

PRELIMINARY COMMUNICATION

Unexpected length dependence of the solubility of chain molecules

By D. FRENKEL

FOM-Institute for Atomic and Molecular Physics, Kruislaan 407,
NL-1098 SJ Amsterdam, The Netherlands

and B. SMIT

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), Badhuisweg 3,
NL-1031 CM Amsterdam, The Netherlands

(Received 9 September 1991; accepted 27 September 1991)

We report numerical simulations of the chemical potential of a freely jointed chain molecule in a solvent of monomers, using a novel scheme to compute the chemical potential of arbitrary chain molecules. For short chains, the excess chemical potential increases linearly with the number of segments. However, as the chain length is increased, the slope of the chemical potential versus the number of segments suddenly increases. This change of slope is due to the solvent and appears to signal a solvent-induced collapse of the flexible molecule.

Computer simulations have proven to be a very powerful tool to study the dynamic and structural properties of chain molecules in solution [1]. In contrast, there are only very few numerical studies of the *phase behaviour* of polymer solutions (see e.g., reference [2]). The reason is that such calculations usually require the availability of an efficient technique to compute the chemical potential, μ , of an arbitrary chain molecule. For all but the shortest chains and the lowest solvent densities, such calculations are notoriously difficult. Yet, the "exact" knowledge of the chemical potential even of relatively short chain molecules (10-20 segments) would be of considerable interest because chain molecules of this length, in particular surfactants, exhibit very rich phase behaviour (see, for instance, reference [3]).

In computer simulations of atomic and simple molecular fluids, the excess chemical potential μ^{ex} (referred to an ideal gas mixture at the same temperature, density and composition) is usually determined with the help of the "test-particle method" of Widom [4]. This method is based on the fact that μ^{ex} is related to the change ΔU in potential energy of a system of N particles upon random insertion of a test particle [4]:

$$\beta\mu^{\text{ex}} = -\ln \langle \exp(-\beta\Delta U) \rangle, \quad (1)$$

where $\beta \equiv 1/(k_B T)$ is the inverse temperature and $\langle \dots \rangle$ denotes a canonical ensemble average. In principle, equation (1) is exact but, in practice, it is limited to relatively small molecules. In particular, equation (1) is effectively useless for flexible chains containing more than four segments [5].

In this paper, we report a novel method for calculating the chemical potential of arbitrary chain molecules. In contrast to most earlier schemes, our approach is not limited to lattice models of polymer solutions. Using this technique, we have computed the chemical potential of chains consisting of 1 to 30 segments in a solvent at

puted the chemical potential of chains consisting of 1 to 30 segments in a solvent at infinite dilution. We find that the excess chemical potential of the polymer shows a sudden kink as a function of the number of segments. This kink is absent in the chemical potential of isolated chains. Hence, it is due to the presence of the solvent molecules. Before presenting these results we first give a brief description of the method we have used to compute μ .

Our method is a generalization of Siepmann's method for calculating the chemical potential of chain molecules with a finite number of conformations [6]. Siepmann uses an algorithm due to Rosenbluth and Rosenbluth to generate polymer conformations on a lattice [7]. In a particle insertion, the chain is grown segment-by-segment. During the addition of a segment, *all* accessible orientations of this segment are probed. Clearly, exploring all possible orientations of a new segment is no problem if we deal with a molecule that has only a finite number of conformations. Such an approach would, however, fail for a continuously deformable, flexible molecule. Surprisingly, it turns out that it is nevertheless possible to construct a rigorous scheme to measure the chemical potential of any flexible molecule using only a random subset of all possible segment orientations, *even if the total number of conformations is infinite*. We shall now proceed to prove this crucial result.

It is most convenient to introduce the method by first considering a molecule with a finite number of conformations. In particular, we assume that every segment can have b possible directions. Subsequently, we shall consider the limit $b \rightarrow \infty$.

Consider a system of N solvent molecules in which we try to insert a polymer by sequential addition of segments. In the i th step of this process, we generate a random subset $(\{m_i\})$ of all possible orientations starting from segment $i - 1$. Let us denote the number of elements in $\{m_i\}$ by k ($k \leq b$). From this set, we select one particular orientation (Γ_i) with a probability $\exp[-\beta u_{\Gamma_i}] / \sum_{j=1}^k \exp[-\beta u(m_j)]$, where $u(m_j)$ is the potential energy of the i th segment in orientation m_j . This procedure is iterated until all l segments have been grown. The probability of generating a polymer of length l in conformation Γ is

$$P_{\Gamma} = \prod_{i=1}^l \left[\sum_{\{m_i\} | \Gamma_i \in \{m_i\}} P_{\{m_i\}} \frac{\exp[-\beta u_{\Gamma_i}]}{\sum_{j=1}^k \exp[-\beta u_{\Gamma_i}(m_j)]} \right], \quad (2)$$

where $P_{\{m_i\}}$ denotes the probability of generating the set $\{m_i\}$. In equation (2), the summation runs over all possible sequences of k trial orientations, with the restriction that this sequence should include the actual sequence of segments that corresponds to the conformation Γ . In particular, the set $\{m_i\}$ should include the i th segment of Γ , denoted by Γ_i .

