Effect of permanent entanglements on the equation of state of polymer films

R.M. Velasco

► To cite this version:

R.M. Velasco. Effect of permanent entanglements on the equation of state of polymer films. Journal de Physique, 1976, 37 (2), pp.95-102. 10.1051/jphys:0197600370209500 . jpa-00208407

HAL Id: jpa-00208407

<https://hal.science/jpa-00208407>

Submitted on 1 Jan 1976

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
 Physics Abstracts
 5.620

EFFECT OF PERMANENT ENTANGLEMENTS ON THE EQUATION OF STATE OF POLYMER FILMS

R. M. VELASCO (*)

Physique de la Matière condensée, Collège de France
 75231 Paris Cedex 05, France

(Reçu le 4 juillet 1975, accepté le 29 septembre 1975)

Résumé. — Les films monomoléculaires de polymères avec un groupe latéral hydrophobe montrent une équation d'état pression-surface qui dépend souvent de l'histoire du film. Nous essayons de relier ce comportement aux enchevêtrements entre les chaînes. A cause des groupes latéraux, les enchevêtrements sont *bloqués* et on attend le comportement d'un gel ; nous construisons une équation d'état pour ces gels, fondée sur une généralisation de la théorie de Flory-Huggins où un point d'enchevêtrement est décrit comme un site doublement occupé. Les enchevêtrements sont ainsi simulés par un site doublement occupé et leur nombre est tenu constant. On trouve un accord qualitatif avec des résultats récents sur des films de poly-*n*-octadécyl méthacrylate.

Abstract. — Monomolecular films of polymers with a hydrophobic side group show an experimental pressure-surface equation of state which often depends on the previous history of the film. We attempt to interpret this behaviour in terms of entanglement points where two chains cross over. Because of the side groups, these entanglements are essentially fixed and the system is expected to behave like a gel ; we construct a plausible equation of state for these gels, based on a generalisation of the Flory Huggins theory where double occupation of each site is allowed. The entanglements are thus simulated by doubly occupied points, and their number is kept constant. We find qualitative agreement with some recent data on poly-*n*-octadecyl methacrylate films.

1. Introduction. — Monomolecular films of amphiphilic polymers have been the subject of some recent work. They are obtained in two ways : *a*) by spreading of a linear polymer [1], *b*) by site polymerization of acrylic monomers, for example [1, 2]. We are interested here in both cases, but restrict ourselves to unbranched chains. At first sight it is natural to expect a reversible pressure-surface $\pi(A)$ equation of state. In practice, in both cases we find that the $\pi(A)$ curves depend on the film formation conditions. This fact has been well established by Dubault *et al.* [2] where experimental $\pi(A)$ curves for poly-*n*-octadecyl methacrylate obtained in different experimental conditions are reproduced in figure 1. Our purpose is to suggest an interpretation of these effects based on the existence of entanglements between the chains in the two-dimensional film. The importance of two-dimensional entanglements when the principal chain is hydrophilic and has a lateral hydrophobic group is explained in figure 2*a*. Because of the lateral groups any crossover point between two chains is essentially frozen in. Subsequent changes in the surface pressure π cannot change the number

of entanglements ; in this case the system must behave like a two-dimensional gel. We calculate an approximate equation of state for such gels, assuming the number of entanglements is fixed by the initial conditions. At first sight one might think of discussing the gel in terms of the standard theory for swollen networks. However, *a*) here we are not interested in swollen systems, but rather in situations of relatively high, positive pressure where the gel is dense, and *b*) in our problem, the length of the chains between attachment points is rather short, and a picture in terms of gaussian statistics would not be very adequate. Thus we prefer to use a lattice model, explained in section 2 which is a generalization of the Flory-Huggins [3] model or of the two-dimensional version used by Saraga-Prigogine [4]. In section 3 we calculate the equation of state of an equilibrium state assuming : i) the formation of each entanglement requires a finite energy U , ii) the number of entanglements is not fixed, but determined by the energy U and the density of the system. This equilibrium situation would correspond to $\pi(A)$ curves taken very slowly ; in practice it is unobservable, but we use it as a reference. In section 4 we assume the number of entanglements N_e is fixed : the monolayer achieves an apparent equi-

(*) Supported by CONACYT-UAM Mexico.

