Temperature-concentration diagram of polymer solutions

M. Daoud, G. Jannink

HAL Id: jpa-00208494
https://hal.science/jpa-00208494

Submitted on 4 Feb 2008

TEMPERATURE-CONCENTRATION DIAGRAM OF POLYMER SOLUTIONS

M. DAOUD and G. JANNINK

Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay,
B.P. nº 2, 91190 Gif-sur-Yvette, France

Résumé. — Nous traçons un diagramme (*T*, *C*) des solutions polymériques en partant d'une approche tricritique du point thêta des polymères. *T* est la température, et *C* la concentration en monomères. Nous définissons quatre régions distinctes dans ce diagramme. Nous calculons les dépendances de la valeur moyenne du carré de la distance bout à bout d'une chaîne, de la longueur d'écran, de la pression osmotique, et du second coefficient du viriel en *T*, *N* et *C*. *N* est le nombre de maillons d'une chaîne. Nous donnons également une forme d'échelle pour l'équation d'état.

Abstract. — Starting from a tricritical approach to the polymer theta point, we deduce a (*T*, *C*) diagram for polymer solutions where *T* is the temperature, *C* the monomer concentration. We define four different regions in this diagram. For each of these regions we calculate the *T*, *N*, *C*, dependence of the mean square end to end distance of a chain, the screening length, the osmotic pressure, and the second virial coefficient. We also give a scaling form for the equation of state.

1. **Introduction.** — In a recent set of neutron scattering experiments [1] by polystyrène solutions, the radius of gyration R, the screening length ξ and the compressibility have been measured in the semi-dilute range. New scaling laws for these observables have been established as a function of two independent variables : *a*) the number N of monomers per chain, at different concentrations ; *b*) the monomer concentration C. In all these experiments, and the corresponding theory, the only interaction taken into account between two monomers was the so-called excluded volume interaction. This corresponds to the case where the repulsive part of the potential is much bigger than the attractive part, which is equivalent to a high temperature approximation. In fact, the attractive par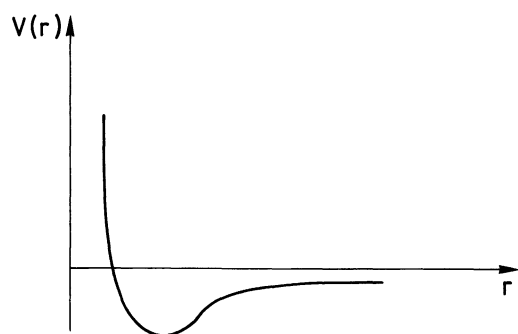t of the potential, shown in figure 1, becomes important as temperature is decreased. For sufficiently low temperatures, the polymer collapses. Typical (*T*, *C*) diagrams of polymer solutions are shown on figure 2, in the low temperature region. As shown in these diagrams, when N increases the maximum of the coexistence curve increases and is shifted towards smaller C values. In the limit of infinite N, the low concentration part of the curve is reduced to a segment of the temperature axis ; the maximum itself is on this axis and has a finite value called the theta temperature (or theta point). For temperature below θ, the chain is collapsed. For temperatures above θ, the problem of a chain is the so-called *self avoiding walk* problem, which is equivalent to a second order phase transition problem [2].

FIG. 1. — Real potential between two monomers. The excluded volume corresponds to the hard core.
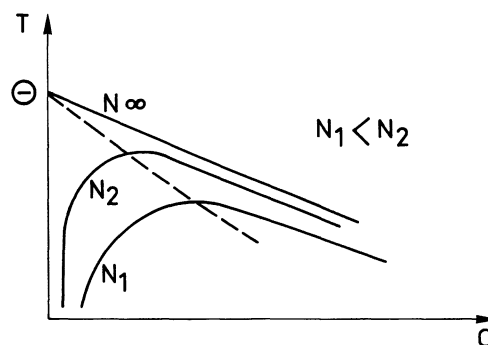

FIG. 2. — Typical phase diagram for dilute polymer solutions. $N_1 < N_2$. When N goes to infinity, the maximum of diagram is on the T axis. The dotted line joins the maximum of the different curves.

