Simple cubic structure in copolymer mesophases

C. Marquest (*) and T. A. Witten

Exxon Research and Engineering Co. Annandale NJ 08801, USA

Résumé. — Les théories classiques de l'organisation micellaire prédisent des réseaux cubiques centrés. Néanmoins des structures cubiques-simples ont été observées dans quelques systèmes de micelles copolymériques. Nous montrons que, quand le potentiel d'interaction entre les micelles est suffisament proche d'un potentiel répulsif en forme de puits carré la structure cubique-simple est la plus stable dans une certaine plage de concentration. Des potentiels d'interaction ayant cette forme peuvent décrire de manière qualitative les micelles dans un solvant. Dans le cas idéal où les bras d'une micelle interagisent seulement avec les cœurs de petite taille des micelles voisines, l'énergie d'interaction du système est bien décrite par un potentiel à deux corps s'exprimant par un potentiel Coulombien écranté par une fonction « erreur-complémentaire ». Mais dans ce cas la structure cubique-simple n'est pas la plus stable.

Abstract. — Classic theories of micellar organization predict body-centered cubic crystal lattices. However simple cubic structures have been reported in some copolymer micellar systems. We show that when the micelle interaction potential is sufficiently close to a repulsive square-well potential, the simple-cubic structure is preferred in a certain range of concentrations. Interaction potentials of this qualitative form are expected for micelles in a solvent. For the idealized case of small-core micelles with noninteracting tails, we show that the interaction energy is well described by a two-body micelle-micelle potential in the form of a Coulomb potential times a complementary error function. But simple-cubic is not the preferred structure in this case.

Introduction.

Diblock copolymers formed from incompatible blocks undergo partial phase separation, in which domains of each block form spatially periodic structures [1]. When one block occupies a small fraction of the total volume, this block resides in small spherical domains or cores. The majority blocks form a corona around each core. The spheres in this phase are observed to form a body-centered cubic lattice. Several arguments for this structure have been proposed in the literature. These arguments require that the underlying phase separation be weak [2, 3, 4], or that the majority chains extend over many periods of the lattice [5]. Neither of these limits describes the observed systems very well ; thus the problem of understanding the lattice structure is still open.

(*) Permanent address : E.N.S.L., 46, allée d'Italie, 69364 Lyon Cedex, France.

Recently two groups have reported *simple* cubic structure in copolymers with added homopolymer [6] or solvent [7] compatible with the coronas. Further dilution of the copolymers leads to loss of crystalline order. Increasing the concentration of copolymer restores the body-centered cubic structure of the neat phase. Apparently the concentration of cores plays a strong role in selecting the structure. The reason for crystalline order has been explained [8, 9], but the reason for the particular crystal structure has not.

Simple cubic order is uncommon in nature. Among the chemical elements only polonium forms this structure. Simple cubic order is more common in compounds with two or more atomic constituents. Thus a diatomic picture is one approach to explaining the simple-cubic structure in copolymers. One might suppose that the added component — homopolymer or solvent — segregates in the complementary space to that of the lattice sites so as to relieve the distortion of the corona chains. In a simple-cubic phase these segregated « droplets » would be farther from the cores than in a face-centered or body-centered cubic structure with the same core concentration [10]. But we are far from being able to justify such a structure theoretically.

In this note we investigate a simpler mechanism for simple-cubic ordering of micelles. We first mention some cases in which micelles interact *via* a potential which rises weakly at short distances and falls steeply beyond a certain distance. In one of these cases the interaction potential may be derived explicitly. This is an idealized model in which the coronas may be treated as ideal random walks which must avoid the micellar cores. We show that the interaction of many such micelles is well described by the sum of pairwise potentials.

Potentials of the same qualitative form as these can give rise to simple-cubic ordering in a certain window of core concentrations, as we show here. But the explicit potential derived for our ideal-chain micelles does not admit a simple-cubic phase.

