Osmotic Pressure of Solutions Containing Flexible Polymers Subject to an Annealed Molecular Weight Distribution

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Abstract. – The osmotic pressure \(P\) in equilibrium polymers (EP) in good solvent is investigated by means of a three dimensional off-lattice Monte Carlo simulation. Our results compare well with real space renormalisation group theory and the osmotic compressibility \(K \propto \phi d\phi/dP\) from recent light scattering study of systems of long worm-like micelles. We confirm the scaling predictions for EP based on traditional physics of quenched monodisperse polymers in the dilute and semidilute limit. Specifically, we find \(P \propto \phi^{2.3}\) and, hence, \(K \propto \phi^{-0.3}\) in the semidilute regime — in agreement with both theory and experiment. At higher concentrations where the semidilute blobs become too small and hard-core interactions and packing effects become dominant, a much stronger increase is evidenced and, consequently, the compressibility decreases much more rapidly with \(\phi\) than predicted from semidilute polymer theory, but again in agreement with experiment.

Introduction. Superficially, it would seem that the colligative properties of quenched and annealed polymers must differ vastly, because the former have a fixed molecular weight distribution, whilst the latter are in equilibrium with each other, and continually exchange material \(\text{[1]}\). In this paper, where we study by means of computer simulations the osmotic pressure of “equilibrium polymers” (EP) in a good solvent, we demonstrate that systems of EP, as widely varying as giant polymer-like surfactant micelles, and supramolecular aggregates of dyes, dipolar colloids and proteins \(\text{[2]}\), behave in essence like conventional polymers. The work presented here complements earlier simulation studies, focusing on the density distribution of sizes in dilute, semidilute and concentrated solution, covering both cases with \(\text{[3]}\) and without ring closure \(\text{[4]}\). Our motivation for studying the osmotic pressure is that it is a

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physical quantity that is more readily accessible experimentally than a distribution function or a mean size, in particular in the regimes where the chains strongly overlap. In addition, since conformation space renormalization group (RG) predictions for the pressure are available \cite{6}, as well as experimental data of the osmotic compressibility covering at least two concentration regimes \cite{7}, a fairly comprehensive comparison between theory, simulations and experiment is possible. The agreement we find is remarkably good, strongly suggesting that our simulations not only accurately describe the size distributions of EP, as in fact already shown in previous work \cite{3,5}, but also capture their colligative properties correctly.

After very briefly presenting the simulation method, we first present our results for the pressure, and discuss these in the framework of the scaling theory of polymers. Both systems with and without ring closure have been investigated. (We recall that in the magnetic analogy, used to model EP, rings are suppressed \cite{8}.) Our focus will mainly but not exclusively be on the findings for the EP with suppressed ring closure. The reason is that ring closure is thought not to play a significant role in giant micellar systems \cite{2,3}, for which the most extensive experimental data are available. Also, for reasons to be discussed, although differences in the behavior of EP with and without rings do show up in the dilute regime, the scaling functions remain for all practical purposes the same. Also presented in this Letter is the scaling behavior of the mean length of the EP, on the one hand because it is directly related to the chemical potential of polymerizing materials and on the other because it is subject of controversy \cite{9}. The combined pressure and chemical potential data fully describe the thermodynamics of the system in hand. We stress the success of the ideas borrowed from the scaling theory of polymers in the dilute and semidilute regimes, but also show that in the high-density limit the properties of EP are dominated by packing effects, and not by chain connectivity or self-assembly.

