traces of water becomes greater the lower the solubility of water in the solvent.[14]

Conclusion

From the results presented here it turns out that the real dry ternary solutions of the blend system PMA–PVAc investigated by Nandi et al. and the newly discovered miscible pair PEA–PVPr are homogeneous at all compositions in the solvents investigated, testifying to the compatibility of these blend systems. The inhomogeneity of some of the ternary solutions reported by Nandi et al. earlier was due to the presence of traces of water in the systems.

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Registry No. PMA, 9003-21-8; PVAc, 9003-20-7; PEA, 9003-32-1; PVPr, 25035-84-1; toluene, 108-88-3; chlorobenzene, 108-90-7; water, 7732-18-5.

References and Notes

(1) Zeman, L.; Patterson, D. *Macromolecules* **1972**, *5*, 513.
(2) Hsu, C. C.; Prausnitz, J. M. *Macromolecules* **1974**, *7*, 320.
(3) Robard, A.; Patterson, D.; Delmas, G. *Macromolecules* **1977**, *10*, 706.
(4) Koningsveld, R.; Kleintjens, L. A.; Schoffeleers, H. M. *Pure Appl. Chem.* **1974**, *39*, 1.
(5) Koningsveld, R.; Chermin, H. A. G.; Gordon, M. *Proc. R. Soc. London, Ser. A* **1970**, *319*, 331.
(6) Aharoni, S. M. *Macromolecules* **1978**, *11*, 277.
(7) Nandi, A. K.; Mandal, B. M.; Bhattacharyya, S. N. *Macromolecules* **1985**, *18*, 1454.
(8) Robard, A.; Patterson, D. *Macromolecules* **1977**, *10*, 1021.
(9) Djadoun, S.; Goldberg, R. N.; Morawetz, H. *Macromolecules* **1977**, *10*, 1015.
(10) Bhattacharyya, C.; Bhattacharyya, S. N.; Mandal, B. M. *J. Ind. Chem. Soc.* **1986**, *63*, 157.
(11) Bhattacharyya, C. Ph.D. Thesis, 1987, Jadavpur University, Calcutta.
(12) Weissberger, A.; Proskauer, E. S. "Technique of Organic Chemistry"; *Organic Solvents*; Interscience: New York, 1955.
(13) Su, C. S.; Patterson, D. *Macromolecules* **1977**, *10*, 708.
(14) The solubilities of chlorobenzene, toluene, and ethyl propionate in water reported in the literature are 0.0488 (30 °C), 0.057 (30 °C), and 1.7 (22 °C), respectively (Seidell, A. *Solubilities of Organic Compounds*, 3rd ed.; 1941; Vol. II). The same sequence of increasing solubility would follow for the reverse case, i.e., for the solubility of water in these solvents.

End-Confined Polymers: Corrections to the Newtonian Limit

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In recent papers Milner et al.[1,2] described a new method to determine the statistics of "end-confined" polymers, such as polymers densely grafted to a surface. The method augments the established approaches of Helfand and Wasserman[3,4] and of Scheutjens and Fleer.[5] These authors reduce the many-chain problem to that of a single chain in a space-dependent monomer chemical potential. This chemical potential must be determined self-consistently in terms of the local concentration of monomers. The statistical mechanics of such a polymer was shown by Edwards[6] to be equivalent to the quantum mechanics of a Schrödinger particle moving in a potential proportional to the monomer chemical potential. The Helfand–Wasserman and Scheutjens–Fleer treatments provide explicit procedures for solving this self-consistent quantum-mechanics problem. Our new method amounts to the observation that for large molecular weight the quantum mechanics reduces to classical Newtonian mechanics. The new method then solves the Newtonian problem without further reference to the underlying quantum mechanics.

The new approach leaves some important formal issues unsettled. Since the connection to Newtonian mechanics is made at the most general level, it is not clear how the Newtonian solution of ref 1 emerges explicitly from the quantum-mechanical description. In particular, our Newtonian description treats the probability density of the free chain end as a quantity to be determined self-consistently, in addition to the chemical potential profile. This end density may vary *independently* of the potential. Thus for chains of given molecular weight and coverage, the potential profile is a fixed parabola, but the required end density is different for a melt, for an Edwards solvent,[7] and for a Flory–Huggins equation of state. This contrasts with the quantum description, where only the potential is to be determined; the free-end probability density is fixed in terms of this potential. The two pictures appear mutually contradictory; one implies that there are two independent functions to be determined; the other states that there is only one.