Interaction between two polymeric micelles

Micelles in which the copolymers are of very different length can be viewed as many-armed star polymers. The shorter block becomes merely a point of attachment of the corona chains or tails. (The same is true of long polymers grafted to a colloidal particle core.) The statistics of these starlike polymers was worked out by Benoit [11] for ideal chains without excluded volume. The scaling properties of stars in a good solvent were worked out by Daoud and Cotton [12, 13]. In the Daoud-Cotton picture, the tails of the micelle radiate outward through regions of progressively lower concentration. The concentration at a given radius r is governed partly by osmotic pressure tending to reduce the tail concentration and thus stretch out the tails. In order for the osmotic energy and the chain-stretch energy to be in balance the concentration must fall off as $r^{1/\nu - 3}$, for a wide range of distances r. Here ν is the Flory swelling exponent. This law breaks down at the outer boundary of the star, where the finite length of the tails becomes important. It also breaks down at short distances. In this inner « core region » the concentrations become higher than the semidilute regime. This Daoud-Cotton description is applicable to a θ solvent, provided one uses $\nu = 1/2$. Even in theta conditions there is strong osmotic pressure within the star [12, 14], and the chains are much different than the ideal chains of the Benoit picture.

The interaction energy of two such micelles was discussed recently by Witten and Pincus [15]. They found that the effective interaction potential diverges logarithmically for small separations (beyond the core radius) and drops off steeply beyond the radius R of the star. There is a large range of separations r within this dropoff radius where the interaction energy is moderate. This behavior contrasts with that seen for interatomic potentials. These have a hard repulsive core regions which prohibites approaches much closer than the range R of the potential. There is no wide region of gradually decreasing potential as with the micelles.

The strength of the micelle-micelle interaction may be [15] many times the thermal energy kT if the number of tails is large. We show below that such potentials can favor simple-cubic crystalline order.

In one idealized situation we may find the form of the micelle-micelle interaction explicitly. This is the Benoit model of f ideal random chains attached to a central core of radius b. Two micelles of this type must experience a mutual repulsion, because the tails of each micelle must avoid the core of the other.

To estimate the free-energy cost of this avoidance, we consider an N-step random walk from the origin of a simple cubic lattice which is excluded from a small spherical region of radius b, centered at distance R. The probability $\psi(r, N)$ that the walk survives N steps and that the N-th step is at r obeys

$$\frac{\partial \psi}{\partial N} - \frac{a^2}{6} \nabla^2 \psi = - \delta(r) \delta(N) \tag{1}$$

with the boundary condition $\psi = 0$ on the sphere and at infinity. Here a is the lattice spacing. Because of the absorbing boundary condition on the sphere, the spatial integral of ψ decreases with time. The survival probability $\int d^3 r \, \psi(r, N)$ is the fraction of all walks which obey the constraint of avoiding the sphere. This survival probability is evidently the partition function $Z(r)$ for one of the micelle tails relative to the free partition function $Z(\infty)$. For $b \ll R$, ψ may be expressed simply in terms of the solution ψ_0 of the free diffusion equation :

$$\psi(r, N) = \psi_0(r, N) - \psi_0(r, N) \frac{\psi_0(\mathbf{r} - \mathbf{R}, N)}{\psi_0(b, N)}$$

where

$$\psi_0(r, N) = \left(\frac{3}{2 \pi N a^2} \right)^{3/2} \exp\left(-\frac{3}{2} \frac{r^2}{N a^2} \right) .$$

It is clear by inspection that this ψ vanishes as required on the absorbing sphere. One may also verify that it solves (Eq. (1)) by substitution. Using this ψ, we find

$$\frac{Z(r)}{Z(\infty)} = \int \psi(r', N) \, d^3 r' = 1 - \frac{b}{r} \operatorname{erfc}\left(\left(\frac{3}{2} \right)^{1/2} \frac{r}{r_0} \right)$$

with $r_0 = aN^{1/2}$. The erfc is the complementary error function [16]. Since $b \ll r$, $Z(r)$ is reduced only slightly by the constraint of avoiding the sphere, regardless of the chainlength N.

If f chains emanate from the origin, the partition function of each is reduced by the same factor $\frac{Z(r)}{Z(\infty)}$. The reduction in the total Z gives rise to a potential of mean force $U(r)$:

$$U(r) = kT \log \left(\frac{Z(r)}{Z(\infty)} \right)^f \approx kTf \frac{b}{r} \operatorname{erfc}\left(\left(\frac{3}{2} \right)^{1/2} \frac{r}{r_0} \right) . \tag{2}$$

This pair potential is perturbed but little by the presence of other micelles. To estimate this perturbation, we interpose a third micelle midway between the two micelles treated above. Chains from the left hand micelle must avoid both of the others. Chains which avoid the middle micelle are automatically depleted slightly (by a factor $1 - O\left(\frac{b}{r} \right)$) near the right hand micelle. Thus the constraint of avoiding the right hand micelle is slightly easier to satisfy because the middle one is present. But if $b \ll r$, this co-operative interaction may be neglected.

