer melts and semidilute solutions of wormlike micelles.

**5 Application 1: Polyethylene Melts**

In Sect. 3 we have introduced the coarse-graining of a melt of $C_{120}H_{242}$ chains into a melt of chains consisting of 6 coarse-grained particles each. The point
of coarse-graining, of course, is to reach larger time and length scales. Having found the interactions between CG particles in a $C_{120}H_{242}$ melt, we now simulate chains of higher molecular weight, assuming that the same interactions hold. We then measure various dynamic properties and compare with theoretical (scaling) predictions and experimental results.

5.1 Diffusion Results

Pearson et al. have experimentally determined the self-diffusion coefficient $D$ in alkane and polyethylene melts at 450 K [25], and found that over the range from $M_w = 600$ up to 120000 it follows a power law,

$$D^{\text{exp}} = 1.65/M_w^{2.65} \text{ (cm}^2/\text{s}).$$

(37)

This result is plotted as a dashed line in Fig. 7. Atomistically detailed simulations [27,28] generally find good agreement (open symbols), but can only be performed in the lower part of the molecular weight range. The CG simulations can go to much larger $M_w$ and are in excellent quantitative agreement (black squares) [26]. The uncrossability of chains is essential: without the Twentanglement constraint, the CG model yields diffusion coefficients which are much too large and scale as $D \propto M_w^{-1}$ instead of the observed $M_w^{-2}$.
5.2 Rheology Results

Much theoretical and simulation effort has been spent to predict or reproduce the zero shear relaxation modulus $G(t)$, which measures the relaxation of stress after applying a small step shear strain. Experimentally its Fourier transform is measured by applying small oscillatory shear, yielding the storage and loss moduli $G'(\omega)$ and $G''(\omega)$. A prominent feature of viscoelastic liquids is the (temporary) plateau that appears in $G(t)$, signifying the elastic part of the relaxation behaviour that sets in after a liquid-like initial relaxation. The crossover time between the liquid-like and the plateau regime is identified as the entanglement time $\tau_e$. Fig. 8 shows $G(t)$ for four different polyethylene melts. These were obtained from the fluctuations of the stress tensor $S$ in equilibrium simulations [3,26]:

$$G(t) = \frac{V}{k_B T} \langle S_{xy}(t) S_{xy}(0) \rangle,$$  

where $V$ is the volume of the (periodic) simulation box. For a melt of $C_{80}$ chains no plateau is observed and the shear relaxation corresponds well to predictions of the Rouse model (dashed lines) [3]. For a melt of $C_{120}$, deviations start to emerge for $t > \tau_e \approx 6$ ns. These deviations grow into plateau-like behaviour for melts of longer chain lengths. The deviations can be explained well if one assumes reptation relaxation for all modes larger than the tube size and Rouse relaxation for the other modes [26].

Pearson et al. have also measured the zero shear viscosity $\eta_0$ in polyethylene melts [25]. They found that at low molecular weight $M_w < M_c \approx 5000$ g/mol, the viscosity is well described by the power law

$$\eta_0 = 2.1 \times 10^{-5} M_w^{1.8} \text{ (cP)},$$  

while at high molecular weight, $M_w > M_c$, the $M_w$ dependence is much stronger:

$$\eta_0 = 3.76 \times 10^{-12} M_w^{3.64} \text{ (cP)}.$$  

The experimental fits are plotted as dashed lines in Fig. 9. In simulations the zero shear viscosity can be obtained either in nonequilibrium, by shearing at sufficiently low shear rates, or in equilibrium, by integrating the measured zero shear relaxation modulus:

$$\eta_0 = \int_0^\infty G(t) dt.$$  

The results of an atomistically detailed simulation (open symbol) [29] and the CG simulations (filled squares) [26] are shown in Fig. 9. Again the agreement is very good.

