

Theory of adsorption of macromolecules in cylindrical pores and at surfaces of cylindrical shape

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A rigorous theory of adsorption of a Gaussian chain of infinite length into cylindrically shaped pores and onto cylindrical surfaces of arbitrary diameter, D , has been developed for any energy of interaction $-\epsilon$. The change in the conformational free energy of a chain arriving inside the pores from an unrestricted volume is proportional to $(D^*)^{-2}$ (D^* is the effective pore width) over the entire molecular-sieve range ($-\epsilon < -\epsilon_c$). In the exclusion range ($-\epsilon < 0$), when the interaction of chain units with the adsorbent exhibits repulsive type forces, D^* is approximately equal to D . As the adsorption forces of attraction increase ($0 < -\epsilon < -\epsilon_c$) the value of D^* increases and becomes infinite at the critical point. This makes it possible to use a *single* adsorbent for effective chromatographic separation of polymers over a wide range of molecular weights. In the adsorption range, where $-\epsilon > -\epsilon_c$, the conformational free energy of the chain is virtually independent of the width and shape of the pores and is determined mainly by the value of $-\epsilon$. At the critical point, $-\epsilon = -\epsilon_c$, the probability of the arrival of a polymer chain in the pore is independent of both the width and shape of the pore and is determined only by the ratio of geometrical volumes of the free volume to the pore volume. For cylindrical pores, a weak dependence of $-\epsilon_c$ on D is observed only for narrow pores. This dependence virtually disappears on passing to adsorbents with wide pores. Consideration of the adsorption of the macromolecule on the outer surface of the cylinder showed that at any finite value of the diameter of the cylinder, D , adsorption occurs as an 'infinite-order' phase transition. The maximum value of the specific heat

$$\frac{(C_p)_{\max}}{k} = \frac{25}{3} = \epsilon_c^2$$

does not depend on D . The degree of bonding of the macromolecule to the adsorbent increases with decreasing curvature of the surface, rapidly attaining values characteristic of chain adsorption on a plane.

Keywords Macromolecules; adsorption; cylindrical pore; cylindrical surface; chromatography; phase transitions

INTRODUCTION

Development of the chromatography of polymers has led to the publication of many theoretical¹⁻⁵ and experimental papers⁶⁻¹¹ dealing with the interaction between macromolecules and a porous medium (adsorbent). In the theoretical analysis a Gaussian chain is generally used to model the polymer molecule and a slit-like or cylindrical pore serves to model the adsorbent.

A theory² (see also ref 3) has been developed for slit-like pores which describes the equilibrium properties of an infinitely-long single macromolecule at an arbitrary energy of interaction between the polymer and the adsorbent. The corresponding theory for cylindrical pores has been developed only for a sorption-inactive surface, i.e. entropy losses of the macromolecule only are taken into account¹.

Here a rigorous analytical theory is developed, describing the behaviour of macromolecules in cylindrical pores with an arbitrary energy of interaction (attraction or repulsion) between the polymer chain units and the adsorbent surface. Comparison of various theories permits us to establish features of the behaviour of macromolecules on porous adsorbents that are common

to adsorbents with different pore geometry.

A theory for the adsorption of flexible chains onto the outer surface of a cylinder of arbitrary radius is also proposed. The limiting cases of this theory are the adsorption of macromolecules on a plane^{1,2} and on a thin adsorbing thread^{1,3}.

MODEL USED AND CALCULATION

We consider a flexible polymer chain without volume interactions, modelled by a random walk on a simple cubic lattice. The inner (or outer) surface of a tube of square section with side $D=2R+1$ (Figure 1) serves as adsorbent. The length of the lattice constant which for this model coincides with the size of the statistical (Kuhn) chain segment is taken as unit length.