The purpose of the present paper is to resolve this apparent contradiction. We show that the end density profile in the Newtonian limit is indeed determined by the potential. But variation in this potential required to shape the end density profile becomes indefinitely small relative to the potential as calculated in ref 1. The required perturbing potential may be expressed as a simple integral transform of the logarithm of the end density.

An end-confined polymer of N statistical segments with one end attached at the position $z = 0$ may be described by its Edwards propagator $G(n;z,z')$. This G is the partition function for a section of n segments beginning at height z and ending at height z', relative to the overall partition function of a free random walk of n segments. The propagator G for an end-confined chain is nontrivial because the chain interacts with the other chains. Each monomer of the chain in question displaces other chains; the free energy cost to place a monomer at z amounts to a position-dependent monomer chemical potential, which we denote $V(z)$ (in units of kT).

The Edwards propagator of a chain in the potential $V(z)$ obeys the heat or Schrödinger equation:

$$\partial G/\partial n = \nabla_z^2 G + V(z)G$$

Thus G behaves much like the wave function of a quantum particle in the potential $-V$. From this G one may calculate the local monomer concentration $\phi(z)$ and finally impose the requirement of consistency between the local monomer chemical potential $V(z)$ and the local concentration $\phi(z)$; e.g., $V(z) = \sigma w \phi(z)$, where σ is the number of chains per unit area and w measures the strength of the interaction.

Once a self-consistent $V(z)$ has been found, the free energy of the chain passing from the attachment point to some z_0 is simply $[\log G(N; 0, z_0)]$. For large N and fixed coverage σ we found[1] that the "quantum" propagator G attains the limiting behavior describing classical Newtonian motion. Then the free energy of a chain becomes the action $S(z_0)$ of a Newtonian particle of unit mass starting from rest at z_0 in the potential $-V(z)$ and ending at $z = 0$. We found that $V(z)$ must be parabolic with a curvature independent of σ in this limit. For this parabolic potential, the action S is independent of z_0 and is of order N. But viewed in another way, $S(z_0)$ cannot be completely independent of z_0, since the free energy of a chain at z_0 controls the probability $\epsilon(z_0)$ that a chain ends there:

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$$\epsilon(z_0) = (\text{constant}) \exp[-S(z_0)]$$

As noted above, this end density must vary with z_0 in a specified way in order to achieve self-consistency.

The variation required in $S(z_0)$ is relatively small. Since the end density ϵ varies only by factors of order unity over almost all of the profile, $S(z_0)$ must have a z_0-dependent term of order unity added to any part independent of z_0. This independent part is of order N and is hence much larger. We may thus suppose that the weak z_0 dependence in $S(z_0)$ arises from a weak perturbation in the potential $V(z)$. Accordingly, we write $V(z)$ as the parabola of ref 1 plus a small perturbation $v(z)$:

$$V(z) = A - Bz^2 + v(z)$$

Since $v(z)$ is small, it can make only a small change in the Newtonian trajectory representing a polymer. To lowest order, the effect of $v(z)$ on the action $S(z_0)$ can be found[8] by using the unperturbed trajectory:

$$S(z_0) \equiv \int \mathrm{d}n\, [1/2(\mathrm{d}z/\mathrm{d}n)^2 + V(z(n))] = S_0 + \int \mathrm{d}n\, v(z(n)) \quad (1)$$

where $z(n) = z_0 \cos (\pi n/(2N))$.

To find the $v(z)$ which reproduces the $S(z_0)$ for a desired end density we must invert this integral equation. This inversion may be simplified by labeling a position z by its energy U relative to the grafting surface: $U \equiv Bz^2$, where[1] $B = \pi^2/(8N^2)$. Then eq 1 takes the form

$$S(U) = S_0 + \frac{1}{\pi}\int_0^U \frac{\mathrm{d}U'}{(U - U')^{1/2}}\left[\frac{Nv(U')}{U'^{1/2}}\right] \quad (2)$$

We denote the quantity in [ ] as $w(U)$. This integral transform has the simplifying property of homogeneity: it transforms a power $w(U) = U^p$ into another power: $(S(U) - S_0) \sim U^{p+1/2}$. It is also invariant under shifts in U, in a certain sense. Thus a shifted power law also transforms into another shifted power law: $w(U) = (U - U_0)^p\Theta(U - U_0)$ transforms into $(S(U) - S_0) \sim (U - U_0)^{p+1/2}\Theta(U - U_0)$. Here $\Theta(x)$ is the unit step function: 1 for positive x; 0 for negative x. Evidently the transform applied *twice* to this $w(U)$ gives (constant)$(U - U_0)^{p+1}\Theta(U - U_0)$; i.e., it is the indefinite integral of the function, up to a multiplicative constant independent of U_0. Since this is true for arbitrary U_0, i.e., for a complete set of functions, it is true in general: the transform applied twice to an arbitrary function is merely the indefinite integral times a constant. Or differentiating a function and then applying the transform twice give back the original function (times a constant). Or the inverse of the transform is the transform of the derivative. In terms of $S(U)$ and $w(U)$

$$\frac{Nv(U)}{U^{1/2}} \equiv w(U) = \int_0^U \frac{\mathrm{d}U'}{(U - U')^{1/2}} \frac{\mathrm{d}}{\mathrm{d}U'}[S(U') - S_0] \quad (3)$$