These ideal, interpenetrating micelles may evidently be regarded as point particles interacting by the pairwise potential $U(r)$. The energy per pair can be substantially greater than kT, since the arm number f is large. Thus it is natural for the micelles to adopt that lattice structure which minimizes the total interaction energy. We now investigate lattices which are favored by $U(r)$ above, and by related potentials.

The favored structure is easy to infer for large or for small polymer concentration ϕ. If the average micelle separation $d \equiv \phi^{1/3}$ is much greater than the radius r_0, the nearest-neighbor interaction becomes very small and crystalline order is lost. In the opposite limit only the b/r prefactor in $U(r)$ is important, and $U(r)$ is essentially a Coulomb interaction. Since Coulomb crystals are body-centered cubic (BCC) [17], our ideal micellar crystal must be also in this limit. Coulomb crystals with the $\frac{1}{r}$ potential modified by the screening factor $\exp(-\kappa r)$ have also been well studied [17]. Sufficiently strong screening (large κ) changes the favored structure from BCC to a close-packed face-centered cubic (FCC). Simple cubic (SC) structure is never favored by such screened potentials.

The $U(r)$ of (Eq. (2)) is reminiscent of a screened Coulomb potential, except that $U(r)$ falls off much faster at large distances. It falls off like a Gaussian rather than like a
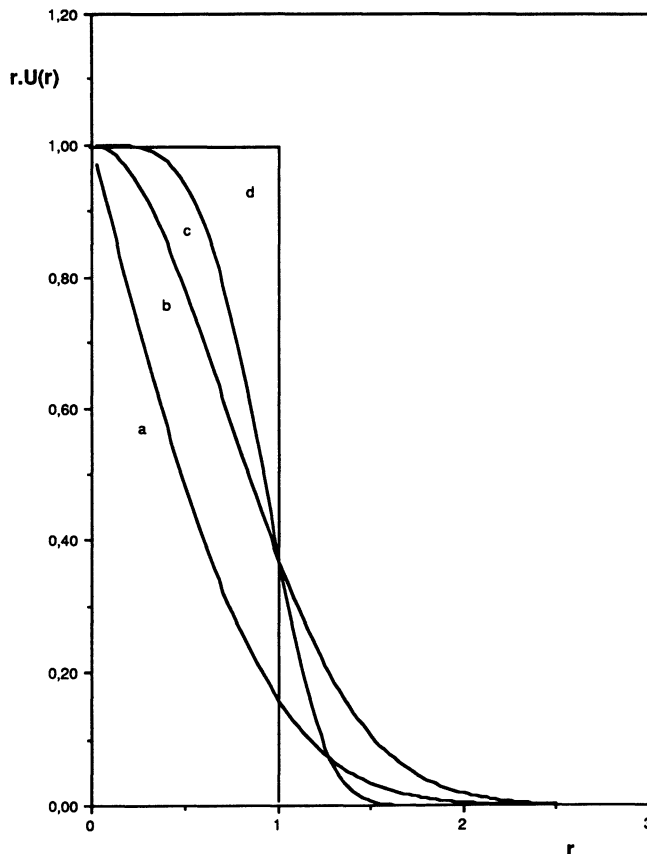

Fig. 1. — The four types of cutoff function compared in this study. a) the Error function of (Eq. (2)) ; b) the Gaussian potential, c) the « hard Gaussian » $\exp(-r^4)$; d) the square well. The full pairwise interaction is obtained by multiplying these cutoff functions by $\frac{b}{r}$.