Macromolecule in a cylindrical pore

Recurrent equations^{2,12,13} are used to describe the configuration of a polymer chain within the space enclosed by the tube walls. The first chain unit is placed

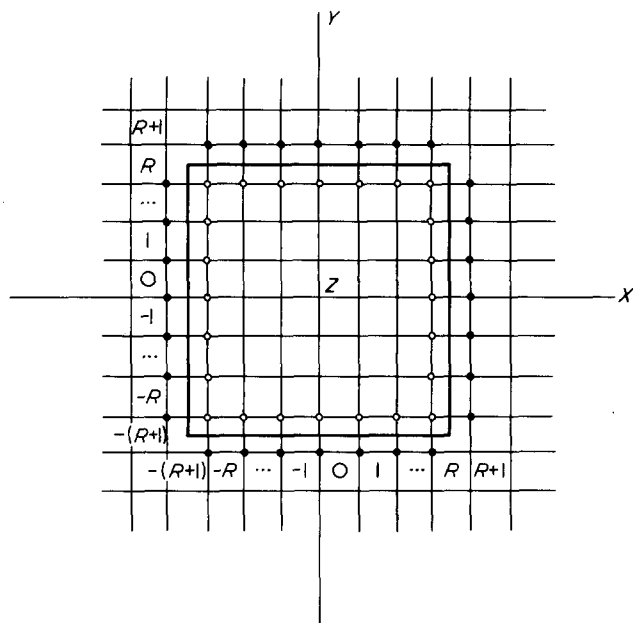


Figure 1 Section of a cylindrical pore. Open circles designate junctions on the inner surface and filled circles designate junctions on the outer surface

along the axis of the cylinder Z . Any unit arriving at the inner surface of the tube (open circles in Figure 1) including its 'corners' gains the adsorption energy $-\epsilon$ (here and below energy values are expressed in units of kT). The statistical properties of this chain ensemble are determined entirely by the two-dimensional discrete probability distribution function. Let $P(X, Y; N)$ be the unnormalized probability of the arrival of the chain at the axis $x = X, y = Y, -\infty < Z < \infty$, at the N th step.

Let us introduce the operator \hat{E}_x^+ which changes the x coordinate to $x + 1$:

$$P(x + 1, y; N) = \hat{E}_x^+ \{P(x, y; N - 1)\}$$

Similar operators $\hat{E}_x^-, \hat{E}_y^+, \hat{E}_y^-$ are also introduced.

Then the operator

$$\hat{E} = \hat{E}_x^+ + \hat{E}_x^- + \hat{E}_y^+ + \hat{E}_y^- + 2$$

is the sum of single chain shifts per step. In the absence of contact with the tube surface the walks in all six directions are equally probable

$$P(x, y; N + 1) = \frac{1}{6} \hat{E} \{P(x, y; N)\} \quad (1)$$

For the arrival of chain units at the tube surface boundary conditions should be fulfilled:

$$P[\pm R, y; N + 1] = \frac{1}{6} e^{-\epsilon} \{ \hat{E} [P[\pm R, y; N]] - P[\pm R + 1, y; N] \} \quad |y| < R$$

$$P[x, \pm R; N + 1] = \frac{1}{6} e^{-\epsilon} \{ \hat{E} [P[x, \pm R; N]] - P[x, \pm R + 1; N] \} \quad |x| < R \quad (2)$$

$$P[\pm R, \pm R; N + 1] = \frac{1}{6} e^{-\epsilon} \{ \hat{E} [P[\pm R, \pm R; N]] - P[\pm(R + 1), \pm R; N] - P[\pm R, \pm(R + 1); N] \}$$

The initial condition

$$P(x, y; 0) = \delta_{x,0} \cdot \delta_{y,0} \quad (3)$$

reflects the attachment of one chain end to the axis of the cylinder Z and $\delta_{ik} = \begin{cases} 1 & i=k \\ 0 & i \neq k \end{cases}$ is the Kronecker delta.

Equations (1)–(3) take into account all possible configurations of a polymer chain in a tube with adsorbing walls. To facilitate the solution of the system of equations (1)–(3), equations describing the random walk outside the tube are added

$$P(x, y; N + 1) = \frac{1}{6} \hat{E} \{P(x, y; N)\} \quad |x| > R \vee |y| > R \quad (4)$$

The introduction of equation (4) means that some configurations of the polymer chain pass to the outside through the tube walls but do not return into the tube. These configurations will be denoted as 'absorbed' by the adsorbent.

