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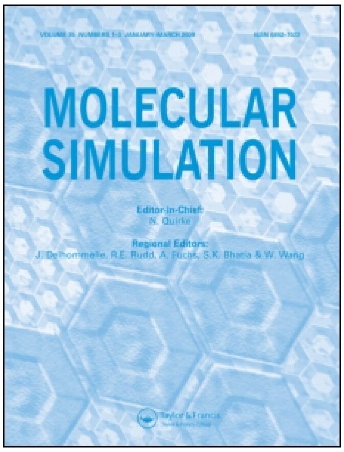

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REPRESENTATION OF COARSE-GRAINED POTENTIALS FOR POLYMER SIMULATIONS

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In order to be able to simulate long time and large space scale properties of polymer melts one has to resort to coarse grained models, for example by subdividing all polymers into parts and restricting attention to the center of mass positions and velocities of these parts. The dynamics of these variables is governed by Langevin equations in which the free energy obtained by integrating the remaining variables provides the potential of the conservative forces. In general this leads to many particle interactions on the coarse-grained level. Methods suggested in the literature to represent these many particle interactions by effective two body interactions are reviewed and a new method, based on the Gibbs-Bogoliubov inequality, is proposed. The reason why none of these methods is able to reproduce the pressure of the underlying atomistic model is discussed.

Keywords: Coarse graining; Thermodynamic variation principle; Virial distribution

I. COARSE GRAINING OF POLYMERS

Their length and flexibility make polymers notoriously difficult to simulate. With increasing polymer length all relevant characteristic times of the system increase extremely fast. Very large systems have to be simulated, exhibiting very slow dynamics. As a result computational times needed to reliably equilibrate and sample the system become prohibitively large. Fortunately, in many cases one is not interested in all the details provided by an atomistic simulation, and one may study the polymer on a coarser scale.

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Also in those cases, in which one actually is interested in atomistic details, it may be advantageous to first run a coarse model in order to quickly obtain equilibration on large length scales, and then to reinstate atomistic details and continue the simulation to obtain equilibration on a small length scale and finally perform the production run. We refer to a recent review paper [1] for further motivation and details.

In order to coarse-grain our system, we subdivide each polymer into parts, called blobs, and concentrate on the center of mass positions and velocities of these blobs. For simplicity we assume that all blobs are of equal size. We collect the center of mass coordinates in one vector R of dimension $3N$, and the remaining coordinates in a vector q of dimension $3M$. The q may always be chosen such that the Jacobian of the transformation of the original atomic coordinates to the $\{R, q\}$ variables is constant, thereby greatly simplifying all equations to be written down in this paper. Denoting by $\Phi(R, q)$ the potential energy of the atomic system, we define the potential of mean force

$$\chi(R) = -kT \ln\left\{ \int \mathrm{d}q \, e^{-\beta\Phi(R,q)} \right\} \tag{1}$$

It is easy to see that $-\partial\chi/\partial R$ indeed gives the average forces on the coordinates R (remember that the Jacobian is constant). Moreover, using $\chi(R)$ as potential, we may calculate all structural properties involving only R coordinates and all thermodynamic properties of the underlying atomic system. Finally, we may also calculate all dynamic properties involving only R coordinates and their time derivatives by performing a Langevin simulation in which $\chi(R)$ serves to provide the conservative forces [2]. It is mainly with this application in mind, that we are interested in coarse-graining of polymers.

In order to perform the Langevin simulation just mentioned, besides the potential of mean force, one needs to know the dissipative and random forces. The calculation of these forces from the underlying atomistic simulation, in the simple case of one chain in a melt coarse grained to a blob-dumbbell, has been the subject of a previous paper [2]. In this paper we concentrate on the potential of mean force. It is easily appreciated that in a melt of chains, each consisting of many blobs, one has to take special care in order to make sure that chains do not cross. The way to prevent these crossings will be the subject of a forthcoming paper [3]. In this paper, by coarse-graining each chain to just one blob, we will restrict ourselves to systems in which on the coarse-grained level no entanglements, resulting from the non-crossability constraint, can occur.