The coarse-grained simulations have enabled us to study the dynamics of (in this case) polyethylene melt in great detail. We observed that the dynamics
Fig. 8. Shear relaxation modulus of a polyethylene melt, calculated from equilibrium stress fluctuations, for four different chain lengths. Negative data are represented by black symbols in these logarithmic plots, to indicate when the (noisy) stress correlation decays to zero. Dashed lines are Rouse model predictions, solid lines are reptation model predictions. The arrows indicate estimates for the entanglement time $\tau_e$.

is in approximate agreement with reptation theory, but one should be careful of literal interpretation of the tube concept. The chains are interacting with their neighbours on many different length scales, even on scales smaller than the (interpreted) tube diameter. Proper care should also be taken of the fact that the chains are not Gaussian, caused by chain stiffness and other sources of non-harmonicity. For more details the reader is referred to [26].

6 Application 2: Wormlike Micelles

6.1 Wormlike Micelles as a Polymer System

Let us briefly consider another application. Under some circumstances surfactant molecules in aqueous salt solutions self-assemble reversibly into elongated structures. The average contour length of such a so-called wormlike micelle increases rapidly with increasing surfactant concentration. Above the overlap concentration entanglements form between the wormlike micelles, leading to a steep increase of the viscosity with surfactant concentration and a wealth of peculiar viscoelastic effects [30,31].
In many respects a wormlike micellar network resembles a polymer network as treated in the previous section. The major difference is that strands in the micellar network can reversibly break. In the presence of oil, the wormlike micelles reassemble into spherical form, resulting in a low viscosity fluid. This responsive behaviour makes them ideal for many industrial applications, such as hydraulic fracturing in the oilfield [32]. From both a fundamental and practical point of view it is therefore important to understand the relation between structure and chemistry of the surfactants and the dynamics and rheology of the macroscopic fluids. Simulations may provide this understanding.

6.2 Simulation Models

As usual, atomistic models are limited to small length (10 nm) and time (10 ns) scales, whereas wormlike micelles have contour lengths in the range of micrometers and relaxation times of at least milliseconds. The only way forward is to coarse-grain. A few coarse-grained models have been proposed in the literature [34,35], but all of them may be classified as top-down models, where no reference is made to any specific wormlike micellar system. Again, in our opinion, great care must be taken if quantitative or even qualitatively realistic results for the dynamics and rheology are required. There are often multiple relevant length scales which must be taken into account.
The philosophy behind the so-called Mesoworm model [33] is that the length scales and, more generally, the material properties of individual wormlike micelles can in principle be measured from detailed simulations or targeted experiments. Relevant properties include the solvent viscosity, worm diameter, bending rigidity (or persistence length), compressibility, and free energies associated with the breaking and fusion process of wormlike micelles. Allowing the model to have these parameters as input, the rheology can be predicted from realistic input, with as few assumptions as possible.

In the Mesoworm model, a wormlike micelle is represented by a string of (rigid) rods, each rod representing one persistence length $L_p$ of wormlike micelle. This degree of coarse-graining is as large as possible to permit a larger integration step and fewer particles, while it is still small enough to allow for an accurate description of the overall conformation of the wormlike micelle. Each rod has the possibility to fuse with other rods at its ends, forming breakable bonds each with a “scission” energy $-E_{sc}$. The scission energy is a very important parameter because it determines the size of the wormlike micelles. In the simplest mean-field theory, a wormlike micelle is treated as a random walk on a lattice, with an energy penalty $E_{sc}$ for each pair of chain ends [31]. By variationally minimising the free energy, under the constraint of fixed volume fraction $\phi$, the theory then predicts an exponential contour length distribution with an average contour length given by [31]

$$\bar{L}/L_p \approx \phi^{1/2} \exp\left(\frac{E_{sc}}{2k_BT}\right).$$

This scaling has been confirmed experimentally.