The method of generating functions¹³ is used to solve the system of equations (1)–(4). We introduce functions:

$$G(\alpha, \beta; t) = \sum_{N=0}^{\infty} t^N \sum_{x=-\infty}^{\infty} \sum_{y=-\infty}^{\infty} P(x, y; N) e^{i(\alpha x + \beta y)} \quad (5)$$

and

$$g(x, y; t) = \sum_{N=0}^{\infty} t^N \cdot P(x, y; N)$$

It follows from equation (5) that $g(x, y; t)$ is the grand partition function of an ensemble of chains arriving at the axis with coordinates (x, y) . Hence, the grand partition function $\Xi(t)$ of chains in the pore is given by:

$$\Xi(t) = \sum_{\substack{|x| \leq R \\ |y| \leq R}} g(x, y; t) \quad (6)$$

If summing over $-\infty < x, y < \infty$ is carried out, the result is a grand partition function $\Xi(t) = G(0, 0; t)$ for an ensemble containing both chains in the tube and chains 'absorbed' by the adsorbent.

Since the functions $g(x, y; t)$ are the Fourier series coefficients of the function:

$$G(\alpha, \beta; t) = \sum_{x=-\infty}^{\infty} \sum_{y=-\infty}^{\infty} g(x, y; t) e^{i(\alpha x + \beta y)} \quad (7)$$

it is possible to find $g(x, y; t)$ using an inverse Fourier transformation:

$$g(x, y; t) = \frac{1}{4\pi^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} G(\alpha, \beta; t) e^{-i(\alpha x + \beta y)} d\alpha d\beta \quad (8)$$

The closed expression for the generating function $G(\alpha, \beta; t)$ can be obtained from equations (1)–(4). For this purpose equations (1), (2) and (4) are multiplied by $\exp[i(\alpha x + \beta y)]$ and summed over all $-\infty < x, y < \infty$. These expressions multiplied by t^{N+1} are summed over values of N from zero to infinity, subsequently applying the initial condition (3) and resulting in a symmetrical problem:

$$g(l_1, l_2; t) = g(l_2, l_1; t) \tag{9}$$

$$g(l_1, l_2; t) = g(-l_1, l_2; t)$$

Omitting intermediate transformations similar to those described previously^{1,3} we obtain:

$$G(\alpha, \beta; t) = \sum_{m=0}^R 2^{-\delta m, R} (1 - e^{-\varepsilon}) g(m, R; t) - \frac{t}{6} g(m, R + 1; t) \cdot 2^{-\delta m, 0}$$

$$\sum_{k_2 = \pm 1} \sum_{k_1 = \pm 1} \frac{\exp[i(k_1 \alpha + k_2 R \beta)] + \exp[i(k_1 m \beta + k_2 R \alpha)]}{1 - t(1 + \cos \alpha + \cos \beta)^3}$$

$$+ [1 - \frac{t}{3}(1 + \cos \alpha + \cos \beta)]^{-1} \tag{10}$$

Let us introduce the vector \vec{g} , comprised of two subvectors the components of which are: $g(m, R; t)$, $g(m, R + 1; t)$; $m = 0, 1, \dots, R$.

Integration of equation (10) successively multiplied by $\exp[-i(\alpha x + \beta y)]$ and equation (8) gives a system of equations:

$$\vec{g} = \Psi^{-1} \cdot \vec{I} \tag{11}$$

where the matrix Ψ , comprised of four submatrices, is given by

$$\Psi = \left\{ \begin{array}{c|c} \delta_{l,m} - 2^{-\delta m, l} \cdot q \cdot \mathcal{F}_{R,R,m,l} & \frac{t}{6} \mathcal{F}_{R,R,m,l} \\ \hline -2^{-\delta m, l} \cdot q \cdot \mathcal{F}_{R,R+1,m,l} & \delta_{l,m} + \frac{t}{6} \mathcal{F}_{R,R+1,m,l} \end{array} \right\} \tag{12}$$

Coefficients:

$$\mathcal{F}_{\rho, \nu, \mu, \lambda} = 2^{-\delta_{\rho, 0}} \sum_{k_1 = \pm 1} \sum_{k_2 = \pm 1} (I_{k_1 \rho - \nu, k_2 \mu - \lambda} + I_{k_2 \mu - \nu, k_1 \rho - \lambda}) \tag{13}$$

are expressed as the sum of integrals:

$$I_{r,s} = \frac{1}{4\pi^2} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{\exp[i(\alpha r + \beta s)] d\alpha d\beta}{1 - \frac{t}{3}(1 + \cos \alpha + \cos \beta)} \tag{14}$$

that are the grand partition functions for an ensemble of chains starting at the origin and walking in an unrestricted space and ending on the line $x = r$, $y = s$ ^{1,3}.

