dimers such as the ones studied here. It is reasonable to think of Si–O–Si inversion as a process by which excimer nonradiative decay may take place.

Registry No. DS, 56-33-7.

References and Notes

(1) (a) Winnik, M. A. *Photophysical and Photochemical Tools in Polymer Science*: NATO ASI Series; D. Reidel: Dordrecht, 1986. (b) Rabek, J. F. *Mechanisms of Phytophysical Processes and Photochemical Reactions in Polymers*; Wiley: New York, 1987. (c) Phillips, D. *Polymer Photophysics*; Chapman and Hall: London, 1985. (d) Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University Press: New York, 1985.

(2) Salôm, C.; Gômez-Antón, M. R.; Horta, A.; Hernández-Fuentes, I.; Piérola, I. F. *Macromolecules* 1987, *20*, 1627.

(3) Fox, R. B.; Price, T. R.; Cozzens, R. F.; McDonald, J. R. *J. Chem. Phys.* 1972, *57*, 534.

(4) David, C.; Piens, M.; Geuskens, G. *Eur. Polym. J.* 1972, *8*, 1019.

(5) Ishii, T.; Handa, T.; Matsunaga, S. *J. Polym. Sci., Polym. Phys. Ed.* 1979, *17*, 811.

(6) Bokobza, L.; Monnerie, L. *Polymer* 1981, *22*, 235.

(7) Tazuke, S.; Ooky, H.; Sato, K. *Macromolecules* 1982, *15*, 400.

(8) Skilton, P. F.; Ghiggino, K. P. *Polym. Photochem.* 1984, *5*, 179.

(9) De Schryver, F. C.; Moens, L.; Van der Auweraer, M.; Boens, N.; Monnerie, L.; Bokobza, L. *Macromolecules* 1982, *15*, 64.

(10) De Schryver, F. C.; Demeyer, K.; Toppet, S. *Macromolecules* 1983, *16*, 89.

(11) Zachariasse, K. A.; Duveneck, G.; Busse, R. *J. Am. Chem. Soc.* 1984, *106*, 1045.

(12) Goldenberg, M.; Emert, J.; Morawetz, H. *J. Am. Chem. Soc.* 1978, *100*, 7171.

(13) Ito, S.; Yamamoto, M.; Nishijima, Y. *Bull. Chem. Soc. Jpn.* 1981, *54*, 35.

(14) Aspler, J. S.; Guillet, J. E. *Macromolecules* 1979, *12*, 1082.

(15) Wu, S. K.; Jiang, Y. C.; Rabek, J. F. *Polym. Bull.* 1980, *3*, 319.

(16) (a) Piérola, I. F.; Radic, D.; Gargallo, L. *J. Photochem.* 1987, *38*, 375. (b) Helfand, E. in Ref 1a, p 151.

(17) Tsitsilianis, C. *Polym. Bull.* 1987, *18*, 183.

(18) Tanabe, Y. *J. Polym. Sci., Polym. Phys. Ed.* 1985, *23*, 601.

(19) Llorente, M. A.; Piérola, I. F.; Saiz, E. *Macromolecules* 1985, *18*, 2663.

(20) Salôm, C.; Horta, A.; Hernández-Fuentes, I.; Piérola, I. *Macromolecules* 1987, *20*, 696.

(21) Kinetic parameters shown in Tables II and III have been obtained from the best fit of results. A single line and two lines with various distributions of points have been tried in every case.

(22) Holden, D. A.; Guillet, J. E. *Developments in Polymer Photochemistry*; Applied Science: Barking, 1980.

(23) Grigoras, S.; Lane, T. H. *J. Comput. Chem.* 1987, *8*, 84.

(24) Rubio, A. M.; Freire, J. J.; Piérola, I. F.; Horta, A., unpublished results.

(25) Debolt, L. C.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* 1988, *26*, 989.