Algorithm and some technical details. As in our previous studies \cite{3,5}, we use an off-lattice Monte Carlo approach, generalizing an efficient bead-spring model for polymers of fixed length. For the direct, non-bonding interactions between the beads we use the repulsive part of a Morse potential. For all practical purposes one may view these beads as hard spheres of diameter $d \approx 0.8$, and effective volume $v = \pi d^3/6 \approx 0.25$. Here, and below, units of length are given in units of the maximum bond length of the bonding potential between two neighboring beads on a chain. This bonding interaction is described by the so-called FENE (finitely extensible nonlinear elastic) potential. In addition to the FENE potential we assign a scission energy $E > 0$ to every bond, to be paid whenever a bond is broken \cite{4}. This scission energy is presumed to be independent of the chain length and the density. In our presentation we choose energy units such that the Boltzmann factor $k_B = 1$, and work at fixed temperature $k_B T = 1$. The two operational parameters which determine the system properties are the number density of beads $\phi$, and the scission energy $E$. Both have been varied over a wide range, $E$ from 3 to 13, and $\phi$ from $2^{-8}$ to 2 to produce a sufficient chain length and density variation allowing for a critical test of the theoretical predictions \cite{3,5,6}. We estimate that in our simulations the effective volume fractions $\nu \phi$ probed range from $\approx 10^{-3}$ to 0.45. The latter value has to be compared with the (only slightly larger) hard-sphere freezing volume fraction of about one half. Therefore, our simulations extend all the way up to the melt regime of a dense liquid. The combined FENE and Morse potentials fix the mean bond length at $l \approx d$, essentially independent of chain length and density \cite{3}. In our model the chains may be regarded as fully flexible \cite{3}.

The osmotic pressure and its scaling with concentration. As is usual in off-lattice Monte Carlo simulations, the pressure $P$ is obtained by evaluating the virial, and adding to that the contribution $k_B T \phi$ from the kinetic degrees of freedom \cite{10}. In Fig. \ref{fig:1} we present the results for the bare pressure of the self-assembled polymers as a function of the number density $\phi$, 
Fig. 1 – Pressure $P$ versus the number density $\phi$ for systems of monodisperse Morse beads (crosses), equilibrium polymers with ring closure suppressed (open symbols) and equilibrium polymers with ring closure allowed (full symbols). Results for various scission energies $E$ are indicated by the symbol shapes listed in the graph. The dashed and full lines indicate the predicted scaling in the dilute and semidilute regimes respectively, and the dotted line the ideal gas behavior of the Morse beads at low densities.

Fig. 2 – Master curve of the reduced pressure $y = P \langle N \rangle / \phi$ versus the reduced mean aggregation number $x = \langle N \rangle / g(\phi)$, based on the notions of the scaling theory of polymers. Same symbols as in Fig. 1. The bottom curve gives all the measured data points, the top curve (shifted for clarity) includes only those data for which $\phi < 1$. The dashed line gives the ideal gas law, and the bold line the power law, expected for a semidilute solution. The data collapse is almost perfect when the data taken in the high density regime (beyond the semidilute range) are excluded. In the top curve we compare our simulations with the estimate $y = 1 + 4.3x$ (thin line), and the RG theory prediction from [6] (dash-dotted line). Both curves virtually coincide.

for various scission energies $E$. For reasons of comparison results are also presented obtained for a gas of monomeric beads, interacting solely via the Morse potential (“Morse beads”).

For the Morse beads (indicated by crosses), we find ideal gas behavior at densities $\phi \ll 1$. At about $v\phi \approx 0.1$ hard-core interactions become important, and $P$ rises steeply. This is to be compared with our results for EP without ring closure (open symbols), and with ring closure (full symbols). Not surprisingly, switching on the polymerization in the EP systems acts to lower the pressure relative to that of the gas of Morse beads. Focusing on the EP without rings first, we observe that in the limit of low densities and low scission energies, i.e., in the weak aggregation limit, the pressure is comparable to that of the Morse beads, as it should (see the data for $E = 3$). As the scission energy and, hence, the mean chain length increases, distinct power laws are observed in the dilute and semidilute regimes. The bold dashed line compares the pressure in the dilute limit with what one expects on the basis of ideal gas behavior $P = \phi / \langle N \rangle$, using the scaling of the mean chain length $\langle N \rangle \propto \phi^{0.46}$ in the dilute regime derived below. At higher densities the pressure becomes independent of $E$. In the limit of sufficiently small densities, but large mean chain length, the measured pressures converge towards $P \propto \phi^{2.3}$. This is in line with the expected scaling behavior of polymers (quenched or annealed) in semidilute solution. In semidilute solution the pressure is governed by the number of blobs or entanglements per unit volume, independent of molecular weight.
It is therefore also independent of any self-assembly process.