Vector \vec{I} in equation (11) consists of integrals $I_{m,R}$ and $I_{m,R+1}$; similarly vector \vec{g} consists of functions $g(m, R; t)$ and $g(m, R + 1; t)$.

The equilibrium value of the chemical potential is found from the grand partition function $\Xi(t)$ divergence condition. Since this sum is expressed by functions g , it follows from equation (1) that for divergence of $\Xi(t)$:

$$\text{Det}(\Psi) = 0 \tag{15}$$

The smallest root in equation (15) determines the free energy of a chain unit, which depends on the energy of

interaction between the polymer and the adsorbent, $-\varepsilon$, and the pore size, D .

Adsorption on a cylindrical surface

We consider a macromolecule located outside the cylindrical sorbent which can be adsorbed on its outer surface (Figure 1, filled circles).

Outside the sorbent random walks are equally probable in all directions:

$$P(x, y; N + 1) = \frac{1}{6} \hat{E} \{ P(x, y; N) \} \tag{16}$$

$$|x| > R + 1 \vee |y| > R + 1 \vee x = \pm(R + 1) \wedge y = \pm(R + 1)$$

Boundary conditions are given by:

$$P[\pm(R + 1), y; N + 1] = \frac{1}{6} e^{-\varepsilon} \{ \hat{E}[P[\pm(R + 1), y; N]] - P[\pm R, y; N] \} \quad |y| < R + 1 \tag{17}$$

$$P[x, \pm(R + 1); N + 1] = \frac{1}{6} e^{-\varepsilon} \{ \hat{E}[P[x, \pm(R + 1); N]] - P[x, \pm R; N] \} \quad |x| < R + 1$$

For convenience the initial conditions are assumed to be symmetrical: chains start at any point on the surface of the adsorbent with equal probability:

$$P[\pm(R + 1), y; 0] = P[x, \pm(R + 1); 0] = e^{-\varepsilon} / 4(2zR + 1) \tag{18}$$

$P[x, y; 0] = 0$ for all other values of x and y .

Recurrent equations for the 'absorbed' chains are given by:

$$P(x, y; N + 1) = \frac{1}{6} \hat{E} \{ P(x, y; N) \} \tag{19}$$

$$|x| < R + 1 \wedge |y| < R + 1$$

The system of equations (16)–(19) is similar to equations (1)–(4) and can be obtained from the latter by substituting indices $R \rightleftharpoons R + 1$. This corresponds to the replacement of the inner surface of the tube by its outer surface. The third equation of equations (2) is an exception. By introducing the generating functions (5) it is possible to write the grand partition functions of 'absorbed' Ξ_p and 'unabsorbed' Ξ_s chains:

$$\Xi_p(t) = \sum_{\substack{|x| \leq R \\ |y| \leq R}} g(x, y; t) \tag{20}$$

$$\Xi_s(t) = \tilde{\Xi}(t) - \Xi_p(t) = G(0, 0; t) - \sum_{|x| \leq R, |y| \leq R} g(x, y; t) \tag{21}$$

Transformations similar to those described above give:

$$G(\alpha, \beta; t) = \sum_{m=0}^R \left\{ (1 - e^{-\varepsilon}) g(m, R + 1; t) - \frac{t}{6} g(m, R; t) + \frac{1}{4(2R + 1)} \right\} \cdot 2^{-\delta_{m, 0}} \times$$

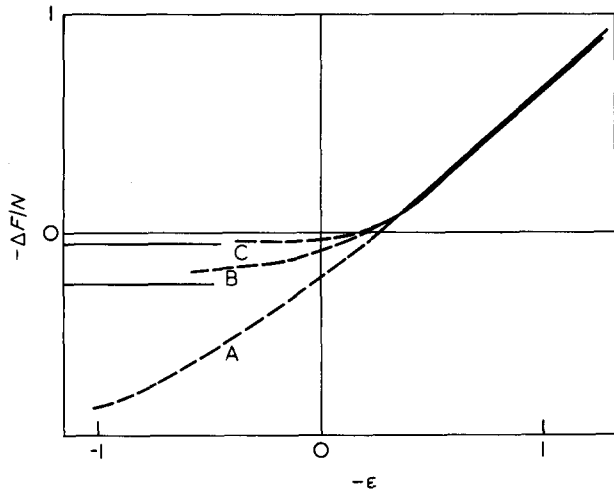


Figure 2 Conformational free energy per unit of a model chain in cylindrical pores of different width vs. polymer-adsorbent interaction energy. $D = 3$ (A), 5 (B) and 11 (C)