Monolayer, Multilayers, and Wetting Film of Poly(phenylmethylsiloxane)

Steve Granick* and Daniel J. Kuzmenka

Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

Stephen J. Clarson[†] and J. A. Semlyen

Department of Chemistry, University of York, York YO1 5DD, U.K.
Received August 2, 1988; Revised Manuscript Received September 27, 1988

ABSTRACT: Surface pressure π has been measured as a function of surface concentration for poly(phenylmethylsiloxane) liquids, M_n = 1470, 2240, 10560, and 19500, spread at the water–air interface at 22.8 °C. For the two fractions of least molecular weight, the surface pressure was independent of concentration at submonolayer coverages, reflecting phase equilibria between aggregated and gaseous molecules. For these fractions π rose abruptly at a concentration consistent with estimates of full monolayer coverage and the transition was smooth to multilayers and eventually to films of macroscopic thickness. However, the two fractions of highest molecular weight did not spread. A desorption, or drying, transition appeared to occur with increasing molecular weight.

Introduction

The desire to study two-dimensional systems motivates studies of insoluble monomolecular films at the water–air interface.[1] Surface pressure π, the amount by which the liquid's surface tension is reduced by presence of film, is measured relatively easily and is analogous to the osmotic pressure characteristic of three-dimensional systems. Much interesting phase information has long been available concerning monolayers of small surfactant molecules (consisting of a polar head and a hydrocarbon tail) but less for amorphous, uncharged polymers because few synthetic polymers[2] spread to form insoluble monolayers at the water–air interface.

Original studies with polymers[3] emphasized dilute concentrations, where π depends on the density of molecules; the interest was to determine the molecular weight and the second virial coefficient. More recently, more attention was paid to a region of much higher concentrations, where surface pressure is found experimentally to rise as a power law in the surface concentration and to be independent of molecular weight; this transition region has been interpreted as a "semidilute" region of concentration in two dimensions,[4,5] although this interpretation has been questioned.[2] At high surface concentrations there begins a plateau region of relatively constant surface pressure, generally interpreted to reflect "collapse" of the monolayer to the three-dimensional state.

The study reported below concerns a polymer that has not been studied previously, poly(phenylmethylsiloxane). One purpose of the study was to obtain additional data

†Present address: Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH 45221.

Table I
Characterization of the Poly(phenylmethylsiloxane)
Samples

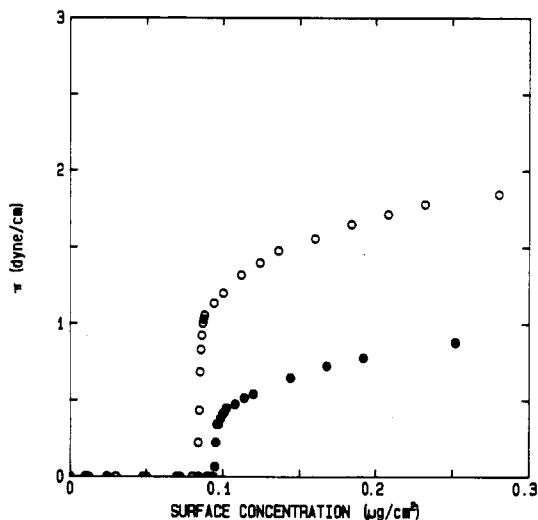| code	M_n	M_w/M_n	code	M_n	M_w/M_n
A	1470	1.09	C	10 560	1.16
B	2 240	1.08	D	19 500	1.12

Figure 1. Surface pressure at 22.8 °C plotted against surface concentration of polymer: open circles, polymer A; filled circles, polymer B.

on the phase behavior of an uncharged polymer at submonolayer coverages. A second purpose was to investigate the passage from the monolayer state to multilayer and eventually to truly three-dimensional states. This in turn is connected to questions of wetting, which have been of recent renewed interest.[6,7]

Experimental Section

Experiments were performed at the University of Illinois. The traditional Wilhelmy plate method was used to measure surface pressure. The resolution in π was 0.01 dyn/cm. A sand-blasted platinum foil 2 cm long was flamed and then suspended with one end in the water and the other end hanging from a Sartorius 1712 electronic balance. The water was distilled and deionized before use. Experiments were performed inside a Teflon trough inside a thermostated chamber. Polymer solutions were prepared by weight in distilled chloroform or benzene (findings were the same using either solvent), and π was inferred from lessened vertical force per length after the films were spread. Surface concentration was controlled by adding film solution at fixed surface area; this has advantages over the compression method, in regard to making equilibrium measurements when the surface coverage is high, because it avoids metastable compression of the film. That polymer did not dissolve was inferred from stability in the readings of π after the solvent had evaporated (2 min). To test the reliability of the Wilhelmy plate measurements, the film was spread on one side to $c > 0.2$ $\mu g/cm^2$, baked talc powder was sprinkled on the clean water side, and finally the thread was lifted rapidly. The powder was swept to the sides of the trough by film, verifying that the finite π reported below was not an artifact of altered Pt–water contact angle.