Of course, the blob picture is only valid for sufficiently low densities and large chain lengths. Our simulation data confirm this: the larger the scission energy $E$, the better the semidilute scaling regime is discernible, in essence because the chains then overlap at lower densities. At densities above $\phi \approx 1$, roughly when the packing effects make themselves felt in the gas of Morse beads, the pressure of EP rises more strongly than predicted by scaling theory, but still remains independent of $E$. This is the melt regime discussed in the introduction.

In Fig. 2 we attempt to construct a master curve covering all our data for the EP, essentially inspired by standard scaling theory for conventional polymers [8], and elucidated in more detail in the next section. The vertical axis gives the pressure divided by the ideal gas pressure $\phi/\langle N \rangle$. Given on the horizontal axis is the ratio of the mean aggregation number $\langle N \rangle$ and the number of monomers per blob $g \sim \phi^{-1}/(3\nu - 1)$, where $\nu \approx 0.588$ is the Flory exponent of a self-avoiding walk in three dimensions. The bottom curve includes results from all densities probed, while the top curve excludes data for densities $\phi \geq 1$, i.e., those data outside of the dilute and semidilute regimes. Not surprisingly, the data collapse is only successful if the data of the melt regime are excluded.

Included in both figures are also results obtained for EP in which ring closure was allowed, and polymer rings compete with linear chains for the available monomers. (The data are indicated by the filled symbols for a single value of $E = 7$.) In a previous study [3] we found that in the dilute limit most of the monomers are assembled in trimer rings (the lower cutoff), and that the polymerization transition and the crossover to the semidilute regime roughly coincide. The pressure data are consistent with this, since we find at small densities $P = \phi/3$. Beyond the crossover to the semidilute regime almost all of the additionally added monomers are included in linear chains. The fact that a finite amount of monomers remains bound in closed loops in the semidilute regime appears to be irrelevant, for we observe within statistical accuracy the same pressure with and without rings. The data collapse perfectly in Fig. 2, although a huge amount of trimer rings are present at low and intermediate densities. Apparently, and perhaps surprisingly [11], the presence of loops does not significantly affect the excluded volume screening.

**Theoretical considerations.** Our findings for EP without rings can be understood from the following Ansatz for the grand potential density

$$\Omega[c(N)] = \sum_{N=1}^{\infty} c(N) \left( \log(c(N)^{\gamma}) - 1 - \mu N + E + f_N(N, \phi) \right) - R(\phi). \tag{1}$$

The sum over monomer mass $N$ describes the self-assembly in terms of an ideal mixing entropy, a Lagrange multiplier or chemical potential $\mu \leq 0$ that ensures conservation of mass, and a free energy penalty $E + f_N(N, \phi)$ associated with the chain ends [3]. Of the latter, $f_N(N, \phi)$ renormalizes the bare scission energy $E$ due to differences in the micro-environment of the ends and central parts of the chains. This term is different in the dilute, semidilute and concentrated regimes [3]. Applying the well-known statistical properties of self-avoiding walks, we infer that in the dilute limit $f_N$ decreases logarithmically with the degree of polymerization, i.e., $f_N(N) = - (\gamma - 1) \log(N)$ with $\gamma \approx 1.158$ the susceptibility exponent of the $n \to 0$ vector model in three spatial dimensions [5]. Entering the semidilute regime, one expects excluded volume effects to be screened out, and $f_N$ should level off to $f_N(\phi) = (\gamma - 1)(3\nu - 1)^{-1} \log(\phi)$ [3]. It is not known theoretically how $f_N(\phi)$ behaves in the melt regime, so we focus first our analysis to the dilute and semidilute regimes.