The theta point is thus a tricritical point as was recently pointed by de Gennes [3]. Earlier predictions for the temperature dependences were made using mean field theories, in the range of very dilute solutions [4, 5], or in very concentrated solutions near the θ temperature [9]. However the development about the tricritical point is a very powerful tool which allows us to make a systematic investigation of the temperature dependence : from the scaling form of the free energy near the tricritical point, we can deduce the equation of the cross-over line between critical and tricritical behaviours. Combined with previous results [1] recalled in appendix B, this allows us to draw a phase diagram in a (τ, C) plane, τ being the reduced temperature $\dfrac{T - \theta}{\theta}$. Writing down the scaling forms of the free-energy and correlation length near the tricritical point [5], we then deduce by continuity the temperature dependence of the correlation function and free energy in the critical domain, that is for temperatures above the θ point. This leads us to predictions for the screening length, mean square end to end distance, and osmotic pressure, and to distinguish between three regions of different characteristic behaviours near the θ temperatures. Variations in N, C, τ of osmotic pressure, screening length, and mean square end to end distance in the different regions are given.

The problem of polymer solutions has a magnetic analogue [7, 1]. We will use this correspondence. Therefore, in the following we use the language of magnetism, unless explicitly specified. The correspondence with polymer solution is given at any step. This correspondence is derived in appendix B. M is the magnetization, μ is the temperature of the magnetic system. τ is an external relevant parameter, in the magnetic analogue it always turns to be the temperature of the polymer solution. The subscript « t » denotes tricritical [11], whereas the absence of subscript means that we are in the critical domain. ν and ν_t are the exponents of the correlation length. ν is also called the excluded volume exponent. φ_t is the cross-over exponent. ν_t and φ_t are close to $1/2$ for $d = 3$ [10], ν is close to $3/5$ for $d = 3$. d is the dimensionality of space. $\tau = \dfrac{T - \theta}{\theta}$.

2. The diagram.

— The free energy of the magnetic analogue is related to the osmotic pressure of the polymer solution. The relation is

$$\pi = - \Delta F = - \Delta G + M \frac{\partial}{\partial M} \Delta G$$

$$\Delta F = \Delta G - MH$$

where ΔF is the free energy and π the osmotic pressure. In the vicinity of a tricritical point, the potential may be written in the form [8]

$$\Delta G(M, \mu, \tau) = \mu^{2 - \alpha_t} f\left(\frac{M}{\mu^{\beta_t}} \cdot \frac{\tau}{\mu^{\varphi_t}}\right) \tag{1}$$

the notation is the same as in reference [8]. Here μ, which is called μ_1 in reference [8], is simply the reduced temperature of the magnetic analogue, τ is the reduced temperature of the polymer solution, as indicated above. Eq. (1) immediately gives the equation of the cross-over line, which is

$$\tau \sim \mu^{\varphi_t}. \tag{2}$$

Now, for low concentrations, that is concentrations for which the chains do not overlap, it is shown in appendix B that

$$\mu \sim N^{-1}$$

so that the equation of the cross-over line is

$$\tau \sim N^{-\varphi_t} \tag{3}$$

$$\simeq N^{-1/2} \quad \text{for} \quad d = 3. \tag{3'}$$

For high concentrations, that is for concentrations for which the chains do overlap, it is also shown in appendix B that