In the next section, we will represent the potential of mean force by an effective two-body potential. Since in future applications we are interested in stresses occurring in our system, the effective potential should provide realistic force distributions among the blobs. In order to study these force distributions in a first approximation, we concentrate on the pressure and the virial distribution in particular. We therefore mention at this point the expression for the pressure $P = -(\partial A/\partial V)_{3(N+M),T}$ in terms of the potential of mean force

$$\begin{aligned} P &= \frac{NkT}{V} - \frac{1}{3V}\left\langle \frac{\mathrm{d}}{\mathrm{d}\lambda}\Phi(\lambda R, q)\bigg|_{\lambda=1}\right\rangle \\ &\quad + \frac{MkT}{V} - \frac{1}{3V}\left\langle \frac{\mathrm{d}}{\mathrm{d}\lambda}\Phi(R, \lambda q)\bigg|_{\lambda=1}\right\rangle \\ &= \frac{NkT}{V} - \frac{1}{3V}\left\langle \frac{\mathrm{d}}{\mathrm{d}\lambda}\chi(\lambda R)\bigg|_{\lambda=1}\right\rangle + \left\langle \frac{\partial\chi(R)}{\partial V}\right\rangle \end{aligned} \tag{2}$$

It is not difficult to show [4] that in the present case, where infinite values of the q variables correspond to infinite energies, actually $\partial\chi(R)/\partial V = 0$.

II. EFFECTIVE POTENTIALS

Averaging over the q variables, from now on called the bath, in general leads to complicated many-body terms in the potential of mean force. In order to keep simulations tractable, one would like to replace the complicated potential of mean force by a simple effective two-body potential

$$U(R) = \sum_{i<j} u(R_{ij})$$

In order to fix $u(r)$, one needs a criterion to be fullfilled by the effective potential. Usually it is required that the effective potential produces a radial distribution function among the blobs, which is as close as possible to the one produced by the underlying microscopic model [1, 4]. Actually it is not difficult to show [5] that any radial distribution function, regardless of the actual potential from which it resulted, can exactly be reproduced by an effective two-body potential. For this one only has to notice that the radial distribution function describes the density around a fixed particle that interacts with the mobile particles in the same way as the mobile particles interact with eachother. If the only interactions are two-body interactions, the fixed particle acts as an external field. According to density functional theory this field is uniquely related to the density distribution produced by it.

In a previous study [4] we found that pressures in the effective system, calculated by means of the virial equation, *i.e.*, replacing χ in Eq. (2) by U, are smaller than the microscopic pressures, roughly by a factor equal to the degree of coarse graining. We therefore propose a different criterion to fix the effective potential by minimizing the variational free energy

$$A_{\mathrm{var}} = A_U + \langle \chi(R) - U(R) \rangle_U \tag{3}$$

which according to the Gibbs-Bogoliubov inequality is always larger than the actual free energy A [6, 7]. A_U in Eq. (3) is the free energy of the effective system and $\langle \ldots \rangle_U$ denotes an average in the effective system. In doing so, we hope that the difference between the exact and estimated free energies does not change very much with the thermodynamic state, and that consequently the pressure is well represented.

We make the above criterion operational by putting equal to zero the functional derivative [8]

$$\begin{aligned} \frac{\delta A_{\mathrm{var}}}{\delta u(r)} = -\frac{1}{2}\beta N(N-1)\langle \delta(R_{12} - r)[(\chi(R) - U(R)) \\ - \langle \chi(R) - U(R) \rangle_U] \rangle_U \end{aligned} \tag{4}$$

In order to solve the resulting equation we start with some guess for $u(r)$ and calculate

$$\delta u(r) = -\frac{2kT}{N(N-1)} \frac{1}{\langle \delta(R_{12} - r) \rangle_U} \frac{\delta A_{\mathrm{var}}}{\delta u(r)} \tag{5}$$

In the next step we replace $u(r)$ by $u(r) + \delta u(r)$, and repeat the whole procedure until $\delta A_{\mathrm{var}}/\delta u(r) = 0$. The choice made in Eq. (5) makes sure that in each step of the iteration

$$\delta A_{\mathrm{var}} = \int_0^\infty \mathrm{d}r \frac{\delta A_{\mathrm{var}}}{\delta u(r)} \delta u(r) \tag{6}$$

will be negative.

In order to calculate $\delta u(r)$, we need to be able to calculate $\langle \delta(R_{12} - r) \times (\chi(R) - \langle \chi(R) \rangle_U) \rangle_U$. For this we make use of the representation [9]

$$\chi(R) = -kT \lim_{n \to 0} \frac{\mathrm{d}}{\mathrm{d}n} \left(\int \mathrm{d}q \, e^{-\beta\Phi(R,q)} \right)^n \tag{7}$$