FIG. 1. — Experimental surface-pressure area curves for poly-*n*-octadecyl methacrylate. Curve (a) : initial conditions $A_i = 41.0 \text{ Å}^2$, $\pi = 3.16 \text{ dynes cm}^{-1}$; curve (a') : obtained from (a) waiting for 150 mn; curve (b) : initial conditions $A_i = 26.5 \text{ Å}^2$, $\pi = 8.3 \text{ dynes cm}^{-1}$.

a)

b)

FIG. 2. — a) Entanglements in two-dimensions; b) Idealized entanglements.

brum state corresponding to a minimum in the thermodynamic potential for N_c fixed. We calculate the equation of state $\pi(A)$ and show that it is very different from $\pi_{eq}(A)$. In particular, for large A , we find negative pressures as in a gel which can support tractions. We show in section 5 that the calculated curves for $\pi(A)$ give a rough agreement with the experimental results of reference [2].

2. Statistical model. — We consider a two-dimensional lattice model similar to that used by Flory and by Huggins [3] in the three-dimensional problem. The main difference between the Flory-Huggins or Saraga-Prigogine models and ours rests on the possibility of entanglements which we have idealized as in figure 2b. All the chains lie in a plane with each chain segment occupying a lattice site. Two segments may occupy the same lattice site but the penalty for this energetically unfavorable situation is represented in the partition function by a factor $\eta < 1$. We also consider the less probable case in which p ($p > 2$) segments occupy the same site which corresponds to a simultaneous entanglement of $p - 1$ chains.

We have considered two versions of the model :

a) In the first we permit the simultaneous entanglement of $p - 1$ chains, but as mentioned this is energetically unfavorable and we assume the statistical factor is η^{p-1} which makes a large number of simultaneous entanglements improbable.

b) In a more general version we consider that the $p > \delta$ (δ a fixed integer) simultaneous entanglements are completely forbidden and we conserve the statistical factor η^{p-1} for $p \leq \delta$. The case $\delta = 2$ (i.e. the simplest entanglement) seems closest to the real problem.

We present the calculation for all values of δ but develop only the case $\delta = 2$ (the selection of δ is important only when ρ is large).

In order to calculate the partition function we consider a lattice with n_0 sites, each of surface A_0 . The n_2 polymer molecules each having x segments are added successively. Then the partition function is given by the number of possible arrangements for the n_2 chains in the lattice. The interaction between the monomers on the same site is represented by a statistical factor η .

Following the Flory approach [3] let us write the partition function of our system in the representation in which the density and the factor η are the independent variables :

$$Z_\eta(\rho, \eta) = \frac{1}{n_2!} \prod_{i=1}^{n_2} v_i(\rho_i, \eta) \quad (1)$$

where the factor $\frac{1}{n_2!}$ appears because the n_2 chains are equivalent, $v_i(\rho_i, \eta)$ is the expected number of x contiguous sites available to the molecule i , $\rho = \frac{n_2 x}{n_0}$

is the total density and $\rho_i = \frac{ix}{n_0}$ is the density when we have inserted i molecules in the lattice.

According to the ideas we have discussed before, the factor $\eta = \exp(\mu_c/kT)$ is the entanglement fugacity and μ_c a chemical potential or the negative of the interaction energy U between the monomers, which is the same for all monomers.