The linear poly(phenylmethylsiloxane) (PPMS) was synthesized at the University of York and was methyl-terminated. The synthesis, fractionation, and characterization procedures have been reported.[8,9] Proton NMR shows the PPMS fractions to be stereochemically atactic.[10] Table I lists the number-average molecular weights M_n and the ratios M_w/M_n of weight-average to number-average molecular weight for the samples used in this study.

Results

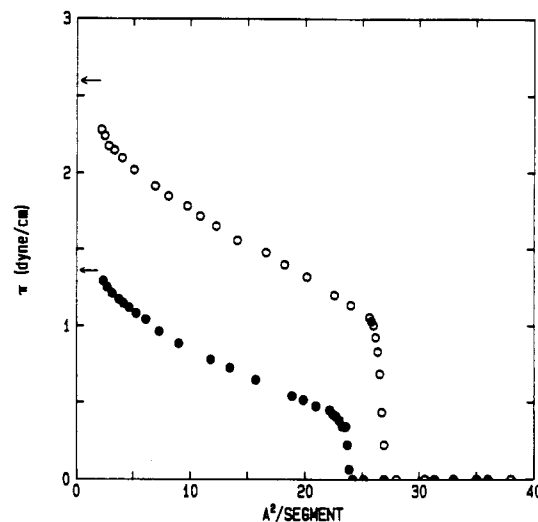Results at submonolayer coverage and just above are illustrated in Figure 1. Even the highest surfaces pressures

Figure 2. Surface pressure at 22.8 °C plotted against area per polymer segment. Points same as in Figure 1. Arrows indicate π_e measured separately.

are exceptionally low, approximately one-tenth those typical[2-5] of spread polymer films. For polymer B (M_n = 2240), no surface pressure was detectable for a considerable range of surface concentration, but then π jumped abruptly. For example, π = 0.00, 0.07, and 0.30 dyn/cm at c = 0.0936, 0.0948, and 0.0957 $\mu g/cm^2$, respectively, so that the step, though not strictly discontinuous, had a slope of about 150 on a log–log basis. The precise concentration at the step usually differed in separate experiments, ranging from 0.095 to 0.100 $\mu g/cm^2$; this is believed to reflect the difficulty of achieving complete spreading to the two-dimensional state. For polymer A (M_n = 1470) the step in π was also abrupt but occurred at the somewhat lesser concentration of 0.085–0.088 $\mu g/cm^2$. In addition, for this species of least molecular weight, π was demonstrably finite even at lesser c, where a surface pressure π = 0.02 ± 0.01 dyn/cm was barely measurable. At a concentration just below the step in π, this is 2 orders of magnitude less than the ideal gas prediction, π = cRT (≈1.4 dyn/cm).

Results for polymers A and B including regions of still higher coverage are shown in Figure 2. Surface coverage is represented now as specific area per segment, A (proportional to $1/c$). Past the step, surface pressure rises monotically, while the surface elasticity $-\partial\pi/\partial \ln (A)$ (not shown) diminishes monotonically. The curves extrapolate to π_e, the equilibrium film pressure measured independently when undiluted polymer was placed onto the surface in quantity sufficient to form a film thousands of angstroms thick. For small surfactant molecules, π_e reflects lenses or crystals in equilibrium with a monolayer.[1] That this was not the case here emerged when the films were visualized by sprinkling them with small inert particles of talc. Whenever undiluted polymers A and B (but not C or D) were added, no matter how much had been added previously, the talc was swept to the sides of the trough. Films of polymers A and B appeared to cover the entire surface with contact angle θ = 0; i.e., the films appear to have wet the water substrate.

The behavior of polymers C and D was decidedly different. In experiments where a large excess of undiluted polymers C and D was deposited onto water by pipette, no surface pressure could be detected, and these liquids of low viscosity visibly formed numerous lenses.