We then obtain

$$
\begin{aligned}
&\langle\delta(R_{12}-r)\chi(R)\rangle_U \\
&\quad= -kT\lim_{n\to 0}\frac{\mathrm{d}}{\mathrm{d}n}\frac{\int \mathrm{d}R\, e^{-\beta U(R)}\delta(R_{12}-r)\left(\int \mathrm{d}q\, e^{-\beta\Phi(R,q)}\right)^n}{\int \mathrm{d}R\, e^{-\beta U(R)}\left(\int \mathrm{d}q\, e^{-\beta\Phi(R,q)}\right)^n} \\
&\quad\quad \frac{\int \mathrm{d}R\, e^{-\beta U(R)}\left(\int \mathrm{d}q\, e^{-\beta\Phi(R,q)}\right)^n}{\int \mathrm{d}R\, e^{-\beta U(R)}} \\
&\quad= -kT\lim_{n\to 0}\frac{\mathrm{d}}{\mathrm{d}n}\langle\delta(R_{12}-r)\rangle_n + \langle\delta(R_{12}-r)\rangle_U\langle\chi(R)\rangle_U
\end{aligned}
\tag{8}
$$

Introducing this into Eqs. (4) and (5) we obtain

$$
\delta u(r) = -kT\lim_{n\to 0}\frac{\mathrm{d}}{\mathrm{d}n}\frac{\langle\delta(R_{12}-r)\rangle_n}{\langle\delta(R_{12}-r)\rangle_U} - \frac{\langle\delta(R_{12}-r)[U(R)-\langle U(R)\rangle_U]\rangle_U}{\langle\delta(R_{12}-r)\rangle_U} \tag{9}
$$

In this equation only averages occur, which can all be calculated from simple simulations. The average

$$
\langle\delta(R_{12}-r)\rangle_n = \frac{\int \mathrm{d}R \int \mathrm{d}q_1 \ldots \int \mathrm{d}q_n\, \delta(R_{12}-r) e^{-\beta\{U(R)+\Phi(R,q_1)+\cdots+\Phi(R,q_n)\}}}{\int \mathrm{d}R \int \mathrm{d}q_1 \ldots \int \mathrm{d}q_n\, e^{-\beta\{U(R)+\Phi(R,q_1)+\cdots+\Phi(R,q_n)\}}} \tag{10}
$$

must be calculated from a simulation with variables $\{R, q_1, q_2, \ldots, q_n\}$ and potential $U(R)+\Phi(R,q_1)+\cdots+\Phi(R,q_n)$.

We have implemented the above procedure, and successfully tested the iteration part on a system of pair potentials (*i.e.*, when $\chi(R)$ is a two-body potential). Next we have applied the method to a box consisting of 200 decamers. All pairs of beads interacted through a WCA interaction. Two adjacent beads in a chain in addition felt a WCA interaction on extension of their distance above $r_m = 2^{1/6}\sigma$. The system was generated using the methods of Akkermans *et al.* [12]. The temperature was kept constant with a Hoover thermostat at $T = 1.0\varepsilon/k_B$ and the density was $\rho = 0.8\sigma^{-3}$. In Figure 1 are given the potentials resulting from the first three iterations; $u^{(1)}(r)$ is the potential resulting from the first iteration step which was run with $u(r) = u^{(0)} = 0$, $u^{(2)}(r)$ the one resulting from the second iteration step with $u(r) = u^{(1)}(r)$ *etc*. The dashed line represents the result of an earlier study [4] where $u(r)$ was fitted to $g(r)$. Although obviously the iteration was not yet converged, it is not very likely that the final potential will very much surpass the dashed line, if it does so at all. Remarkably, the radial distribution functions (not shown) corresponding to the successive potentials quickly converged to the exact one. In Figure 2 is shown the virial distribution corresponding to $u^{(2)}(r)$. The dashed line represents the virial distribution of

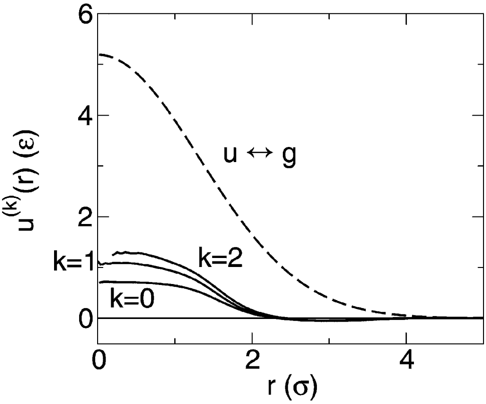

FIGURE 1 Successive pair potentials obtained with the variational method. The dashed line represents the pair potential obtained by fitting to the radial distribution function.