We note that the details of the scission and fusion kinetics are very important for the resulting dynamics and rheology of the micellar solution [36,37]. In real wormlike micelles, before their ends can fuse, there are specific demands on the conformations of the surfactants in the spherical endcaps, giving rise to a considerable free energy barrier $E_{act}$ associated with fusion. By increasing this activation barrier, not only the time-scales associated with scission and fusion increase, but also the physics of the scission-fusion process changes from diffusion limited, where immediate self-fusion predominates, to reaction limited, where fusion is mostly with other chain ends [37]. Since most experimental wormlike micelles belong to the latter class [36], it is important to include such an activation barrier in the model.

Finally, entanglements are very important for the rheology of a solution of wormlike micelles. In fact, the relaxation of stress in wormlike micellar solutions is believed to be determined for a large part by the balance between reptation and breaking of the micellar chains [31]. Entanglements emerge naturally when two wormlike micelles try to cross. In the Mesoworm model, the entanglements are handled by the Twentanglement algorithm.

### 6.3 Results

A snapshot of a typical simulation box is shown in Fig. 10. This model repre-
Fig. 10. Snapshot of a Mesoworm simulation box.

sents wormlike micelles of the cationic surfactant erucyl bis-(hydroxyethyl)-
methylammonium chloride (EHAC) in aqueous solution of sodium chloride [38]. Most of the mechanical properties have been calculated from detailed atomistic molecular dynamics simulations of a small segment (about 10 nm) of wormlike micelle [33]. For example, the bending rigidity was determined, and corresponds to a persistence length of about 30 nm. A typical coarse-grained box contains 4000–32 000 persistence length units, at a box size of 300–600 nm. This allows for realistic micellar contour lengths in the range of micrometers. The computational speed is typically of the order of 0.1 - 1 ms per week on a single PC processor.

The linear rheology can be measured similarly to the case of polymers from fluctuations in the stress tensor, while the non-linear rheology can be measured by applying sheared periodic boundary conditions. Particularly, the transient rheology may be studied by suddenly applying shear to a sample initially at rest. If the shear rate is high enough, characteristic overshoots in the transient shear stress are observed [33]. After some time a steady state is established, when the shear viscosity is obtained from the ratio of shear stress to shear rate. An example is given in Fig. 11, where the shear-thinning behaviour of a wormlike micellar solution is studied as a function of surfactant concentration. These results are in good agreement with experimental viscosities obtained from rheometry [39].

Supported by the quantitative agreement with experiment, the coarse-grained model now enables us to test various hypotheses about the dynamics and rheology of these wormlike micelles.

7 Conclusion

Simulations are very helpful in understanding the link between microscopic interactions and processes on the one hand, and the macroscopic fluid be-

4 It should be noted that, for computational reasons, the scission and activation energies were chosen lower than their realistic values, corresponding to a higher effective temperature. It has been observed, however, that this does not influence the viscosity at high shear rates, but merely the critical shear rate where the transition from the Newtonian plateau to the shear thinning region takes place [38].
haviour on the other hand. Sometimes they provide us with qualitative or quantitative predictions, but more importantly they enable us to verify or falsify assumptions that are made in approximate theories.

Simulation studies of fluids composed of relatively small molecules have traditionally focused on the Molecular Dynamics method. Such simulations are performed more or less routinely with accurate force fields that are readily available in the literature. For polymer systems, however, the time and length scales associated with collective dynamics and rheology are so large that an atomistic description is unfeasible and coarse-graining of the interactions becomes absolutely necessary.

Unfortunately, this coarse-graining is neither unique nor trivial. The potential of mean force is, in principle, a complicated function of all coarse-grained coordinates. Additionally, the friction may have complicated memory terms. These problems may be overcome by a careful choice of approximations, always keeping an eye on the essential physics. In particular, we have shown that a correct treatment of the relative length and energy scales (persistence length, scale of bonded and nonbonded interactions) combined with the important uncrossability of bonds can lead to quantitative agreement of simulations with experimental results.

Fig. 11. Viscosity vs shear rate for wormlike micellar solutions at various concentrations. Results were obtained by coarse-grained Mesoworm simulations (see text). Reprinted with permission from [33]. Copyright (2001) Institute of Physics.
References