To test whether failure to observe spreading of polymers C and D might stem from lack of equilibration (long equilibration times have been reported for spreading of

poly(dimethylsiloxane) melt[11]), other attempts were made to deposit these polymers from spreading solution. Under this condition, spreading is known to occur on the scale of minutes. Even poly(dimethylsiloxane) of molecular weight as high as 9×10^6 spreads rapidly from solution.[2] No surface pressure was detected. Unfortunately, from the present experiments one cannot determine whether polymers C and D failed completely to spread at the water–air interface or whether an equilibrium was established between lenses and a monomolecular film of exceedingly low ($\pi < 0.01$ dyn/cm) surface pressure.

Discussion

Submonolayer Coverages. To what should one attribute the step in π? This step occurred at 26.1 ± 0.5 Å^2/segment for polymer A and 23.2 ± 0.6 Å^2/segment for polymer B. These areas are consistent with estimates of the close-packed area per segment using molecular models. We note, however, as emphasized elsewhere,[12] that such estimates are inevitably uncertain quantitatively in view of the unknown extent to which the monolayers are strictly two-dimensional and the unknown compressibility of a two-dimensional layer. However, from scaling considerations, a rise in π occurs at the concentration of average overlap between two-dimensional (2D) chains.[4] As noted below, the density of these aggregated chains is expected to be that of chains in the 2D melt, a condition under which a step in π^4 is predicted. The two-dimensional version of the Flory–Huggins theory[13] will also predict, if the interaction parameter is so large as to result in two-dimensional phase separation, an abrupt rise in π at the close-packed area. Thus it is probable that the area at the step does correspond to close-packed coverage.

The different numerical areas at the step may be owing to molecular weight distribution in polymers A and B. Since it is known that polymers C and D failed to spread, to the extent that polymers A and B also certainly contained a minority of species of long chain length, reflecting molecular weight distribution, these also may have failed to spread. This would be a larger influence for polymer B than for polymer A because of the difference in average molecular weight.

The phase diagram at submonolayer coverage appears to be as follows for polymer A and B. Monolayers must be gaseous when sufficiently dilute.[1] A phase transition, from the gaseous state to an equilibrium between the gaseous and 2D aggregated state, occurs then at low coverage—unfortunately, with π too low to be measured. The phase equilibrium is manifested as constant π as the surface coverage is raised. At full monolayer coverage there exists a continuous 2D liquid film, whose low compressibility is manifested as the step in π. Thereafter the path is continuous to a film of macroscopic thickness. Owing to insolubility of these polymers in the water substrate, the films form multilayers in the air direction rather than dissolve into the water as does[12] water-soluble poly(ethylene oxide).

On the other hand, the fact that $\pi = 0$ (within experimental resolution) at all concentrations for the two species of higher molecular weight suggests that they did not adsorb to the water substrate. The picture thus emerges that in this system the polymer–polymer interactions are far stronger than the polymer–substrate interactions (leading to collapse of polymers C and D and aggregation of polymers A and B), yet the polymer–substrate interactions are barely sufficient, for polymers A and B, to induce wetting. These essential features describe the weak-substrate system, considered, for a lattice gas, by Pandit and co-workers.[6]

More Than Monolayer Coverage. We have shown in Figure 2 the smooth passage from submonolayer coverage to a film of effectively infinite thickness, as indicated by the smooth rise in the surface pressure. This is the signature of a film which "wets" the substrate.[6,7] Qualitatively, this behavior reflects adsorption of the spreading liquid to the interface, even when this means adsorption onto other molecules of the same kind. This contrasts with the behavior of more common surface-active molecules, such as long-chain alcohols and fatty acids (both liquid and crystalline[1]), for which layers beyond the monolayer do not form. In those systems, if the total mass on the surface is increased to a level too high to sustain a single monolayer, the system partitions so that there is coexistence between the monolayer and crystals or lenses. In those systems, the surface pressure does not rise even though mass is added to the surface.

As noted by Wortis,[14] it is peculiar that we fail to see a coexistence between monolayer and multilayer after the step. This would be reflected in a second zone of constant π. Such a plateau zone indeed characterizes poly(dimethylsiloxane),[2] and it is interesting to speculate why it is not found for PPMS. One interesting possibility[14] is that when the monolayer reaches a state of high pressure and surface coverage, there occurs a reorientation of the molecules to form a distinctly new phase upon which additional molecules can then grow continuously. If this transition is an *internal* order parameter of the film were second-order, there would be no requirement for coexistence of phases at constant π. The present thermodynamic experiments cannot, of course, provide direct evidence of such a steric transition.