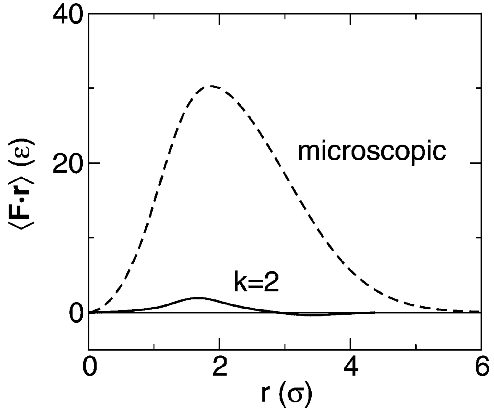

FIGURE 2 Virial distribution function of the potential after the third iteration step. The dashed line represents the virial distribution function of the underlying microscopic system.

the underlying atomistic system. Obviously the result is not very promising. Just like in the case of a potential fitted to the radial distribution function our method seems to produce a virial distribution which is too small by a factor of the order of the number of monomers mapped on one blob.

III. DISCUSSION

Referring to earlier work of Reatto [10], in a recent paper Louis *et al.* [11] claim that the effective pair potential which exactly reproduces the radial distribution function, in a variational sense provides the best pair potential. The variational principle referred to, in our notation reads

$$\int \mathrm{d}R\{e^{-\frac{1}{2}\beta\chi(R)} - e^{-\frac{1}{2}\beta U(R)}\}^2 \geq 0 \tag{11}$$

After putting equal to zero the functional derivative with respect to $u(r)$, we find

$$e^{-\beta A_U} g_U(r) = e^{-\beta A_{\frac{1}{2}(\chi+U)}} g_{\frac{1}{2}(\chi+U)}(r) \tag{12}$$

Since for large values of r all radial distribution functions tend to one, this condition implies that A_U must equal $A_{(1/2)(\chi+U)}$, and consequently $g_U(r)$ must equal $g_{(1/2)(\chi+U)}(r)$ for all values of r. The first of these conditions is not necessarily implied by the second, meaning that an effective pair potential U for which $g_U(r) = g_{(1/2)(\chi+U)}(r)$ for all values of r, not necessarily minimizes the left hand size of Eq. (11). In a second step, Reatto notices that to first order in $U - \chi$ the condition on the radial distribution function may be replaced by $g_U(r) = g_\chi(r)$. This step seems to be doubtful, since there is no reason why $U - \chi$ should be small.

From the discussion above, it is clear that our treatment of the thermodynamic variation principle is much more sound than the one invoked by Louis *et al.* [11]. Still our results seem to indicate that our method produces an effective potential which is very similar to the one obtained by fitting U to $g(r)$. The virial distribution corresponding to U is much too small, and consequently also the pressure calculated from it. Let us therefore have a better look at the equations to be used to calculate the pressure. Since A_{var} is our estimate of the actual free energy, we calculate the pressure by taking minus the derivative of A_{var} with respect to V. While doing so, we have to realize that U may parametrically depend on V. After some lengthy algebra we arrive at

$$\begin{aligned} P = \frac{NkT}{V} - \frac{1}{3V}\left\langle \frac{\mathrm{d}}{\mathrm{d}\lambda}\chi(\lambda R)\bigg|_{\lambda=1}\right\rangle_U \\ + \beta\left\langle\left[\frac{1}{3V}\frac{\mathrm{d}}{\mathrm{d}\lambda}U(\lambda R)\bigg|_{\lambda=1}\right.\right. \\ \left.\left. + \frac{\partial U(R)}{\partial V}\right][(\chi(R) - U(R)) - \langle\chi(R) - U(R)\rangle_U]\right\rangle_U \end{aligned} \tag{13}$$

Since the first factor in the last term is a sum of pair terms, it can be taken out of the averaging brackets, leaving a factor $\delta(R_{12} - r)$. It then follows from the variation principle [see Eq. (4)] that the last term in Eq. (13) equals zero. Our result is remarkably similar to Eq. (2), the only difference being that the average is taken over the effective system instead of the exact system. The important point is that the virial contribution has to be calculated using $\chi(R)$ instead of $U(R)$. As long as $U(R)$ is a soft potential, which it most probably is in case it only has to reproduce $g(r)$, it will never produce the right virial contribution. After all it would have been very surprising if just one pair function would have been enough to capture all the information kept by the many complicated many-body forces acting in the coarse grained system.

Finally, let us notice that of course one may include the pressure in the list of object functions to be reproduced by some optimised pair potential. The more information one puts into the optimisation, however, the larger is the danger of producing an unrealistic potential, which can not be used to calculate properties other than those which have been included in the list of object functions.

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