$$\mu \sim C^{1/(\nu_t d - 1)}$$

and the equation of the cross-over line is

$$\tau C^{** - \varphi_t/(\nu_t d - 1)} \sim 1$$

or

$$C^{**} \sim \tau^{(\nu_t d - 1)/\varphi_t} \tag{4}$$

$$\simeq \tau \quad \text{for} \quad d = 3. \tag{4'}$$

For a given value of N, we can then draw a (τ, C) diagram of polymer solutions, which is shown on figure 3.
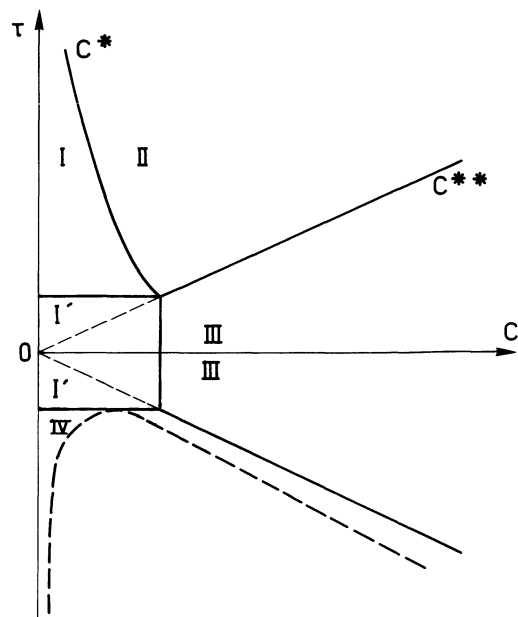

FIG. 3. — Typical phase diagram of a polymer solution. In the high negative τ region there is a coexistence curve; τ is $\dfrac{T - \theta}{\theta}$. Region I' is the so-called θ region.

— Region I is the dilute region, it is limited by $\tau \sim N^{-1/2}$ and by the line $C^*(\tau)$. $C^*(\tau)$ is the monomer concentration at which the chains begin to overlap [1]. The dependence $C^*(\tau)$ will be given later.

— Region II is the semi-dilute region. It is limited by the lines $C^*(\tau)$ and $C^{**}(\tau)$.

— Region I' is the dilute tricritical region. It is the so-called theta region [4].

— Region III is the semi-dilute and concentrated tricritical region, which had not yet been mentioned before, to our knowledge.

3. The equations of state.

— 3.1 TRICRITICAL DOMAIN. — The tricritical domain is defined by the inequality $\tau/\mu^{\varphi_t} \ll 1$ (regions I' and III in Fig. 3). The scaling law for ΔG then reads

$$\Delta G(M, \mu, \tau) = \mu^{2-\alpha_t} g\left(\frac{M}{\mu^{\beta_t}}\right). \tag{5}$$

We can deduce from this equation and from the equations of the magnetic equivalence between the polymer problem and a critical magnetic problem, the form of the equation of state. The derivation is given in appendix A.

$$\frac{\pi}{T} \mu^{-v_t d} = f(C\mu^{1-v_t d}). \tag{6}$$

We immediately find a special concentration C_t^*,

$$C_t^* \sim \mu^{v_t d - 1}$$

which is the concentration above which the chains overlap. If C is less than C_t^*, the chains do not overlap and the solution is called a dilute solution. If C is more than C_t^*, the chains overlap and the solution is called semi-dilute solution.

For dilute solutions

$$\mu \sim \frac{1}{N}$$

and

$$C^* \sim N^{1 - v_t d}$$

$$\simeq N^{-1/2} \quad \text{for} \quad d = 3.$$

For dilute solutions, it is shown in appendix B that $\mu \sim N^{-1}$, and $f(x) \sim x$. Then

$$\pi \sim \frac{C}{N} \tag{7}$$

for concentrations $C > C_t^*$, it is also shown in appendix B that

$$\mu \sim C^{1/(v_t d - 1)}$$

then

$$\frac{\pi}{T} \sim \mu^{v_t d} \sim C^{v_t d/(v_t d - 1)}$$

$$\frac{\pi}{T} \sim C^{v_t d/(v_t d - 1)} \tag{8}$$

$$\simeq C^3 \quad \text{for} \quad d = 3. \tag{8'}$$

3.2 CRITICAL DOMAIN. — This domain is defined by $\tau/\mu^{\varphi_t} \gg 1$ (regions I and II in Fig. 3). In this domain, relation (1) may be written

$$\Delta G_c(M, \mu, \tau) = \mu^{2-\alpha_t}\left(\frac{\tau}{\mu^{\varphi_t}}\right)^x g\left(\frac{M}{\mu^{\beta_t}}\left(\frac{\mu^{\varphi_t}}{\tau}\right)^y\right) \tag{9}$$

which is to be compared with the critical scaling law for the potential

$$\Delta G(M, \mu, \tau) = \mu^{2-\alpha} g_1\left(\frac{M}{\mu^{\beta}}\right) \tag{10}$$

it is easy to deduce x and y from these two relations, then ΔG may be written in the form

$$\Delta G(M, \mu, \tau) = \mu^{2-\alpha} \tau^{(\alpha-\alpha_t)/\varphi_t} g\left(\frac{M}{\mu^{\beta}} \tau^{(\beta-\beta_t)/\varphi_t}\right) \tag{11}$$

and by applying the same treatment as in the tricritical case we deduce the form of the equation of state in the critical region.