We note, following Cohen-Stuart,[15] that the discrepancy between π_e and π in the multilayer region reflects the disjoining pressure[16] between the water and air interfaces, i.e. the interaction between these interfaces with confined PPMS in between. This aspect of the experiments is under continuing investigation, and no quantitative explanation is attempted at the present time.

The physical significance of π_e remains to be discussed. We recall that experimentally, the determination of π involves measuring the reduction of surface tension of water covered by the polymer film from that characteristic of the bare water–air interface. When a film of effectively infinite thickness covers the water, the inferred π_e is characteristic of a film with two well-defined independent interfaces, water–polymer and polymer–air. Let us define σ_{W-A}, σ_{W-P}, and σ_{P-A} to be interfacial tensions of the water–air, water–polymer, and polymer–air interfaces, respectively. Then from the method of measurement, it follows by definition that

$$\pi_e = \sigma_{W-A} - [\sigma_{W-P} + \sigma_{P-A}] \qquad (1)$$

The right-hand side of this equation is of course also an expression for the well-known spreading coefficient S.[1,7] $S > 0$ corresponds to complete wetting and $S < 0$ to partial wetting, i.e. lens formation. The equilibrium film pressure, from a film of effectively infinite thickness, is thus identified with the spreading coefficient. Equation 1 provides a method to determine the spreading coefficient without knowing all the quantities on the right-hand side of eq 1.

Evidently, π_e and therefore also S decreased with increasing molecular weight. This spreading transition, which might be studied in detail if it were possible to vary the molar mass with more finesse, would then represent a noncritical drying transition,[6,7] i.e. a transition from preferential wetting of water by polymeric liquid, to its preferential wetting by air. We conjecture that the observed decrease of π_e with increasing polymer molecular

weight could be a natural corollary of the theoretical expectation[17] that polymer interfacial tension, i.e. surface free energy, should increase with increasing chain length (owing to entropic constraints at the surface). Data do not appear to be available for σ_{W-P}, but this has long been known to occur for σ_{P-A}.[18]

In summary, a phase diagram not previously reported for amorphous polymers at submonolayer coverage has been described. A spreading transition was observed with increasing molecular weight.

References and Notes

(1) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*: Interscience: New York, 1966.
(2) Granick, S. *Macromolecules* 1985, *18*, 1597.
(3) Crisp, D. J. In *Surface Phenomena in Chemistry and Biology*; Danielli, J. F., Pankhurst, K. G. A., Riddiford, A. C., Eds.; Pergamon: New York, 1958.
(4) Vilanove, R.; Rondelez, R. *Phys. Rev. Lett* 1980, *45*, 1502.
(5) Takahashi, A.; Yoshida, A.; Kawaguchi, M. *Macromolecules* 1983, *15*, 1196.
(6) Pandit, R.; Schick, M.; Wortis, M. *Phys. Rev. B; Condens. Matter* 1982, *26*, 5112.
(7) de Gennes, P.-G. *Rev. Mod. Phys.* 1985, *57*, 827.
(8) Clarson, S. J.; Semlyen, J. A. *Polymer* 1986, *27*, 1633.
(9) Clarson, S. J.; Dodgson, K.; Semlyen, J. A. *Polymer* 1987, *28*, 189.
(10) Clarson, S. J.; Mark, J. G.; Clarson, S. J.; Dodgson, K.; Semlyen, J. A. *Polymer*, in press.
(11) Aussere, D.; Picard, A. M.; Léger, L. *Phys. Rev. Lett.* 1987, *57*, 2671.
(12) Kuzmenka, D. J.; Granick, S. *Macromolecules* 1988, *21*, 779.
(13) Ter-Minassian-Saraga, L.; Prigogine, I. *Mem. Serv. Chim. Etat (Paris)* 1953, *38*, 109.
(14) Wortis, M., private communication.
(15) Cohen-Stuart, M. A., private communication.
(16) Derjaguin, B. V.; Churaev, N. V.; Müller, V. M. *Surface Forces*; Consultants Bureau: New York, 1987.
(17) Theodorou, D. *Macromolecules* 1988, *21*, 1400.
(18) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982; Chapter 3.