Then we can write the partition function in eq. (1) as

$$Z_\eta(\rho, \eta) = \sum_{N_c} \eta^{N_c} Z_{N_c}(\rho, N_c) \quad (2)$$

where N_c is the number of entanglements and $Z_{N_c}(\rho, N_c)$ is the partition function in the (ρ, N_c) representation. Eq. (1) and (2) lead us to write the corresponding thermodynamic relationships

$$\begin{aligned} F_\eta(\rho, \eta) &= -kT \ln Z_\eta(\rho, \eta) \\ dF_\eta(\rho, \eta) &= -S dT + \frac{n_2 x A_0}{\rho^2} \pi d\rho - \frac{kTN_c}{\eta} d\eta, \\ \Pi &\equiv \frac{\pi A_0}{kT} = -\frac{\rho^2}{n_2 x} \left(\frac{\partial \ln Z_\eta}{\partial \rho} \right)_\eta; \\ N_c &= \eta \left(\frac{\partial \ln Z_\eta}{\partial \eta} \right)_\rho \end{aligned} \quad (3)$$

in the representation (ρ, η) and

$$\begin{aligned} F_{N_c}(\rho, N_c) &= -kT \ln Z_{N_c}(\rho, N_c) \\ dF_{N_c}(\rho, N_c) &= -S dT + \frac{n_2 x A_0}{\rho^2} \pi d\rho + \\ &\quad + kT \ln \eta dN_c \quad (4) \\ \Pi &= -\frac{\rho^2}{n_2 x} \left(\frac{\partial \ln Z_{N_c}}{\partial \rho} \right)_{N_c}; \\ \ln \eta &= -\left(\frac{\partial \ln Z_{N_c}}{\partial N_c} \right)_\rho \end{aligned}$$

in the representation (ρ, N_c) , where π is the surface pressure, $\rho = A_0/A$ where A is the average surface occupied by a monomer and T is the constant temperature. We wish now to calculate v_{i+1} i.e. the expected number of x contiguous sites available for the $i+1$ th molecule. To do this we consider the segment j of the $i+1$ molecule. Let z be the lattice coordination number and $\bar{f}_{ki}$ the average probability of finding k monomers on a lattice site, when there are i polymer molecules already in the lattice. We are interested in the expected number of sites available for monomer j of chain $i+1$, $v_{j,i+1}$. The j th monomer may occupy $z-1$ lattice sites with a statistical weight which can be constructed in the following way: if the site is vacant we have a contribution given by the average probability of finding an unoccupied cell, if the site is occupied by one monomer, the contribution is given by the average probability of finding a monomer in a cell $\bar{f}_{1i}$ multiplied

by the fugacity η which measures the interaction between the monomer on the site and the monomer j ; if the site is doubly occupied we have $\eta \bar{f}_{2i}$ which corresponds to the average probability of finding two monomers in a cell and the interaction between the last monomer in the site and the monomer j , etc. If we consider the number of monomers on a site to be restricted, the last contribution to the statistical weight will be given by $\eta \bar{f}_{\delta-1i}$, where δ is the maximum number of monomers which may occupy a lattice site.

Then

$$v_{j,i+1} = (z-1) \left(\bar{f}_{0i} + \eta \sum_{k=1}^{\delta-1} \bar{f}_{ki} \right). \quad (5)$$

If the maximum number of monomers δ on one site is large enough we can write

$$v_{j,i+1} = (z-1) [\bar{f}_{0i} + \eta(1 - \bar{f}_{0i})]. \quad (6)$$

This statistical weight is valid when there is no limit to the density of the system.

The contribution to v_{i+1} coming from $x-1$ monomers in each chain is given by eq. (5) or eq. (6); only the first monomer in each chain has a larger factor because it has n_0 sites to choose from instead of $z-1$, then we have for the $i+1$ chain,

$$v_{i+1} = (z-1)^{x-1} n_0 \left(\bar{f}_{0i} + \eta \sum_{k=1}^{\delta-1} \bar{f}_{ki} \right)^x \quad (7)$$

or

$$v_{i+1} = (z-1)^{x-1} n_0 [\bar{f}_{0i} + \eta(1 - \bar{f}_{0i})]^x. \quad (8)$$