This scheme is strongly biased towards generating polymer conformations that can be successfully inserted in the solvent. In the computation of the excess chemical potential using a particle insertion scheme, we must correct for this bias. This is done by relating the excess chemical potential of the chain molecule to the average of a weight factor W_{Γ} , defined as

$$W_{\Gamma} = \prod_{i=1}^l \frac{1}{k} \sum_{j=1}^k \exp[-\beta u_{\Gamma_i}(m_j)]. \quad (3)$$

We obtain an estimate of the ensemble average of W_{Γ} by averaging over a large number of chain conformations. The configurations of the solvent are sampled using

standard constant- N, V, T Monte Carlo simulation.

$$\langle W_l \rangle \equiv \frac{\sum_{\mathbf{q}^N} [\sum_{\Gamma} P_{\Gamma}(\mathbf{q}^N) W_{\Gamma}(\mathbf{q}^N)] \exp[-\beta U(\mathbf{q}^N)]}{\sum_{\mathbf{q}^N} \exp[-\beta U(\mathbf{q}^N)]}, \quad (4)$$

where the first summation in the numerator runs over all configurations of the system \mathbf{q}^N and the second over all conformations of the test polymer. $U(\mathbf{q}^N)$ is the energy of a configuration \mathbf{q}^N . Note that the test polymer does not form part of the N -particle system. Therefore the probability of finding the solvent particles in a configuration \mathbf{q}^N does not depend on the configuration Γ of the polymer.

For a given configuration of the system \mathbf{q}^N , we can define an average weight factor

$$\bar{W}_l = \sum_{\Gamma} P_{\Gamma} W_{\Gamma} = \sum_{\Gamma} \prod_{i=1}^l \exp[-\beta u_{\Gamma_i}] \left[\sum_{\{\{m_i\} | \Gamma_i \in \{m_i\}\}} \frac{1}{k} P_{\{m_i\}} \right]. \quad (5)$$

Equation (5) has been obtained by combining equations (2) and (3). Note that we have dropped the argument \mathbf{q}^N .

The probabilities $P_{\{m_i\}}$ determine the relative *a priori* probability of the segment orientations. For completely flexible polymers, all segment orientations are generated with the same *a priori* probability, or $P_{\{m_i\}} = 1/b^k$. For polymers with strong intramolecular interactions, for example, stiff polymers ("wormlike chains"), it is straightforward to show [8] that the probabilities $P_{\{m_i\}}$ can be modified in such a way that the probability of generating a given segment orientation is dictated by the Boltzmann factor associated with the intramolecular energy. For the flexible polymer, the total number of possible sets of orientations which include orientation Γ_i is kb^{k-1} . This gives for the average weight factor in equation (5)

$$\bar{W}_l = \sum_{\Gamma} \prod_{i=1}^l \exp[-\beta u_{\Gamma_i}] \frac{kb^{k-1}}{kb^k} = \sum_{\Gamma} \frac{1}{b^l} \exp[-\beta U_{\Gamma}]. \quad (6)$$

Upon substitution of this expression in equation (4) we obtain

$$\langle W_l \rangle = \frac{\sum_{\mathbf{q}^N} [\exp[-\beta U_{\Gamma}(\mathbf{q}^N)]] \exp[-\beta U(\mathbf{q}^N)]}{\sum_{\mathbf{q}^N} b^l \exp[-\beta U(\mathbf{q}^N)]} \quad (7)$$

We recall that b^l is simply the number of possible conformations of an ideal (non-interacting, nonself-avoiding) polymer. Therefore, the denominator in equation (7) is equal to the partition function of the N -particle system plus an ideal polymer, and the numerator is equal to the partition function of the N -particle system plus an *interacting* chain molecule. This shows that the average of the W_l factor is directly related to the excess chemical potential of a polymer

$$\beta \mu^{\text{ex}}(l) = \beta \mu(l) - \beta \mu(\text{ideal pol}, l) = \ln \langle W_l \rangle. \quad (8)$$

Note that equation (8) does not depend on the number b of trial directions. This implies that the above expression remains valid if we consider any finite subset of k trial directions, even if $b \rightarrow \infty$.