The remaining contribution $R(\phi)$ accounts for excluded volume interactions which depend only on density $\phi$, and are not conjugate to $c(N)$. Minimizing eq. (1) gives in the limit of long
chains an exponential equilibrium distribution function $c_{eq}(N) \propto \exp(-E-f_N(N, \phi)+\mu N)$ \cite{3}, and an osmotic pressure $P = -\Omega[c_{eq}] = \phi/\langle N \rangle + R(\phi)$. Following De Genes \cite{8}, we assume a constant free energy density of $k_B T \approx 1$ per blob, giving $P/\phi = F(x) = 1 + x$ with $x \propto \langle N \rangle/g(\phi)$. This simple estimate can fit remarkably well the observed master curve of Fig. 2 and is barely distinguishable from the more elaborate RG treatment of ref. \cite{6}, also shown in the figure. Note that the functional eq. (1) may be readily generalized to include the possibility of ring closure \cite{3}, or even chain branching. However, as long as the excluded volume term $R(\phi)$ remains dominated by entanglements, the equation of state should be independent of chain architecture, in line with our observations.

Scaling behavior of mean chain length and chemical potential. To help analyzing the concentration and scission energy dependence of the pressure we evaluated the mean chain length $\langle N \rangle$ as a function of these parameters, the results of which are given in Fig. 3. From the equilibrium length density distribution given in the previous section, we easily find that $\langle N \rangle \propto \phi^\alpha \exp(\delta E)$ with $\alpha = \delta = 1/(1+\gamma) \approx 0.46$ in the dilute, and $\alpha = (1 + (\gamma - 1)/(3\nu - 1))/2 \approx 0.6$, $\delta = 1/2$ in the semidilute limit \cite{3,5}. This also fixes the chemical potential of the polymerizing material: $-1/\mu = \gamma \langle N \rangle$ in dilute, and $-1/\mu = \langle N \rangle$ in semidilute solution, at least for sufficiently large mean aggregation number. (The chemical potential has also been obtained directly from the exponential cutoff of the distribution functions, confirming these relations and yielding a similar scaling plot.) In Fig. 3 both the mean aggregation number and the density are scaled by their values at the crossover from the dilute to the semidilute regimes, obtainable by a matching procedure described elsewhere \cite{4}. The slopes
giving the \( \alpha \) exponents in both regimes are clearly visible. Also included in the figure is the RG result of \([13]\). As expected, the agreement is reasonable but not perfect, because the theory is based on an approximation valid in the vicinity of four spatial dimensions. Extrapolated to three dimensions the growth exponents become \( \alpha \approx 0.44 \) in the dilute, and \( \alpha \approx 0.56 \) in the semidilute regime, slightly underestimating the results from our simulations in both regimes. The astounding accuracy of the scaling function for the pressure calculated from the RG theory, plotted in Fig. 2 is due to the circumstance that the inherent inaccuracies of the theory are hidden in the scaled pressure and the scaled mean chain length.

As in Fig. 2 we have in Fig. 3 only included data for densities \( \phi < 1 \) to avoid entering the melt regime, where the scaling and RG theories are known to be no longer accurate \([3]\). This is illustrated in the inset of Fig. 3, where we have plotted for three values of \( E \) the concentration dependence of the free energy penalty \( f_N \), which in the simulations may be measured either from the relation \( \langle N \rangle^2 \propto \phi \exp( E + f_N ) \) or from fitting the length distribution \( c(N) \), which turns out to remain purely exponential in the melt regime at variance with recent lattice simulations \([12]\), attempting to support a questionable modeling assumption proposed by Bouchaud et al. \([13]\) to rationalize the observed Levy flight dynamical behavior in giant micelles. The figure shows that in this regime the free energy penalty \( f_N \) increases more or less linearly with concentration, \( f_N(\phi) \propto \phi \). We speculate that packing effects give rise to the free energy penalty, disfavoring chain ends because they disturb the local structure of the chain fluid. A crude estimate for \( f_N \) can be gotten in terms of the work required to create two new chain ends against the ambient pressure. In the inset of Fig. 3, we compare \( f_N \) with this estimate \( P \delta V \), presuming that the additional free volume \( \delta V \approx 1/\phi \) associated with free ends is of the order of the mean monomer volume. Although our argument is certainly simplistic and further study is warranted, the qualitative agreement does suggest that packing effects rule at such high densities – this may of course also be inferred from Fig. 1, which hints at the convergence of the monomer and EP pressures in the melt regime.