At this stage we require an explicit form for the average probabilities $\bar{f}_{ki}$ in terms of ρ_i, η . We consider the problem of inserting independent monomers when the lattice already contain i chains. Let ξ_i be the fugacity (the same for all monomers) associated with the introduction of a monomer to a lattice site, when there are i chains in the lattice. Let us insert a monomer in the lattice, if it finds a vacant site the contribution to the statistical weight z_i is unity, or if it finds a site with one monomer its contribution is ξ_i ; with two monomers it is proportional to ξ_i^2 , but according to the rule we have chosen to take into account the interaction between two monomers in the same site we have also a factor η and $\frac{1}{2!}$ because the independent monomers are indistinguishable, then the contribution must be $\frac{1}{2!} \eta \xi_i^2$, etc., if there are δ monomers the corresponding contribution is $\frac{1}{\delta!} \eta^{\delta-1} \xi_i^\delta$, then we can write the statistical weight in the following way

$$z_i = 1 + \xi_i + \frac{1}{2!} \eta \xi_i^2 + \dots + \frac{1}{\delta!} \eta^{\delta-1} \xi_i^\delta \quad (9)$$

if we take δ large enough the statistical weight is

$$z_i = 1 + \frac{1}{\eta} (e^{\xi_i \eta} - 1) \quad (\delta \rightarrow \infty) \quad (10)$$

the average probabilities $\bar{f}_{ki}$ are given by

$$\bar{f}_{0i} = \frac{1}{z_i}; \quad \bar{f}_{ki} = \frac{1}{z_i} \frac{1}{k!} \eta^{k-1} \xi_i^k \quad (11)$$

the density $\rho_i = \frac{x_i}{n_0}$ can be written in terms of the probabilities $\bar{f}_{ki}$ as

$$\rho_i = \sum_j j \bar{f}_{ji} = \xi_i \left(\frac{\partial \text{Ln } z_i}{\partial \xi_i} \right)_\eta \quad (12)$$

this relation defines ξ_i in terms of the average density and it leads us to express the average probabilities in terms of (ρ_i, η) . For arbitrary δ values the structure of eq. (9), (10) and (12) does not permit an analytical calculation. From on we restrict our attention to the case of $\delta = 2$, which is more tractable, and which seems to be the most realistic.

3. Equilibrium thermodynamic properties. — *Flory's problem.* — Let us return first to the problem studied by Flory, which in our language corresponds to $\eta = 0$. This means that the monomers experiences an infinite repulsion from an occupied site as in a fermion problem. According to eq. (9)

$$z_i = 1 + \xi_i \quad (\eta = 0)$$

which can be expressed directly in terms of the density ρ_i since

$$\xi_i = \frac{\rho_i}{1 - \rho_i} \quad \text{and} \quad \bar{f}_{0i} = 1 - \rho_i.$$

Substitution of these relations in eq. (7) with $\delta = 1$ leads us to the expected number of x contiguous sites calculated by Flory

$$v_{i+1} = \left(\frac{z-1}{n_0} \right)^{x-1} (n_0 - xi)^x \quad (13)$$

substituting eq. (13) in eq. (1) and (3) we obtain the free energy

$$F_\eta(\rho, \eta = 0) = kTn_0 \left[(1 - \rho) \text{Ln}(1 - \rho) + \frac{\rho}{x} \text{Ln} \rho \right] \quad (14)$$

where we have written just the terms depending on the density.

— *The simplest entanglement* ($\delta = 2$). — Now we consider the simplest entanglement, i.e. the maximum number of monomers δ in a lattice site is two, then the statistical weight z_i becomes

$$z_i = 1 + \xi_i + \frac{1}{2} \eta \xi_i^2$$

and the average probabilities

$$\bar{f}_{0i} = \frac{1}{z_i}, \quad \bar{f}_{1i} = \frac{\xi_i}{z_i}, \quad \bar{f}_{2i} = \frac{\eta \xi_i^2}{2 z_i} \quad (15)$$

the density

$$\rho_i = \frac{\xi_i(1 + \eta \xi_i)}{z_i}.$$

The equation for the density permits us to write ξ_i directly in terms of ρ_i and η

$$\xi_i = \frac{1}{\eta(2 - \rho_i)} \times \left[- (1 - \rho_i) \mp \sqrt{(1 - \rho_i)^2 + 2 \eta \rho_i (2 - \rho_i)} \right]. \quad (16)$$