We have used the procedure outlined to compute the excess chemical potential at infinite dilution of a fully flexible chain molecule in a moderately dense atomic fluid. In our model, both the solvent and the polymer segments interact via a Lennard-Jones potential [9, 10]. Adjacent polymer segments are connected with an infinitely stiff spring with length σ . We have considered two systems. In system 1, the Lennard-Jones potential is truncated at $R_c = 2.5\sigma$. At larger separations, the solvent is treated as a continuum (see e.g., reference [5]). System 2 is purely repulsive: the Lennard-

Table 1. The excess chemical potential ($\beta\mu^{\text{ex}}$) as a function of the number l of beads for various values of k for system 1. The density is $\rho^* = \rho\sigma^3 = 0.6$, the temperature is $T^* = k_B T/\varepsilon = 1.2$, the number of solvent molecules is 500, the number of MC cycles is 3000. The number of trial insertions per Monte Carlo cycle is 250. The small subscript gives the accuracy of the results, so -2.43_5 means -2.43 ± 0.05 .

l	$k = 1$	$k = 2$	$k = 10$	$k = 20$	$k = 50$	$k = 100$
1	-2.45_5	-2.45_8	-2.43_4	-2.45_6	-2.44_4	-2.43_5
2	-5.3_5	-5.0_8	-5.0_2	-5.0_1	-5.05_7	-5.05_9
3	-8_2	-7_1	-7.3_3	-7.3_2	-7.3_2	-7.4_1
4	—	—	-9.5_4	-9.8_4	-9.9_2	-9.9_2
5	—	—	-11.8_7	-12.0_7	-12.3_3	-12.2_3
6	—	—	-13_1	-14_1	-14.8_4	-14.5_5
7	—	—	-16_2	-17_2	-18_1	-17_1
8	—	—	-18_2	-18_1	-19.7_9	-18.9_7
9	—	—	—	-21_3	-22_2	-22_1
10	—	—	—	—	-23_1	-24_1
11	—	—	—	—	-26_2	-27_2
12	—	—	—	—	-28_2	-28_1
13	—	—	—	—	-30_2	-28_1
14	—	—	—	—	-32_2	-29_2

Jones potential is truncated (and shifted) at its minimum ($R_c = 2^{1/6}\sigma$). Technical details of the simulations are described in a forthcoming publication [8].

In table 1, the results for the chemical potential are given for various values of k . An important result, shown in table 1, is that within the accuracy of our calculations the results are indeed independent of the particular choice of k . In contrast, the statistical error depends strongly on k . In particular, table 1 shows that the conventional Widom particle insertion method (i.e., $k = 1$) only yields a reliable estimate of μ for chains with less than 3 segments. In contrast, the present method yields reliable estimates of the chemical potential for chains that are an order of magnitude longer. We have performed several tests to verify that our results do not depend on N , the number of solvent particles (the present results pertain to $N = 500$). For more details, the reader is referred to reference [8].

In figure 1, results for the excess chemical potential as a function of the chain length are presented for system 2. This figure shows that the chemical potential increases linearly for chains with $l < 11$ but, surprisingly, the slope of μ^{ex} suddenly increases as the chain length is increased. For an isolated polymer chain of the same length, this effect is not observed (see figure 2). This indicates that the change in slope is a solvent effect. This conclusion is supported by the observation that at a higher solvent density (see figure 1) the change of slope occurs for a shorter chain length ($l \approx 8$). Moreover, we observe a similar effect in system 1 (see reference [8]).

As the excess chemical potential determines the solubility of the polymer in the liquid of monomers, our calculations indicate a rather sudden change in the dependence of polymer solubility on chain length. The observed change of slope in μ^{ex} indicates that, beyond a certain length, it becomes more difficult to add additional segments to a chain molecule. As the probability of insertion decreases rapidly with increasing density, the most obvious interpretation is that, beyond a certain length, additional segments are inserted in a denser fluid. The sudden change in slope in μ^{ex} suggests that there is a change of the segment density of the polymer in solution. In itself, such an

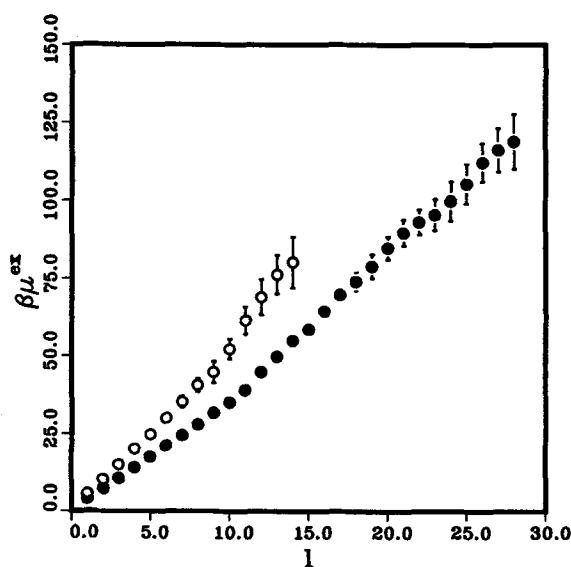


Figure 1. The excess chemical potential $\beta\mu^{ex}$ as a function of the number l of beads of the chain for system 2: only repulsive interactions. \bullet , $\rho^* = 0.5$, and \circ , $\rho^* = 0.6$.