Matrix Representation of the Dynamical Structure Factor of a Solution of Rodlike Polymers in the Isotropic Phase

Tadakazu Maeda

Mitsubishi Kasei Institute of Life Sciences, 11 Minami-ooya, Machida-shi, Tokyo 194, Japan. Received July 11, 1988; Revised Manuscript Received October 10, 1988

ABSTRACT: The dynamical structure factor of a solution of rodlike polymers, recently derived by Doi, Shimada, and Okano (*J. Chem. Phys.* 1988, *88*, 4070), was rewritten in matrix form, the evaluation of which is quite easy and straightforward. With this formulation, it is possible to compute the dynamic light scattering spectrum of rigid rod suspensions in the entire region of **k**, t, and ν, where **k** is the scattering vector, t the delay time, and ν the number concentration of the rods. Results of numerical computation show that the excluded-volume interaction affects only the spatially long and temporarily slow modes of fluctuation in the solution and suggest that it is necessary to generalize the osmotic virial coefficient A_2 as a function of kL, where L is the rod length. The present analysis raises the possibility of studying the concentration dependence of $D_{\parallel}$, $D_{\perp}$, and D_r individually, where $D_{\parallel}$ and $D_{\perp}$ are self-diffusion coefficients for the lengthways and sideways translation of a rod, respectively, and D_r is the rotational one.

1. Introduction

When we theoretically construct the dynamic light scattering (DLS) spectrum of rod suspensions at finite concentration, we have to take into account the translation–rotation coupling of rod diffusion and various types of rod–rod interactions: In general, the translational and rotational diffusive motions of a rod in solution are coupled with each other, because the friction constant parallel to the rod axis is smaller than that perpendicular to the axis. When the rod concentration increases, we can no longer neglect such types of rod–rod interactions as the excluded-volume interaction (the steric repulsion and van der Waals attraction between polymers), the entanglement effect (the topological constraint that filaments cannot pass through each other), and the hydrodynamic interaction.

Doi, Shimada, and Okano[1] (DSO) recently studied the dynamics of rodlike polymers in solution under the influence of other polymers, taking all the above four factors into account: They started from a kinetic equation for the average number density $f(\mathbf{r}, \mathbf{u}, t)$ of rods, where $\mathbf{r}$ is the position vector of the center of a rod and $\mathbf{u}$ the orientation unit vector of the long axis of the rod. The equation they adopted is the one that expresses the coupled diffusion of

the translation and rotation of a rod:

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \mathbf{r}}[D_{\parallel,0}\mathbf{u}\mathbf{u} + D_{\perp,0}(\mathbf{I} - \mathbf{u}\mathbf{u})]\left[\frac{\partial f}{\partial \mathbf{r}} + \frac{f}{k_B T}\frac{\partial h}{\partial \mathbf{r}}\right] + D_{r,0}\mathcal{R}\left[\mathcal{R}f + \frac{f}{k_B T}\mathcal{R}h\right] \quad (1)$$

where $D_{\parallel,0}$ and $D_{\perp,0}$ are the lengthways and sideways translational diffusion coefficients, respectively, h is the potential of an external field, $D_{r,0}$ is the rotational diffusion coefficient, and $\mathcal{R}$ the rotational operator. The subscript 0 of $D_{\perp,0}$, $D_{\perp,0}$, and $D_{r,0}$ denotes zero polymer concentration, and since eq 1 includes no interactions between rods, it holds only in the dilute regime.

Next, they took into account the excluded-volume effect, using the mean-field approximation. Let $W(\mathbf{r} - \mathbf{r}', \mathbf{u}, \mathbf{u}')$ be the interaction potential between two polymers in the configurations $(\mathbf{r}, \mathbf{u})$ and $(\mathbf{r}', \mathbf{u}')$. In the mean-field approximation, the molecular field for a polymer in the configuration $(\mathbf{r}, \mathbf{u})$ is written as

$$\bar{W}(\mathbf{r}, \mathbf{u}, t) = \int d\mathbf{r}' \int d\mathbf{u}'\, W(\mathbf{r} - \mathbf{r}', \mathbf{u}, \mathbf{u}')f(\mathbf{r}', \mathbf{u}', t) \quad (2)$$