$$\frac{\pi}{T} \mu^{-vd} \tau^{(v-v_t)d/\varphi_t} = f\left[\frac{C\mu^{1-vd}}{\tau^{(v_t-v)d/\varphi_t}}\right] \tag{12}$$

$$\left(\frac{\pi}{T} \mu^{-9/5} \tau^{3/5} = f(C\mu^{-4/5} \tau^{3/5} \quad \text{for} \quad d = 3\right). \tag{12'}$$

Again a special concentration C^* appears immediately.

$$C^* \sim \tau^{(v_t-v)d/\varphi_t} \mu^{vd-1}$$

which is the concentration above which the chains overlap. The difference between C_t^* and C^* lies in the fact that for C_t^*, the chains are brownian chains, whereas in the case of C^* the chains are swelled.

For concentrations below C^* the chains do not overlap the polymer solution is said to be dilute.

For concentrations above C^* the chains overlap the solution is then called semi-dilute solution.

For dilute solutions, $\mu \sim N^{-1}$, and

$$C^* \sim \tau^{(v_t-v)d/\varphi_t} N^{1-vd}$$

$$= \tau^{-3/5} N^{-4/5} \quad \text{for} \quad d = 3.$$

(i) For low concentrations, $\mu \sim N^{-1}$ and $f(x) \sim x$. Then

$$\frac{\pi}{T} \sim \frac{C}{N} \tag{13}$$

a result which is not surprising since it just recalls the analogy of dilute solutions with perfect gases.

(ii) For high concentrations,

$$\mu \sim C^{1/(\nu d - 1)} \, \tau^{(\nu' - \nu_t)/(1 - \nu d)d/\varphi_t}$$

and $f(x)$ becomes a constant, then

$$\frac{\pi}{T} \sim C^{\nu d/(\nu d - 1)} \, \tau^{(\nu - \nu_t)/(-1 + \nu d)d/\varphi_t} \tag{14}$$

$$(= C^{9/4} \, \tau^{3/4} \qquad \text{for} \qquad d = 3) \, . \tag{14'}$$

One can then make two remarks concerning the osmotic compressibility, the elastic modulus, and the number of chain contact points.

(i) In a neutron scattering experiment, the zero momentum transfer intensity is related to the osmotic compressibility [12] :

$$S(q = 0) = TC \frac{\partial C}{\partial \pi} \tag{15}$$

by eq. (14) one then obtains

$$S(q = 0) \sim C^{(2 - \nu d)/(\nu d - 1)} \, \tau^{(\nu - \nu_t)/(1 - \nu d)d/\varphi_t} \tag{16}$$

$$(\approx C^{-1/4} \, \tau^{-3/4} \qquad \text{for} \qquad d = 3) \, .$$

(ii) The number of chain segment contacts is [1] proportional to π/T

$$n \sim C^{9/4} \, \tau^{3/4} \tag{17}$$

then if one is concerned with viscoelastic properties at low frequencies the elastic modulus is then only due to the entanglements. There are arguments [1] for saying that $E/T \sim n$. Then one finds

$$\frac{E}{T} \sim C^{9/4} \, \tau^{3/4} \, . \tag{18}$$

4. Scaling of the correlation length.

— The scaling law for the correlation length may be written [8] near the tricritical point

$$\xi(\mu, \tau) = \tau^{-\nu_t/\varphi_t} f(\mu/\tau^{1/\varphi_t}) \, . \tag{19}$$