To calculate the partition function we need v_{i+1} which in this case is given by eq. (7) with $\delta = 2$

$$v_{i+1} = (z-1)^{x-1} n_0 (\bar{f}_{0i} + \eta \bar{f}_{1i})^x \quad (17)$$

while substitution of eq. (15) in eq. (17) gives us

$$v_{i+1} = (z-1)^{x-1} n_0 \left(\frac{\rho_i}{\xi_i} \right)^x, \quad (18)$$

so that we see from this equation that only the positive root in eq. (16) has meaning, then the partition function can be written as

$$Z_\eta(\rho, \eta) = \frac{(z-1)^{n_2(x-1)}}{n_2!} n_0^{n_2} \prod_{i=1}^{n_2} \eta(2 - \rho_{i-1}) \rho_{i-1} \left[- (1 - \rho_{i-1}) + \sqrt{(1 - \rho_{i-1})^2 + 2 \eta \rho_{i-1} (2 - \rho_{i-1})} \right]^{-1} \quad (19)$$

substituting eq. (19) in eq. (3) and with the usual approximations we obtain the free energy

$$F_\eta(\rho, \eta) = kTn_2 \text{Ln} \rho - kTn_0 \left\{ \rho \text{Ln} \rho - 2 \text{Ln} \left(1 - \frac{\rho}{2} \right) + \rho \text{Ln} [\eta(2 - \rho)] \right\} - \\ - \text{Ln} 4 \eta - \rho \text{Ln} \left[- (1 - \rho) + \sqrt{2 \eta + (1 - 2 \eta)(1 - \rho)^2} \right] \\ + \text{Ln} [2 \eta - (1 - 2 \eta)(1 - \rho) + \sqrt{2 \eta + (1 - 2 \eta)(1 - \rho)^2}] \quad (20)$$

where we have not written the density independent terms; the first term in eq. (20) is the ideal chain contribution as we shall show later.

From eq. (20) we can obtain the surface-pressure and the number of entanglements N_c . Substitution in eq. (3) leads to

$$\Pi_{eq} = \rho \left(\frac{1}{x} - 1 \right) - 2 \ln(2 - \rho) + \ln \left\{ \frac{1}{\eta} [2\eta - (1 - 2\eta)(1 - \rho) + \sqrt{2\eta + (1 - 2\eta)(1 - \rho)^2}] \right\} \quad (21)$$

for the surface-pressure. In the long chain approximation the ideal contribution may be neglected and figure 3 shows the $\Pi(\rho)$ curves for different values of the fugacity η . We note in $\rho = 2$ that the pressure diverges, as it must do for the maximum density.

FIG. 3. — Theoretical surface-pressure area curves in the long chain approximation. - - - - equilibrium curves (ρ, η) eq. (21). — $\Pi(\rho)$ curves with a fixed number of entanglements (ρ, N_c).

The limit curve corresponds to the pressure in the problem studied by Flory which we can obtain from the free energy in eq. (14) or from the surface pressure in eq. (21) by taking the limit $\eta = 0$. Both ways give us

$$\Pi_{eq} = \rho \left(\frac{1}{x} - 1 \right) - \ln(1 - \rho). \quad (22)$$

If the entanglement fugacity is very small ($\eta \ll 1$) it is easy to obtain the first order correction to the Flory's surface pressure

$$\Pi_{eq} = -\rho - \ln(1 - \rho) - \frac{\eta}{2} \frac{\rho^2}{(1 - \rho)^2} + O(\eta^2). \quad (23)$$

To calculate the number of entanglements we use eq. (3)

$$\frac{N_c}{n_0} = \frac{\rho}{2} + \frac{1}{2(1 - 2\eta)} \times [\sqrt{2\eta + (1 - 2\eta)(1 - \rho)^2} - 1]. \quad (24)$$