simple exponential. A sufficiently rapid falloff can lead to a simple-cubic structure. To illustrate this, we consider a « square-well » potential U, which is 1 for $r < r_0$ and zero beyond. Thus the site at the origin has an interaction energy equal to the number of sites within r_0. If r_0 is larger than the nearest-neighbor distance for FCC (hence also for BCC and SC), but smaller than the second-neighbor distance for SC, then SC, with 6 nearest neighbors is favored over BCC with 8 and over FCC with 12. The favored structure is that with the lowest total interaction energy at fixed concentration ϕ. Figure 2 compares the total energies for the three cubic structures. Simple-cubic is favored over a factor $2^{1/2}$ range of ϕ.
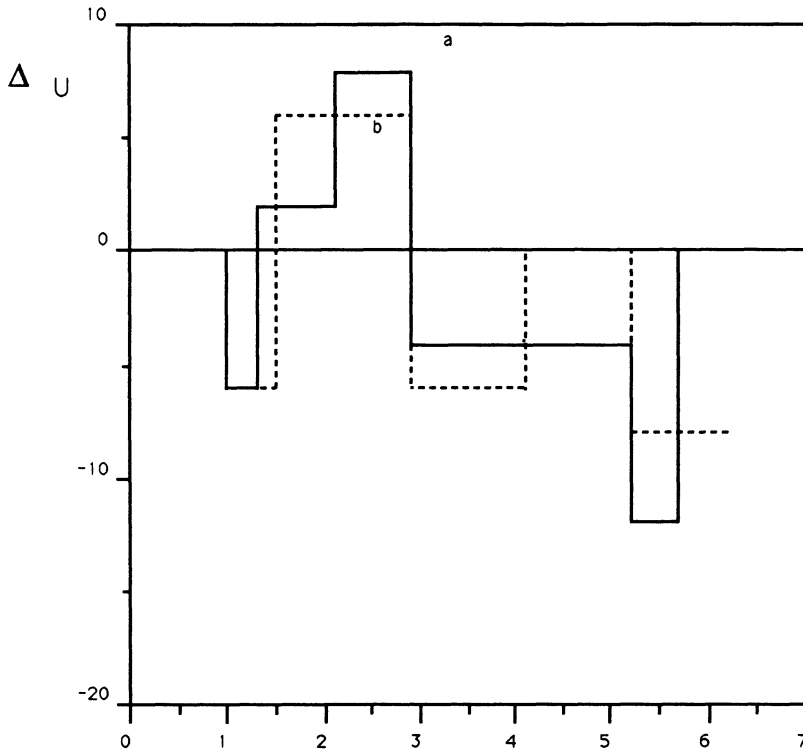

Fig. 2. — Total interaction energy per lattice site using a square-well interaction between sites. The factor $\frac{b}{r}$ is not included ; it only changes the slope of the plateaus. Abcissa is micelle concentration ϕ relative to $\phi_c \equiv r_0^{-3}$. Solid curve : BCC energy minus SC energy. Dashed curve : FCC energy minus SC energy. The SC structure is most stable in regions where both curves are positive.

We investigated the stability of the simple-cubic structure numerically for a variety of potentials $U(r)$. The potentials are shown in figure 1. To obtain the total energy per lattice point we summed the potential $U(r_i)$ for all lattice points r_i within a large boundary sphere. This was done for the three cubic lattices at the same concentration ϕ of lattice points. The boundary sphere was taken large enough to assume that the (small) differences in total energy for the three lattices was constant to 1 % accuracy [18].

The simple cubic region seen with a square-well potential survives well when the sharp cutoff is softened and a $\frac{b}{r}$ factor is included. To show this we investigated the « hard

Gaussian » potential $U(r) = \dfrac{b}{r} \exp(-r^4)$. As figure 3 shows, this potential, like the square well, gives rise to a simple-cubic structure for a thirty-percent « window » of concentration. We expect the derived potential of (Eq. (2)) to favor SC less strongly than these model potentials. This $U(r)$ is cut off less sharply than the hard Gaussian at long distance, and it
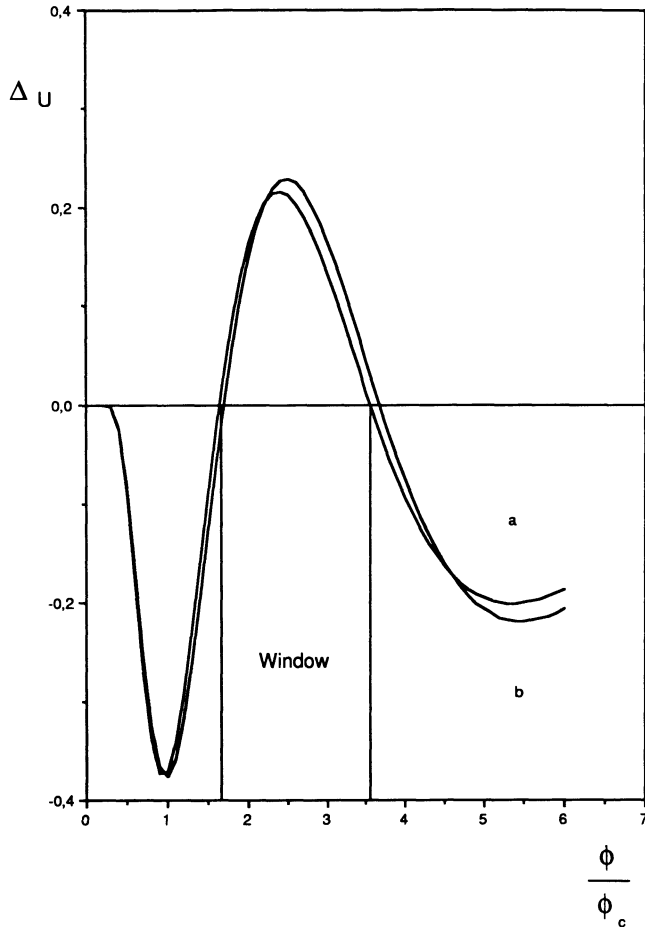