effect is not surprising. What *is* surprising is that this effect appears to take place quite abruptly, even for relatively short chains. At present, a quantitative explanation for this effect is lacking. It would, however, be interesting to see whether recent theories on dilute polymer solutions [11, 12] would reproduce this effect of the solvent on the excess chemical potential of polymers. Recently, Kumar *et al.* [13] have proposed an approximate scheme to compute the chemical potential of systems containing chain

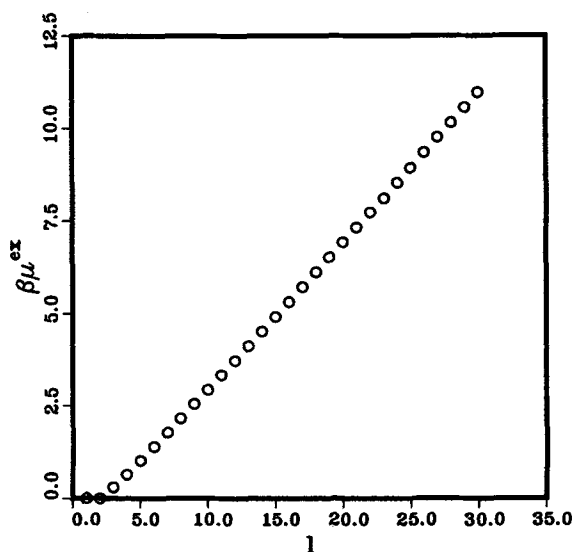


Figure 2. The excess chemical potential $\beta\mu^{ex}$ of an isolated self-avoiding chain of repulsive Lennard-Jones particles, as a function of the number l of 'atoms' in the chain.

molecules. In the latter scheme, it is assumed that the excess chemical potential of a chain molecule of l "beads" is simply l times the free energy required to add one extra segment. If this assumption were correct, we would not observe the change of slope of μ^{ex} versus l shown in figure 1. However, it seems plausible that the method of reference [13] works better for systems of longer chain molecules and for melts rather than solutions. Clearly, it would be of considerable interest to use the rigorous scheme presented above to determine the range of applicability of the method proposed in reference [13].

We thank H. N. W. Lekkerkerker for a critical reading of the manuscript, and we gratefully acknowledge stimulating discussions with I. Szleifer and B. Widom. The work of the FOM Institute is part of the research program of FOM and is supported by Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

References

- [1] For a recent overview, see e.g., 1991, *Computer Simulation of Polymers*, edited by R. J. Roe (Prentice-Hall).
- [2] SARIBAN, A., and BINDER, K. 1988, *Macromolecules*, **21**, 711.
- [3] SAFRAN, S. A., and CLARK, N. A., editors, 1987, *Physics of Complex and Supramolecular Fluids* (Wiley).
- [4] WIDOM, B., 1963, *J. chem. Phys.*, **39**, 2802.
- [5] ALLEN, M. P., and TILDESLEY, D. J., 1987, *Computer Simulation of Liquids* (Clarendon Press, Oxford).
- [6] SIEPMANN, J. I., 1990, *Molec. Phys.*, **70**, 1145.
- [7] ROSENBLUTH, M. N., and ROSENBLUTH, A. W., 1955, *J. chem. Phys.*, **23**, 356.
- [8] FRENKEL, D., and SMIT, B., *J. Phys. Condensed Matter* (in press).
- [9] SMIT, B., VAN DER PUT, A., PETERS, C. J., DE SWAAN ARONS, J., and MICHELS, J. P. J., 1988, *Chem. Phys. Lett.*, **144**, 555.
- [10] SMIT, B., COX, K. R., and MICHELS, J. P. J., 1989, *Molec. Phys.*, **66**, 97.
- [11] SZLEIFER, I., and WIDOM, B., 1989, *J. chem. Phys.*, **90**, 7524.
- [12] SZLEIFER, I., 1990, *J. chem. Phys.*, **92**, 6940.
- [13] KUMAR, S. K., SZLEIFER, I., and PANAGIOTOPOULOS, A. Z., 1991, *Phys. Rev. Lett.*, **66**, 2935.