Figure 4 shows the behaviour of the number of entanglements (density of entanglements) given in eq. (24). The maximum number of entanglements is obtained when the density is maximum ($\rho = 2$) independently of the value of η . Eq. (24) gives $N_c = 0$ when $\eta = 0$ as expected from Flory's problem. When $\eta \ll 1$ we obtain the density of entanglements to first order in η

$$\frac{N_c}{n_0} = \frac{\eta}{2} \frac{\rho^2}{1 - \rho} + O(\eta^2). \quad (25)$$

FIG. 4. — Density of entanglements $\gamma(\rho, \eta)$ and $\gamma_{ideal}(\rho, \eta)$.

It is also interesting to notice the case $\eta = \frac{1}{2}$ which represents a degenerate case. The statistical weight (15) can be written as $z_i(\eta = \frac{1}{2}) = (1 + \frac{1}{2} \xi_i)^2$, the density by $\rho_i = \frac{\xi_i}{(1 + \frac{1}{2} \xi_i)}$, and the average probability to find a vacant site as $\bar{f}_{0i} = (1 - \frac{1}{2} \rho_i)^2$.

By substitution in eq. (7) we obtain

$$v_{i+1} = (z - 1)^{x-1} n_0 (1 - \frac{1}{2} \rho_i)^x$$

which is the same as Flory's factor with a density $\rho_i/2$; then when $\eta = \frac{1}{2}$ we have two independent lattices with a density $\rho/2$, the surface-pressure is twice the pressure in Flory's problem with the density $\rho/2$

$$\frac{1}{2} \Pi_{eq} \left(\eta = \frac{1}{2} \right) = -\frac{\rho}{2} - \text{Ln} \left(1 - \frac{\rho}{2} \right) \quad (26)$$

and the density of entanglements $\frac{N_c}{n_0} = \frac{\rho^2}{4}$ corresponds to the product of probabilities of finding a monomer on a site in each independent lattice.

On the other hand the value $\eta = 1$ gives us a limit curve which corresponds to the minimum interaction between the monomers on the same site but at the same time it does not permit the insertion of a third monomer to the site.

— *Ideal Chains.* — In the case of ideal chains we consider there to be no interaction at all between the monomers so that we can insert an arbitrary number in each lattice site. Then the statistical weight is given by eq. (10) in which we take $\eta = 1$, $z_i = e^{\xi_i}$, $\xi_i = \rho_i$ and the average probability $\bar{f}_{0i}$ reduces to a Poisson distribution, $\bar{f}_{0i} = e^{-\rho_i}$, the factor v_{i+1} , is given by eq. (8) with $\eta = 1$ since we are considering a problem with no restrictions on the maximum number of monomers on each site. We are also interested in a situation near the ideal one, because this will permit us to calculate the number of entanglements. We take

$$\eta = 1 - \varepsilon \quad (0 < \varepsilon \ll 1)$$

which corresponds to a very small interaction, and the first order correction to the ideal case leads us to a free energy,

$$\begin{aligned} F_\eta(\rho, \eta) &= \\ &= kT [n_2 \text{Ln} \rho - n_0 \varepsilon (1 - \rho - e^{-\rho}) + O(\varepsilon^2)] \end{aligned} \quad (27)$$

It is clear that the first term is the ideal one ($\varepsilon = 0$) and the second one represents a first order deviation.

Substituting this equation for the free energy in eq. (3) we find that in the long chain approximation the surface pressure is zero

$$\Pi_{ideal} = 0 \quad (x \gg 1). \quad (28)$$

However we are interested in the case near the ideal and eq. (27) gives us

$$\Pi_{eq} = \varepsilon [e^{-\rho} (1 - \rho) + 2\rho - 1] \quad (29)$$

and the number of entanglements is

$$\frac{N_c}{n_0} = \eta(\rho - 1 + e^{-\rho}) \quad (30)$$

if we take $\eta = 1$ the density of entanglements in the ideal case is given by

$$\gamma_{ideal} \equiv \frac{N_c}{n_0} \Big|_{\eta=1} = \rho - 1 + e^{-\rho} \quad (31)$$

and this value represents the limit curve in figure 4; we note the number of monomers in each site is not restricted and γ_{ideal} can take an arbitrary value.