Fig. 3. — Comparison of lattice energy per site for the « hard Gaussian » potential described in the text. Energies are in units for $\dfrac{b}{r_0}$. Curve a) : BCC energy minus SC energy. Curve b) : FCC energy minus SC energy.

decreases faster at short distance. In fact the window of stability for the SC structure completely disappears, as figure 4 shows. Figure 5 shows the results for the Coulomb potential with Gaussian cutoff : $U(r) = \dfrac{b}{r} \exp(-r^2)$. The only vestige of the stability window is a small shoulder in the interaction energy, and there is no stable region.

To settle the question of the most stable structure for our micellar potential of (Eq. (2)), we compared the very small difference between FCC and BCC energies, as shown in figure 6. As
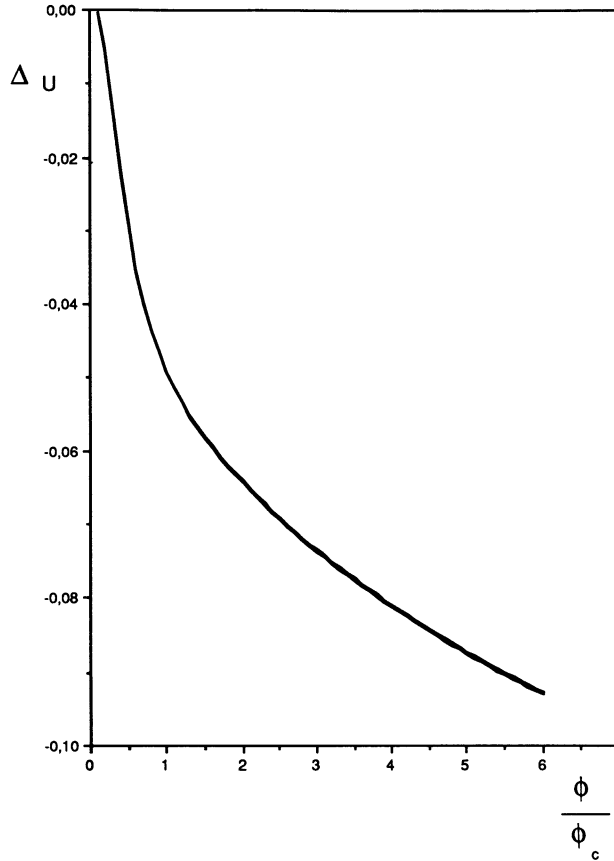
Fig. 4. — Comparison of lattice energy per site using the potential $U(r)$ of (Eq. (2)). BCC and FCC energies are indistinguishable on this plot. Absence of positive values indicates that SC is less stable than BCC or FCC for all concentrations ϕ.

with the screened Coulomb potential, FCC gives way to BCC as the intermicelle distance decreases to less than the range of the potential r_0.

Even when the SC structure is more stable than FCC or BCC, the SC structure may be unstable against a small shear deformation. To investigate this shear stability, we have calculated the three elastic constants C_{11}, C_{12}, and C_{44} of the cubic system. Since our potential is strictly repulsive, we need to have a pressure p to maintain the assumed density. In this case the classic stability conditions [19] on $C_{11} = C_{xxxx}$, $C_{12} = C_{xxyy}$ and $C_{44} = C_{xyxy}$

$$C_{11} > 0 \; ; \; C_{44} > 0 \; ; \; C_{11} - C_{12} > 0 \; ; \; C_{11} + 2 \, C_{12} + p > 0 \tag{3}$$