**Comparison with experiment: Osmotic compressibility.** In Fig. 4 we compare our simulation results with the isothermal osmotic compressibility, \( K \), of a particular giant micellar system, measured by means of light scattering \([4]\). We deduce \( K \) from the computed pressures using the thermodynamic identity \( K \propto \phi \partial \phi / \partial P \). In order to minimize scatter and obtain a numerically meaningful differentiation, we first fit fourth order polynomials to each data set of \( \log P \) versus \( \log \phi \), and then differentiate these polynomials. Because the dilute regime is very small for large \( E \), we have in addition extrapolated these data to lower densities using the well tested relationship for the mean chain length in the dilute limit (see left side of Fig. 3). In other words, we insist on \( K \propto \phi^{1+\alpha} \propto \phi^{1.46} \) in dilute solution for large \( E \). The experimental data have been shifted in such a way to match our semidilute regime where \( K \propto \phi^{(2-3\nu)/(3\nu-1)} \). This is allowed, because (i) the experimental data for \( K \) are not absolute and given in arbitrary units only \([4]\), and (ii) our volume fractions are only effective ones. Reasonable agreement was found over all regimes for the scission energy \( E = 13 \). From this we conclude that we are able to simulate coarse-grained EP comparable in size to real giant micelles. Also included is the result from the RG calculation \([3]\), which fits well to both experiment and simulation in the dilute and semidilute regime. Apparently, the semidilute regime is rather small in both simulations and in the experiments of Buhler and co-workers \([7]\).

**Discussion.** We have investigated the (osmotic) pressure and compressibility of solutions of equilibrium polymers. Results from off-lattice Monte Carlo simulation, renormalisation group theory, and recent light scattering data of giant micelles have been compared. At low density and sufficiently high scission energy, i.e., for long enough chains, the results confirm unambiguously the theoretical predictions based on standard polymer theory \([3]\).

The universal scaling of \( P \) and \( K \) with respect to density \( \phi \) and mean chain-length \( \langle N \rangle \) is
shown to be identical to that of quenched polymers, in agreement with theory \[3\]. Specifically, we find that in the semidilute regime the power law scaling of the pressure \( P \propto \phi^{2.3} \) and compressibility \( K \propto \phi^{-0.3} \), in agreement with experimental findings in many solutions of giant micelles \[2\], but only for sufficiently flexible ones \[14, 15\]. Whether or not rings are present does not seem to alter the scaling of the pressure in semidilute EP. Despite that there is consensus about the growth law in the dilute regime, now and again workers find growth exponents that deviate from the expected value close to one-half, varying from \( \alpha \approx 0.1 \) to \( 1.5 \) \[3\]. From our simulations we put forward that for these systems additional physics must be involved, such as due to ring closure, branching, the presence of charges, or the presence of more than one aggregating component. Clearly, the issue calls for a more detailed experimental investigation.

In our simulations the blob picture breaks down at volume fractions exceeding, say, 0.1. The pressure then increases more rapidly than with the 2.3 power law, although it does stay below that of the monomeric Morse beads at equal concentration. As a consequence, the deduced compressibility decreases more strongly in this limit than with the \(-0.3\) power expected from scaling theory. Our interpretation is that the EP then enter the concentrated or melt regime. The light scattering data of Buhler et al. also point at a crossover to the concentrated regime \[7\]. In real systems the crossover to the concentrated regime is non-universal, and likely to depend on both the persistence length of the aggregates as well as their diameter \[8\]. We intend to investigate by means of computer simulation the influence of chains flexibility on the colligative properties of EP in the near future.

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