In the critical domain II, we recover the critical scaling law. For a given value of τ :

$$\xi(\mu ; \tau) = \mu^{-\nu} \, \xi(1 ; \tau) \tag{20}$$

whereas (19) gives, in this limit

$$\xi_c(\mu ; \tau) = \omega_c \, \mu^{-\nu} \, \tau^{(\nu - \nu_t)/\varphi_t}$$

and, in the tricritical region III

$$\xi_t = \omega_t \, \mu^{-\nu_t} \, .$$

(i) At low concentrations, μ is proportional to N^{-1}. This gives, for low concentrations

$$\xi_c \sim N^{\nu} \, \tau^{(\nu - \nu_t)/\varphi_t} \tag{21}$$

$$(\approx N^{3/5} \, \tau^{1/5} \qquad \text{for} \qquad d = 3) \text{ in region I}$$

$$\xi_t \sim N^{\nu_t} (= N^{1/2} \qquad \text{for} \qquad d = 3) \text{ in region I}' \, .$$

(ii) At high concentrations, μ is proportional to $C^{1/\nu d - 1} \, \tau^{(\nu - \nu_t)/(\nu d - 1)d/\varphi_t}$ in the critical domain and to $C^{1/\nu_t d - 1}$ in the tricritical domain. This gives

$$\xi_c \sim C^{\nu/(-\nu d + 1)} \, \tau^{(\nu - \nu_t)/\varphi_t(1 - \nu d)} \quad \text{in region II} \tag{22}$$

$$= C^{-3/4} \, \tau^{-1/4} \qquad \text{for} \qquad d = 3 \, . \tag{22'}$$

$$\xi_t \sim C^{\nu_t/(1 - \nu_t d)} \quad \text{in region III} \tag{23}$$

$$\simeq C^{-1} \qquad \text{for} \qquad d = 3 \, . \tag{23'}$$

At low concentrations, the unique length scale which is introduced in the problem is the mean square end to end distance. Then, from (21) we deduce

$$\langle R^2 \rangle \sim N^{2\nu} \, \tau^{2(\nu - \nu_t)/\varphi_t} \, (\approx N^{6/5} \, \tau^{2/5}) \tag{24}$$

which is a law already found by Flory [4] and Edwards [5].

From this result we can deduce two other laws.

(i) The concentration at which the chains begin to overlap is

$$C^* \sim \frac{N}{R^d} = N^{1 - \nu d} \, \tau^{d(\nu - \nu_t)/\varphi_t} \tag{25}$$

in agreement with what we found above

$$C^* \sim N^{-4/5} \, \tau^{-3/5} \qquad (\text{for } d = 3) \, . \tag{25'}$$

(ii) The second virial coefficient.

At low concentrations, the osmotic pressure can be developed in powers of the monomer concentration. This development reads

$$\frac{\pi}{T} = \frac{C}{N} + 2 \, A_2 \, C^2 \tag{26}$$

when A_2 is the second virial coefficient. This coefficient varies as R^d, we then find that

$$A_2 \sim N^{\nu d} \, \tau^{d(\nu - \nu_t)/\varphi_t} \tag{27}$$

$$(= N^{9/5} \, \tau^{3/5} \qquad \text{for} \qquad d = 3) \, . \tag{27'}$$

For semi-dilute solutions, there are two length scales corresponding to the longitudinal and transverse correlation lengths. The method gives us only one of these two lengths. Comparison with previous results [1] tells us that we obtain the longitudinal length. A simple model, already described [1], allows us to

TABLE I

Mean square end to end distance, screening length and osmotic pressure in the different regions of the phase diagram. Results for three dimensions are between brackets