where

$$C_{\alpha\beta\gamma\delta} = \frac{1}{2 \, r_0^3} \sum_{i \neq j} \frac{r_\alpha^{ij} \, r_\beta^{ij} \, r_\gamma^{ij} \, r_\delta^{ij}}{r^{ij^4}} \left(- r^{ij} \, U'(r^{ij}) + r^{ij^2} \, U''(r^{ij}) \right) \tag{4}$$

should be written over the Birch-Brillouin coefficients $B_{\alpha\beta\gamma\delta} = C_{\alpha\beta\gamma\delta} + p(\delta_{\alpha\beta} \, \delta_{\mu\delta} - \delta_{\alpha\mu} \, \delta_{\beta\delta} - \delta_{\alpha\delta} \, \delta_{\beta\mu})$. Figure 7 shows the concentration region where the
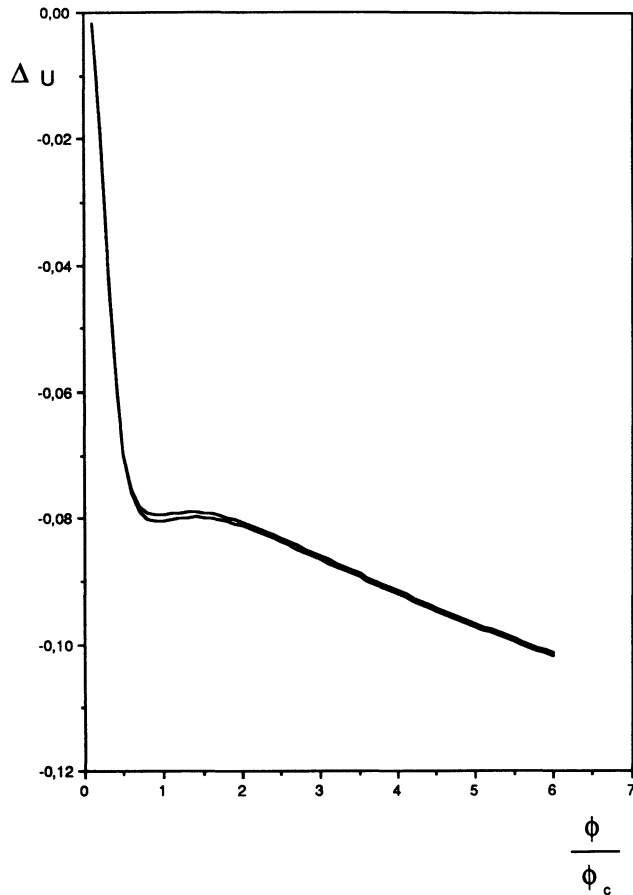
Fig. 5. — Comparison of lattice energy per site using the Coulomb potential with Gaussian cutoff described in the text. Solid curve : BCC energy minus SC energy. Dashed curve : FCC energy minus SC energy.

conditions hold for two different « hardnesses » of the potential. This calculations include up to the third neighbours which, for hard enough potentials and for the relevant range of concentration should be enough. We see that the « hard Gaussian » potential which favored simple cubic order over FCC or BCC order (Fig. 3) still shows instability to shear. But for hard enough potentials $(b/r \exp(-r^9))$ the simple cubic is also stable to shear.

Discussion.