$$\sum_{k_1=\pm 1} \sum_{k_2=\pm 1} \frac{\exp[i(k_1 m \alpha + k_2 (R+1) \beta)] + \exp[i(k_1 m \beta + k_2 (R+1) \alpha)]}{1 - t(1 + \cos \alpha + \cos \beta)/3} \quad (22)$$

The following expression is a specific case of equation (22) at $R=0$,

$$G(\alpha, \beta; t) = \left[(1 - e^{-\epsilon})g(1, 0; t) - \frac{t}{6}g(0, 0; t) + \frac{1}{4} \right] \times \frac{2(\cos \alpha + \cos \beta)}{1 - t(1 + \cos \alpha + \cos \beta)/3} \quad (23)$$

It was obtained previously¹³ for a flexible macromolecule adsorbed on a thread of unit thickness.

Further transformations lead to equation (15) with the matrix

$$\Psi = \left\{ \begin{array}{c|c} \delta_{l,m} - q \cdot \mathcal{F}_{R+1,R+1,m,l} & \frac{t}{6} \mathcal{F}_{R+1,R+1,m,l} \\ \hline -q \cdot \mathcal{F}_{R+1,R,m,l} & \delta_{l,m} + \frac{t}{6} \mathcal{F}_{R+1,R,m,l} \end{array} \right\} \quad (24)$$

Equation (15) was solved using a computer for matrices (12) and (24) with coefficients (13) and (14).

The dependences of the free energy and other thermodynamic characteristics of chains on the adsorption energy $-\epsilon$ and the pore size D were calculated.

RESULTS AND DISCUSSION

Adsorption in cylindrical pores

Free energy. Figure 2 shows the conformational free energy per chain unit, F , versus the energy of interaction between the polymer and the adsorbent, $-\epsilon$, for chains in cylindrical pores of different diameters.

The values are calculated from the conformational free energy $F_0 = -\ln 6$ of an unrestricted chain (per unit). In further discussion we will use the terms 'stationary' and 'mobile' phases (as used in chromatography) to designate the states of macromolecules inside the pores and in the free space, respectively.

Figure 2 shows that two ranges of energy $-\epsilon$ can be distinguished. In the left-hand range (the molecular-sieve range) $-\Delta F = -(F - F_0)$ is less than zero and, hence, the residence of the macromolecule in the pore is thermodynamically unfavourable. In the right-hand range (adsorption range) $-\Delta F$ is greater than zero and the residence of the chain in the pore is thermodynamically more favourable than in solution. The energy $-\epsilon = -\epsilon_c$ separating these regions (where $-\Delta F = 0$) will be called the critical point.

Molecular-sieve range. In the molecular-sieve range below the critical point ($-\epsilon < -\epsilon_c$) the features characteristic of macromolecules in exclusion (gel permeation) chromatography are exhibited: the existence of macromolecules in the mobile phase (in solution) corresponds to thermodynamic equilibrium and the arrival of the macromolecule at the pore is a fluctuation, the probability of which

$$w = \frac{V_p \cdot \exp(-NF_p)}{V_0 \cdot \exp(-NF_0) + V_p \cdot \exp(-NF_p)} \approx \frac{V_p}{V_0} \cdot \exp(-N \cdot \Delta F) \quad (25)$$

decreases exponentially with increasing chain length (V_0 and V_p are volumes of the mobile and the stationary phase, respectively).