Region	$\langle R^2 \rangle$	π/T	ξ^2
I	$N^{2\nu}\,\tau^{2(\nu-\nu_t)/\varphi_t}$ $(N^{6/5}\,\tau^{2/5})$	$\dfrac{C}{N}$	
I'	N	$\dfrac{C}{N}$	Const.
II	$NC^{(\nu-\nu_t)/(1-\nu d)1/\varphi_t}\,\tau^{(\nu-\nu_t)/(1-\nu d)[\nu d(1-2\varphi_t)+2\varphi_t]/\varphi_t^2}$ $(NC^{-1/4}\,\tau^{1/4})$	$C^{\nu d/(\nu d-1)}\,\tau^{\nu-\nu_t/\nu d-1\,d/\varphi_t}$ $(C^{9/4}\,\tau^{3/4})$	$C^{2\nu/(1-\nu d)}\,\tau^{2(\nu-\nu_t)/\varphi_t(1-\nu d)}$ $(C^{-3/2}\,\tau^{-1/2})$
III	N	C^3	C^{-2}

calculate the transverse correlation length. The results are

$$\langle R^2 \rangle \sim NC^{(\nu-\nu_t)/(1-\nu d)\varphi_t}\,\tau^{(\nu-\nu_t)/(1-\nu d)\,[\nu d(1-2\varphi_t)+2\varphi_t]/\varphi_t^2} \tag{28}$$

$$(\approx NC^{-1/4}\,\tau^{1/4} \quad \text{for} \quad d = 3) \text{ in region II} \tag{28'}$$

and

$$\langle R^2 \rangle \sim N \quad \text{in region III}. \tag{29}$$

Logarithmic corrections to relation (29) have already been calculated [6].

Finally, the properties of the different regions are summarized in table I, which shows the main results for osmotic pressure, screening length and mean square end to end distance.

5. Some remarks for low temperatures.

— Let us make some remarks concerning the region where τ is negative and $\tau N^{1/2} \gg 1$. We know that in this region there is a phase separation. Some predictions can be made.

a) In the dilute region the polymer chain is collapsed which imposes that R^2 varies as $N^{2/3}$

$$R^2 \sim N^{2/3} \tag{30}$$

by using relation (19), valid near the tricritical point. One can expand this relation in the form

$$\xi \sim N^{1/2}(\tau N^{1/2})^x \tag{31}$$

and from relation (30) one finds $x = -\frac{1}{3}$.

In the dilute region and for temperatures far below θ, we find that the chains are totally collapsed. They can be put in a sphere of radius

$$R \sim \left(\frac{N}{\tau}\right)^{1/3}. \tag{32}$$

One can remark that the volume inside the sphere is completely filled by the chain. This relation is valid in domain IV (see Fig. 3).

b) We can then evaluate the asymptotic behaviour of the coexistence curve : the volume fraction occupied by one chain is $f = C/\tau$. When there are several chains, as we are in the dilute regime, the chains do not interpenetrate, and the volume fraction occupied by the collapsed chains is $f = c/\tau$.

The demixtion occurs when f is some constant, independent of N and τ, so that we find

$$C_* \sim \tau. \tag{33}$$

We find that the coexistence curve for high concentrations is a linear function. We can assume that this line coincides with the line separating the tricritical domain from the first order domain. We will justify this assumption *a posteriori*. The two phases coexisting are

i) collapsed chains,

ii) ideal chains, i.e. chains with a radius of giration proportional to $N^{1/2}$ and independent of τ.

If we accept this assumption, we can evaluate the coordinates of the critical point, that is the top of the curve (C on Fig. 3).

Point C is the only point where we have both relations (29) and (32) valid :

$$R = \left(\frac{N}{\tau}\right)^{1/3} = N^{1/2}$$

which gives

$$\tau_c \sim N^{-1/2} \tag{34}$$

from which we easily deduce

$$C_c \sim N^{-1/2}. \tag{35}$$

Relation (34) has been verified a long time ago [13]. The asymptotic behaviour of different curves can also be seen on figure 3 of reference [13]. These results justify *a posteriori* the assumption about the two coexisting phases.

Now from the fact that the coexistence curve has two asymptotes, one can guess that the curve is simply an hyperbola.

Knowing the position of the critical point, and the

two asymptotes, we easily find the equation of the curve

$$\tau = - \alpha\left(C + \frac{1}{NC}\right) \qquad (36)$$

where α is some positive constant.

Eq. (36) can be written in the form

$$\frac{\tau N^{1/2}}{-\alpha} = CN^{1/2} + \frac{1}{N^{1/2}C} \qquad (37)$$

that is a scaling equation, or a law of corresponding states for chains of different lengths. It can be written more generally

$$\tau N^{1/2} = f(CN^{1/2}) \qquad (38)$$

where f is an unknown function.