We saw that the only micelle-micelle interaction we could treat explicitly did not result in a simple cubic structure. But we also saw that this structure can be preferred for a broad class of potentials resembling those predicted for polymeric micelles. Favorable potentials are those which increase only weakly at short distances and which fall off steeply beyond some distance. As discussed above, micelles in a solvent are expected to interact in this way. The question whether these micelles should form a simple cubic phase must await more detailed theories. Since the interaction in a solvent arises from the mutual repulsion of the tails, it is distinctly
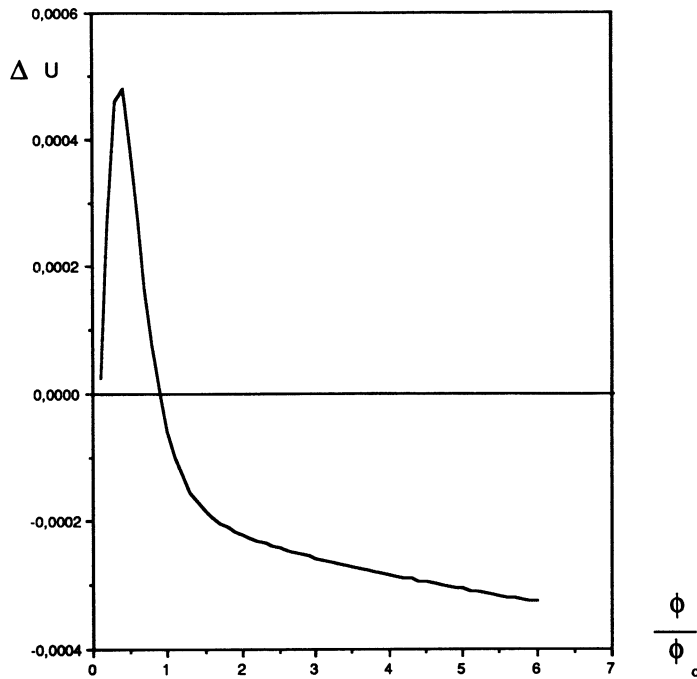
Fig. 6. — Difference in lattice energy between BCC and FCC structure using the potential $U(r)$ of (Eq. (2)). BCC is more stable for negative values.
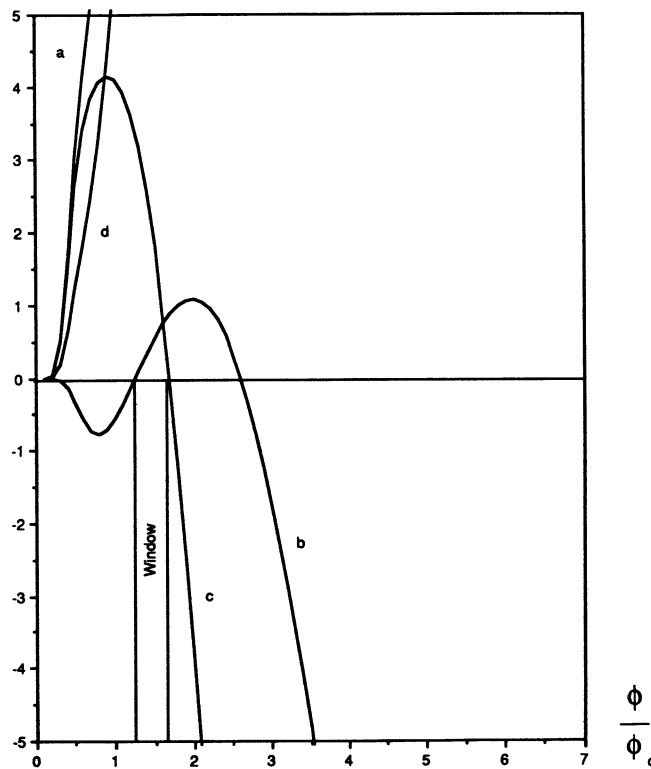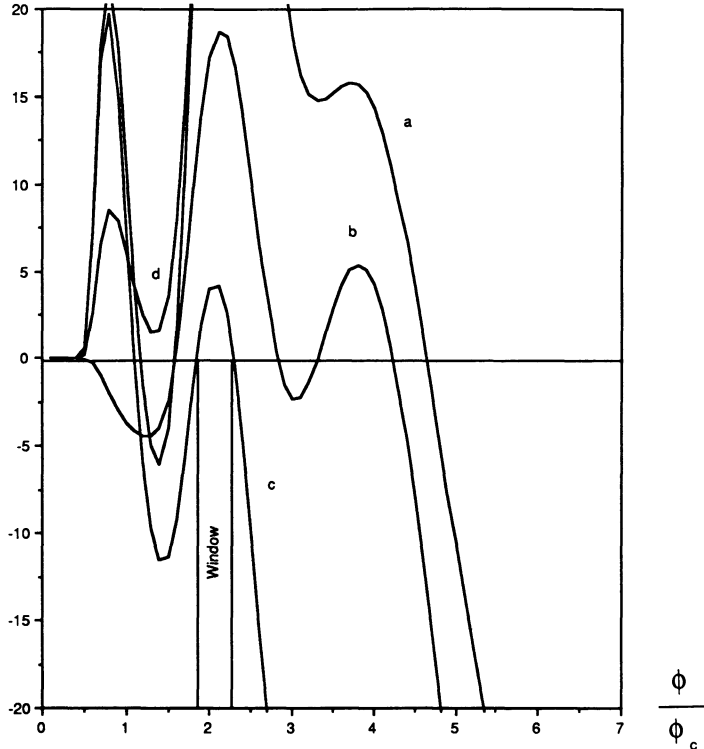
Fig. 7 I.