At $-\epsilon = 0$ the following expansion is valid for long chains in slit-like pores²:

$$-\Delta F = \frac{\Delta S}{k} = \ln \left[\frac{2}{3} + \frac{1}{3} \cos \frac{\pi}{(D+1)} \right] \approx -\frac{\pi^2}{6} (D+1)^{-2} \quad (26)$$

The analysis of expressions obtained for the pores of cylindrical and spherical shapes at $-\epsilon = 0^1$ shows that at $D \geq 5$ the following equation is valid:

$$-\Delta F \approx -\frac{\pi^2}{6} K \cdot (D+1)^{-2} \quad (27)$$

The values of the coefficient K for various models are listed in Table 1.

Using results reported by Di Marzio and Rubin² we analysed the dependence $-\Delta F(D)$ over the entire molecular-sieve range, i.e. at $-\epsilon < -\epsilon_c$. It was found that equation (27) is fulfilled if the geometrical width of the pore D is replaced by:

$$D^* = D - 2 + 2 \cdot \frac{1 - \exp(\epsilon_c)}{\exp(\epsilon) - \exp(\epsilon_c)} \quad (28)$$

The dependences of D^* are shown in Figure 3. The value of D^* can be treated as an effective pore width.

Table 1 Values of K (coefficient in equation 27) for various models

| Pore model | Chain model | |
|------------|-------------|-----------------|
| | Lattice | Without lattice |
| Slit | 1 | 1 |
| Cylinder | 2 | 2.344 |
| Sphere | — | 4 |

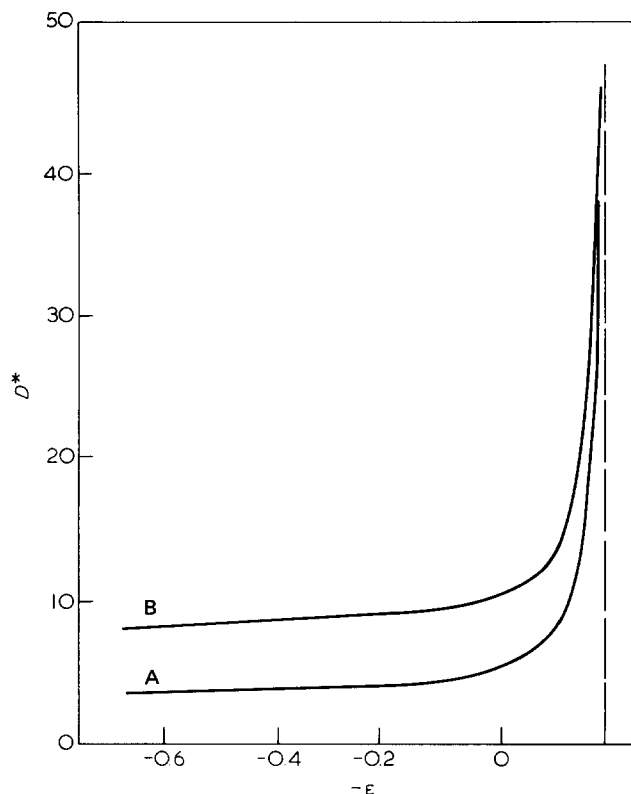


Figure 3 Effective pore width vs. polymer-adsorbent interaction energy. Geometrical width of pores at $-\varepsilon = 0$ are $D = 5$ (A) and 10 (B)

At $-\varepsilon = 0$, D^* is equal to D . When it is assumed that the repulsion energies $-\varepsilon$ are less than zero, the macromolecule avoids contact with the sorbent surface and is located completely inside the pore. This is equivalent to a decrease in the pore diameter (at $-\varepsilon \rightarrow -\infty$ $D^* \rightarrow D - 2$). In contrast, the condition $0 < -\varepsilon < -\varepsilon_c$ is equivalent to a widening of the pore. As $-\varepsilon$ approaches the critical value, $-\varepsilon_c$, the effective width of the pore D^* tends to infinity so that at the critical point the macromolecules are not influenced by the porous structure of the adsorbent.