Because we know that near the critical point the system is equivalent to an Ising system, so that Ising exponents must appear [14], we think that the curve is not an hyperbola near the critical point, but we guess that equation (38) still holds (we hope to come back on these points soon).

6. **Conclusion.** — *a*) Earlier temperature concentration diagrams for polymer solutions were characterized by two sets of lines, depending upon molecular weight :

— below the theta temperature, the coexistence lines, defining a sharp transition ;

— above the theta temperature, the interpenetration lines, indicating a smooth change of behaviour. The connections between these two sets of lines were however never studied.

Use of the tricritical concept has allowed a precise definition of the vicinity of the theta temperature, as a function of molecular weight and monomer concentration. A new set of lines is therefore established, which indicates a smooth change of behaviour caused by the shift from repulsive to attractive interaction.

b) The observables R, ξ and π discussed in reference 1, in the high temperature limit, scale in molecular weight and monomer concentration with critical exponents. In the vicinity of the theta point, the scaling exponents are both critical and tricritical for the semi-dilute range.

The scaling laws in temperature, already calculated in the dilute range [4], are extended to the semi-dilute concentration. They include both critical and tricritical exponents.

c) The calculations suggest an implicit law of corresponding states for the coexistence curve.

d) The line $\tau = 0$ is a line of symmetry for the *Gaussian* behaviour of the chain in the temperature concentration diagram.

e) Experimental evidence for the proposed laws can be obtained from the neutron scattering technique, respectively with and without labeled samples.

APPENDIX A

Equation of state. — In domains I and III, we showed that the potential can scale as

$$\Delta G(M, \mu) = \mu^{2-\alpha_t} g(M/\mu^{\beta_t}) . \qquad (A.1)$$

Des Cloizeaux [7] has shown that there is an equivalence between the magnetic problem described by eq. (A.1) and the problem of a concentrated polymer solution. There is a dictionary between the two problems, which can be read :

$$C = - \Delta S = \frac{\partial}{\partial \mu}(\Delta G) \qquad (A.2)$$

$$C_p = \frac{1}{2} MH = \frac{1}{2} M \frac{\partial}{\partial M}(\Delta G) \qquad (A.3)$$

$$C_p = \frac{C}{N} \qquad (A.4)$$

$$\frac{\pi}{T} = - \Delta G + MH = - \Delta G + M \frac{\partial}{\partial M}(\Delta G) \qquad (A.5)$$

where C_p is the polymer concentration, C the monomer concentration, N the number of segments of a chain, π the osmotic pressure of the polymer solution.

By combining eqs. (A.1) to (A.4), one easily obtains

$$C = \mu^{1-\alpha_t}\left\{(2 - \alpha_t)\, g(x) - \beta_t\, x \frac{\partial g}{\partial x}\right\} \qquad (A.6)$$

$$= \frac{1}{2} N \mu^{2-\alpha_t} x \frac{\partial g}{\partial x} \qquad (A.7)$$

where

$$x = \frac{M}{\mu^{\beta_t}} .$$

Combining eqs. (A.1) and (A.5) gives

$$\frac{\pi}{T} = \mu^{2-\alpha_t}\left[- g(x) + x \frac{\partial g}{\partial x}\right]$$

or

$$\frac{\pi}{T} \mu^{\alpha_t - 2} = h(x) . \qquad (A.8)$$

Eliminating x between eqs. (A.6) and (A.8), one obtains the general form of the equation of state

$$\frac{\pi}{T} \mu^{\alpha_t - 2} = K(C\mu^{\alpha_t - 1}) \qquad (A.9)$$

which is the result used in the text.