4. Thermodynamic properties with the number of entanglements fixed. — Let us now consider the thermodynamic properties of the system with the number of entanglements fixed. Formally this problem is equivalent to a change in the thermodynamic representation which for the partition function is given by the Laplace transformation, and in the thermodynamic relationships by the corresponding Legendre transformation. Then

$$\begin{aligned} F_{N_c}(\rho, N_c) &= F_\eta(\rho, \eta(\rho, N_c)) + \\ &+ kTN_c \text{Ln} \eta(\rho, N_c) \end{aligned} \quad (32)$$

where $\eta = \eta(\rho, N_c)$ is obtained as the solution of eq. (24). The roots of this equation are

$$\begin{aligned} \eta &= \frac{1}{2} + \frac{4\alpha - \rho}{2\rho(2\alpha - 1)^2} \\ \eta &= \frac{1}{2} \end{aligned} \quad (33)$$

where $\alpha \equiv \frac{N_c}{n_2 x}$ is the number of entanglements per monomer. The second value of η leads to the degenerate case, however the first root gives us the fugacity as a function of the density and the number of entanglements, which are now the independent variables.

Substituting this value of η in eq. (32) we obtain the free energy in the (ρ, N_c) representation

$$\begin{aligned} F_{N_c}(\rho, N_c) &= F_{ideal} + \frac{n_2 x kT}{\rho} \times \\ &\times \left[(1 - \rho + \alpha\rho) \text{Ln} (1 - \rho + \alpha\rho) \right. \\ &\left. + \alpha\rho \text{Ln} \left(\frac{2\alpha}{\rho} \right) + \rho(1 - 2\alpha) \text{Ln} (1 - 2\alpha) \right] \end{aligned} \quad (34)$$

the thermodynamic relationships given in eq. (4) reproduce the value of η in eq. (33) and give us the surface-pressure

$$\Pi = \rho \left(\frac{1}{x} - 1 \right) - \text{Ln} (1 - \rho + \alpha \rho) \quad (35)$$

the first term is the ideal chain contribution and, with the approximation $x \gg 1$, is negligible.

We are interested now in the behaviour of the surface-pressure given in eq. (35), first we note a maximum density ($\Pi \rightarrow \infty$) depending on the value of α

$$\rho_{\infty} = \frac{1}{1 - \alpha} \quad (36)$$

which can also be obtained from the following argument. Let us call n_1 the number of vacant lattice sites, $n_2 x - N_c$ is the number of occupied sites,

thus $n_0 = n_1 + n_2 x - N_c$ and the density $\rho = \frac{n_2 x}{n_0}$

is maximum when n_0 is a minimum which corresponds to the case $n_1 = 0$ and leading immediately to eq. (36). Secondly the surface-pressure is zero for a value ρ_0 of the density which satisfies the relation

$$\alpha = \frac{1}{\rho_0} (e^{-\rho_0} + \rho_0 - 1) \quad (37)$$

and coincides with the value obtained in eq. (31) for the number of entanglements ($\gamma_{\text{ideal}} = \alpha \rho_0$).

When the density $\rho < \rho_0$ the surface-pressure eq. (35) is negative, a perfectly acceptable result, since, as mentioned in the introduction, it corresponds to the expected resistance to tractions of a gel. The value ρ_0 for which the pressure is zero corresponds to the gel equilibrium density. On the other hand the behaviour given by eq. (35) for $\rho \ll \rho_0$ is incorrect because eq. (35) predicts $\Pi = -\alpha\rho$, i.e. negative and small. In fact in a gel there exists a limit for elongations corresponding to the completely stretched chains and we must obtain a limit in which $\Pi(\rho) \rightarrow -\infty$ in a certain density $\rho_{\min} \ll \rho_0$ ($A_{\max} \gg A(\Pi = 0)$). These elongation effects are not included in our model. Fortunately they are not important in the positive pressure region which is of main interest to us. In figure 3 we show the curves for the surface pressure given by eq. (35) for different values of the number of entanglements α ; we notice the curves move to the right when the number of entanglements decreases up to the limit curve $\alpha = 0$ corresponding to the Flory's problem, obviously with $\rho_{\infty} = 1$.