From this equation the $v(r)$ needed to reproduce any particular end density $\epsilon(z_0)$, and its corresponding $S(U)$, can readily be found. Of particular interest are the melt[9] and the "moderate density" regime in which the chemical potential is proportional to the concentration. For these cases the end density $\epsilon(z)$ is given by[2]

$$\begin{aligned}\epsilon(z(U)) &= (\text{constant})U^{1/2}(A - U)^{-1/2}, && \text{melt}\\ &= (\text{constant})U^{1/2}(A - U)^{1/2}, && \text{moderate density}\end{aligned} \quad (4)$$

where A is the energy U at the maximal height $z = h$. Thus

$$S(U) = \tfrac{1}{2}[\ln (U) \mp \ln (A - U)]$$

Inserting this in eq 3, we find

$$Nv(z) = -\left[\ln z \pm \left(\frac{z}{h - z}\right)^{1/2} \arctan \left(\frac{z}{h - z}\right)^{1/2}\right] + (\text{constant}) \quad (5)$$

As anticipated, $v(z)$ diverges at $z = 0$ and $z = h$, where $v(z)$ is obliged to force the end density to zero or infinity. From eq 2 we see that $w(U)$ must diverge as $U^{-1/2}$ and as $(A - U)^{-1/2}$ to produce the required logarithmic divergence in $S(U)$. This implies a logarithmic divergence in v at $z = 0$ and an $(h - z)^{-1/2}$ divergence at the maximal height h. The corrections to the classical potential are thus strongest at the tip of the brush.

This discussion shows as claimed that the end density need not be explicitly specified in order to solve our end-confined polymer problem. Instead, it is sufficient to specify the effective potential $V(z)$. But for polymers well described by our Newtonian limit, there are drawbacks in specifying only the potential. If one does choose to specify only the potential, one must take account of two contributions to it which have different orders of magnitude. This would lead to stability problems in numerical procedures which specify only the potential.

One may ask whether the perturbing potential $v(r)$ above constitutes the *complete* leading correction to the parabolic potential of ref 1. Another "quantum correction" also alters the simple Newtonian picture. The free energy of a chain ending at z in the parabola is no longer exactly the Newtonian action S_0 but has a correction due to entropic fluctuations about the lowest energy path. Remarkably,[8,10] this correction is independent of position z. We know of no other source of perturbation of the parabolic potential. Thus the $v(z)$ calculated here is the complete correction to the parabola, up to an additive constant independent of position. As we have seen, this correction diverges badly at the tip of the brush, so that fluctuations cannot be treated as a perturbation in the tip region.

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References and Notes

(1) Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* **1988**, *5*, 413.

(2) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610. Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules*, in press.

(3) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1978**, *5*, 960.

(4) Noolandi, J.; Hong, K. M. *Macromolecules* **1982**, *15*, 482.

(5) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.

(6) Edwards, S. F. *Proc. Phys. Soc.* (*London*) **1965**, *85*, 613; **1966**, *88*, 265. de Gennes, P.-G. *Rep. Prog. Phys.* **1969**, *32*, 187.

(7) By an Edwards solvent we mean one with sufficiently weak excluded volume and sufficiently high concentration that the mean-field approximation is justifiable.

(8) Feynmann, R. P.; Hibbs, A. R. *Quantum Mechanics and Path Integrals*, McGraw-Hill: New York, 1965.

(9) Semenov, A. N. *Sov. Phys.—JETP* (*Engl. Transl.*) **1985**, *61*, 733 [*Zh. Eksp. Teor. Fiz.* **1985**, *88*, 1242].

(10) Merzbacher, E. *Quantum Mechanics*, 2nd ed. Wiley: New York, 1970. The partition function of the chain passing from 0 to z is the time-dependent propagator of eq 8.96 in this reference, evaluated at spatial coordinates $x = 0$ and $x' = z$ and at an imaginary time of magnitude $\pi/(2\omega)$. One readily checks that at this time the width of the wavefunction diverges, and the partition function thus becomes independent of position.