A similar derivation can be used in the critical

domain (I and II). Eq. (A.1) has then to be replaced by the scaling form in the critical region (eq. (11))

$$\Delta G(M, \mu, \tau) = \mu^{2-\alpha} \, \tau^{(\alpha-\alpha_t)/\varphi_t} \, g\left[\frac{M}{\mu^\beta} \tau^{(\beta-\beta_t)/\varphi_t}\right] \quad \text{(A.10)}$$

which leads to a result similar to eq. (A.9)

$$\frac{\pi}{T} \mu^{\alpha-2} \, \tau^{(v-v_t)d/\varphi_t} = K_c\left[\frac{C\mu^{\alpha-1}}{\tau^{(v_t-v)d/\varphi_t}}\right] \quad \text{(A.11)}$$

which is eq. (12) used in the text.

APPENDIX B

Values of μ. — One can draw a line of constant N (isometric line) in an (M, μ) diagram in the magnetic problem. It has been shown (see appendix [1]) that such a line has the form indicated by figure 4. It starts from the τ axis at a point A situated at a distance of order N^{-1} from the critical point and then tends towards the critical curve.

a) For dilute solutions, the representative point is in the vicinity of point A. This can be seen from eqs. (A.6) and (A.7). From these two equations, one finds

$$N \mid \mu \mid = A(X); X \to 0 \quad \text{(B.1)}$$

and $\mid \mu \mid$ is of order N^{-1}.
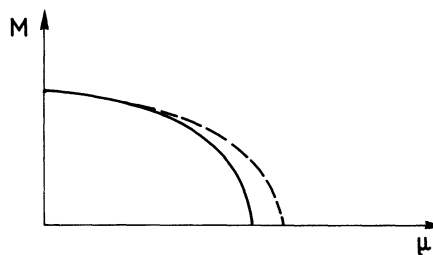
FIG. 4. — The isometric line (N = constant) (dotted line) starts from a point at a distance N^{-1} from the critical point and then goes to the spontaneous magnetization curve.

For high concentrations, the representative point is near the spontaneous magnetization curve. Then x goes to a given value x_0 and eq. (A.6) shows that

$$C = \mu^{1-\alpha_t} h(x_0) = K\mu^{1-\alpha_t} \quad \text{(B.2)}$$

that is

$$\mu \sim C^{1/1-\alpha_t} = C^{1/v_t d-1} . \quad \text{(B.3)}$$

Of course, in the critical domain, a similar derivation gives similar results :

$$\mu \sim N^{-1} \quad \text{in the dilute regime}$$

$$\mu \sim C^{1/vd-1} \, \tau^{(v-v_t)/(vd-1)d/\varphi_t} \quad \text{in the semi-dilute regime .}$$
$$\text{(B.4)}$$

References

[1] DAOUD, M., COTTON, J. P., FARNOUX, B., JANNINK, G., SARMA, G., BENOIT, H., DUPLESSIX, R., PICOT, C., DE GENNES, P. G., *Macromolecules* **8** (1975) 804.

[2] DE GENNES, P. G., *Phys. Lett.* **38A** (1972) 339.

[3] DE GENNES, P. G., *J. Physique Lett.* to be published.

[4] FLORY, P. J., *Principles of Polymer Chemistry* (Cornell University Press, 5th ed.) 1966.

[5] EDWARDS, S. F., *Proc. Phys. Soc.* **85** (1965) 613.

[6] STEPHEN, M. J., *Phys. Lett.* **53A** (1975) 363.

[7] DES CLOIZEAUX, J., *J. Physique* **36** (1975) 281. A more direct

derivation has been given by SARMA, G., Saclay Lecture, to be published.

[8] RIEDEL, E. K., *Phys. Rev. Lett.* **28** (1972) 675.

[9] EDWARDS, S. F., *J. Phys. A* **8** (1975) 1670.

[10] STEPHEN, M., MC CAULEY, J., *Phys. Lett.* **44A** (1973) 89.

[11] GRIFFITHS, R. B., *Phys. Rev. B* **7** (1973) 545.

[12] EGELSTAFF, P. A., *An introduction to the liquid state* (Academic Press, London and New York) 1967.

[13] SCHULTZ, A. R., FLORY, P. J., *J. Chem. Phys.* **74** (1953) 4760.

[14] NAKATA, M., KUWUHARA, N., KANEKO, M., *J. Chem. Phys.* **62** (1975) 4278.