5. Discussion. — In comparing our calculations with the experimental results, we emphasize first of all that the equilibrium equation of state (eq. (21)) is very different from the equation obtained with the number of entanglements fixed (eq. (35)). In the first case the magnitude of the interaction, represented

by the entanglement fugacity is fixed and the system looks for the most probable configuration, corresponding to a state in which the number of entanglements depends on the density and the interaction. However if we constrain the system to have a fixed number of entanglements, the interaction must be adapted and this gives us an apparent equilibrium state which should depend on the formation conditions. The existence of entanglements between the chains makes the system behave like a two-dimensional gel and eq. (35) has the qualitative requirements to represent such gels. We propose therefore to identify the $\pi(A)$ curves in figure 1 as the apparent states given by eq. (35), i.e. as states with a fixed number of entanglements.

The curve (a) in figure 1 was obtained by site polymerization at constant pressure ($3.15 \text{ dynes cm}^{-1}$) and starting from a surface $A_i = 41.0 \text{ \AA}^2$ on the monomer curve, while curve (a') was obtained from (a) waiting for 150 mn. As explained in reference [2], we identify curve (a) as a state with a fixed number of entanglements which depends on the film formation, and curve (a') as a state of the same kind but with a different number of entanglements depending on the time allowed to the system to approach the true equilibrium state. In other words a state with a fixed number of entanglements is not an equilibrium state, but relaxes sufficiently slowly to allow thermodynamic properties to be measured. Then the different experimental curves represent steps in the relaxation to the real equilibrium state.

A rough numerical fit gave us an estimate of the number of entanglements $\alpha = 0.144$ in curve (a) and $\alpha = 0.086$ in curve (a') both with the value

FIG. 5. — Comparison between experimental and theoretical curves. - - - - experimental curves (a) and (a') in figure 1; ——— theoretical curves, eq. (35).

$A_0 = 23.0 \text{ \AA}^2$. On the other hand, curve (b) in figure 1 was obtained by the same experimental method but with different initial conditions ($A_i = 26.5 \text{ \AA}^2$, $\pi = 8.3 \text{ dynes cm}^{-1}$) and the numerical fit with the same value $A_0 = 23.0 \text{ \AA}^2$ gave a different value for the number of entanglements, $\alpha = 0.154$, all in reasonable agreement with the experimental data and with the qualitative picture we have adopted as shown in figure 5. However, it is important to notice that the numerical fit gives only a semi-quantitative idea, because of the two parameters (A_0 , α), α is highly sensitive to the value of A_0 and we have only a very rough estimate of A_0 .

In spite of the limitations in the numerical comparison as well as in the approximations we used to calculate eq. (35) we see that the proposed model can explain the experimental results. One possible source of discrepancy (pointed out to us by a referee) is the following : there are indications that many amphiphilic polymers at the surface of water are *not very flexible* : this may change the rheological behaviour quite independently of entanglement effects.

Acknowledgments. — The author is greatly indebted to P. G. de Gennes, F. Brochard, M. Veyssié, A. Dubault for fruitful discussions.

References

- [1] BEREDJICK, N., BURLANT, W. J., *J. Polymer Sci. A* **8** (1970) 2807.
 - [2] DUBAULT, A., CASAGRANDE, C., VEYSSIÉ, M., *J. Phys. Chem.*, in press.
 - [3] FLORY, P. J., *Principles of Polymer Chemistry* (Cornell University Press) 1966.
 - [4] TER MINASSIAN-SARAGA, L., PRIGOGINE, I., *Mém. Serv. chim. état* **38** (1953) 109.
-