Fig. 7 II.

Fig. 7. — Stability curves for two different potentials : I. « hard Gaussian » ; II. $U(r) = \dfrac{b}{r} \exp(-r^9)$.

Elastic constants are in $\left(\dfrac{b}{r_0}\right)^3$ units. Stability conditions are : a) $C_{11} > 0$; b) $C_{44} - \dfrac{P}{2} > 0$; c)

$C_{11} - C_{12} - P > 0$; d) $\dfrac{(C_{11} + 2\,C_{12} + 2\,P)}{3} > 0$, where P is the pressure.

different from that of our ideal chains. Unlike our ideal chains, the interaction among many micelles may not be expressible as a sum of pairwise potentials.

A regime we have not discussed is the melt regime, where the copolymers are alone or are mixed with homopolymer. Here the corona tails obey ideal-chain statistics, as in the Benoit [11] picture, beyond a small central stretched region. These ideal tails must avoid the micelle cores. Still, the interaction between such micelles is not describes by (Eq. (2)) above. The strong screening effects in this melt environment [20] insure that each tail is practically unaffected by a neighboring excluded region except immediately next to that region. This is unlike the case we treated, where each core has a depletion region of radius roughly b from which chains of other micelles are excluded. We hope to analyze this melt regime in a future publication.

References

[1] For reviews, see GALLOT B. R. M., *Adv. Polym. Sci.,* **29** (1978) 85 ; GOODMAN I., Ed., *Developments in Block Copolymers I,* Applied Science Publishers, New York (1982).

[2] LEIBLER L., *Macromolecules* **13** (1980) 1602.

[3] ALEXANDER S., McTAGUE J., *Phys. Rev. Lett.* **41** (1978) 702.

[4] HIGGINS J. S., BLAKE S., TOMLINS P. E., ROSS-MURPHY S. B., STAPLES E., PENFOLD J. and DAWKINS J. V., Preprint.

[5] SEMENOV A. N., *Sov. Phys. JETP.* **61** (1985) 733.

[6] KINNING D. J., THOMAS E. L., FETTERS L. J., submitted to *J. Chem. Phys.* August 1988.

[7] SHIBAYAMA M., HASHIMOTO T., KAWAI H., *Macromolecules* **16** (1983) 16.

[8] LEIBLER L., PINCUS P. A., *Macromolecules,* **17** (1984) 2922.

[9] LEIBLER L., ORLAND H., WHEELER J. C., *J. Chem. Phys.* **79** (1983) 3550.

[10] Droplets in S.C. phase will be $(3/5)^{1/2} 2^{2/3} = 1.22$ times farther than in B.C.C. and $3^{1/2} 2^{-2/3} = 1.09$ than in F.C.C.

[11] BENOIT H., *J. Polym. Sci.* **II** (1953) 507 ; KOBLOVSKII Y. Y., *Polymer Sci. USSR* **3** (1962) 326.

[12] DAOUD M., COTTON J. P., *J. Phys. France* **43** (1982) 531.

[13] BIRSHTEIN T. M., ZHULINA E. B., *Polymer* **25** (1984) 1453 ;
BIRSHTEIN T. M., ZHULINA E. B., BORISOV O. V., *Polymer* **27** (1986) 1078.

[14] DAOUD M., JANNINK G., *J. de Phys. France* **37** (1976) 973.

[15] WITTEN T. A., PINCUS P. A., *Macromolecules,* **19** (1986) 2509 ;
WITTEN T. A., PINCUS P. A., CATES M. E., *Europhysics Letters* **2** (1986) 137.

[16] ABRAMOWITZ M. and STEGUN I. A., *Handbook of Mathematical Functions* National Bureau of Standards, Washington DC (1964).

[17] FOLDY L. L., *Phys. Rev. B* **3** (1971) 3472 ; erratum **4** (1971) 2833.

[18] It also has been checked that, energy values obtained by replacing $U(r)$ by a Yukawa potential agree up to the fifth decimal with recent literature results. See ROBBINS M. O., KREMER K., GREST G. S., *J. Chem. Phys.,* **88** (1988) 3286.

[19] WALLACE D. C., *Thermodynamics of crystals* John Wiley & Sons, Inc. (1969).

[20] FLORY P., *J. Chem. Phys.* **17** (1949) 303 ; DEGENNES P. G., *Scaling Concepts in Polymer Physics,* Cornell, Ithaca, (1979), Chap. II.