Equations (27) and (28) show that the dependence of $(K/\Delta F)^{1/2}$ on

$$\xi = \frac{1 - \exp(\varepsilon_c)}{\exp(\varepsilon) - \exp(\varepsilon_c)}$$

should be linear and identical for different models. These dependences, plotted as precise equations and as approximate equations (27) and (28) are shown in Figure 4. The value of $\Delta F^{-1/2}(\xi)$ deviates from linearity only for narrow pores or at energies $-\varepsilon \approx -\varepsilon_c$. It follows from equations (27) and (28) that the dependence $\Delta F^{-1/2}(D)$ should also be linear at constant $-\varepsilon$. In this case the value of the intercept

$$(6K\pi^2)^{1/2} \cdot \frac{1 - \exp(\varepsilon_c)}{\exp(\varepsilon) - \exp(\varepsilon_c)}$$

tends to zero in the range of super-exclusion ($-\varepsilon \ll -\varepsilon_c$) and increases as the attractive forces between the polymer and the adsorbent, tending to infinity at $-\varepsilon \rightarrow -\varepsilon_c$. Hence, the low value of the intercept can serve as a criterion for the absence of adsorption effects.

For Gaussian chains the relationship between the molecular weight of the chain and its dimensions (e.g. the mean square radius of gyration, $\overline{S^2}$) is known to be linear. Consequently, in the pre-critical range the probability of the arrival of a macromolecule in the pore is given by:

$$w \approx \frac{V_p}{V_0} \exp\left\{-K\pi^2 \frac{\overline{S^2}}{(D^*)^2}\right\} \quad (29)$$

Equations (29) and (28) show that in the exclusion range (at $-\varepsilon < 0$) the pore is 'open' to a great extent only to those macromolecules of size comparable to the geometrical dimensions of the pore ($\overline{S^2} \leq (D^*)^2 \approx D^2$). At $\overline{S^2} \gg D^2$ the macromolecules arrive only seldom in the pores and are virtually 'excluded' from them.

Figure 5a shows the molecular-weight dependence of retention volume:

$$V_e = V_0 + V_p \cdot K_d = V_0 + V_p \cdot \exp(-N \cdot \Delta F) \quad (30)$$

calculated for cylindrical pores at $-\varepsilon = 0$. Since it is desirable to use the linear part of the dependence $V_e = V_e(N)$ for effective separation, it is necessary to choose adsorbents with different pore sizes for different molecular weight ranges or to use columns containing specifically-selected adsorbent mixtures.

However, there is another method which does not require the use of different adsorbents. In this case a slight attraction energy between the polymer segments and the adsorbent surface should exist. Equation (28) shows that

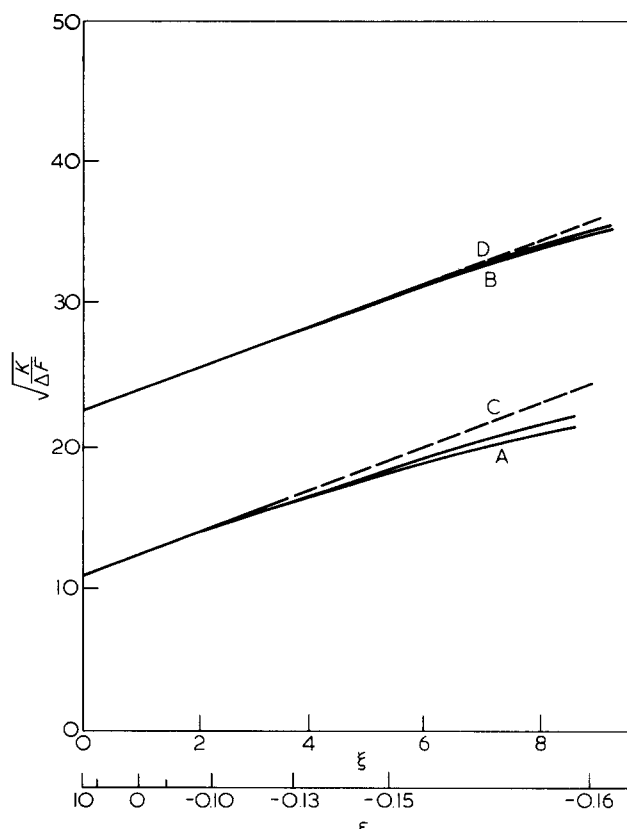


Figure 4 Value of $(K/\Delta F)^{1/2}$ vs. $(1 - \exp(\varepsilon_c))/(\exp(\varepsilon) - \exp(\varepsilon_c))$ for slit-like (A, B) and cylindrical (C, D) pores of width $D = 15$ (A, C) and 30 (B, D). Broken lines correspond to asymptotic equations (27) and (28). The values of K are given in Table 1

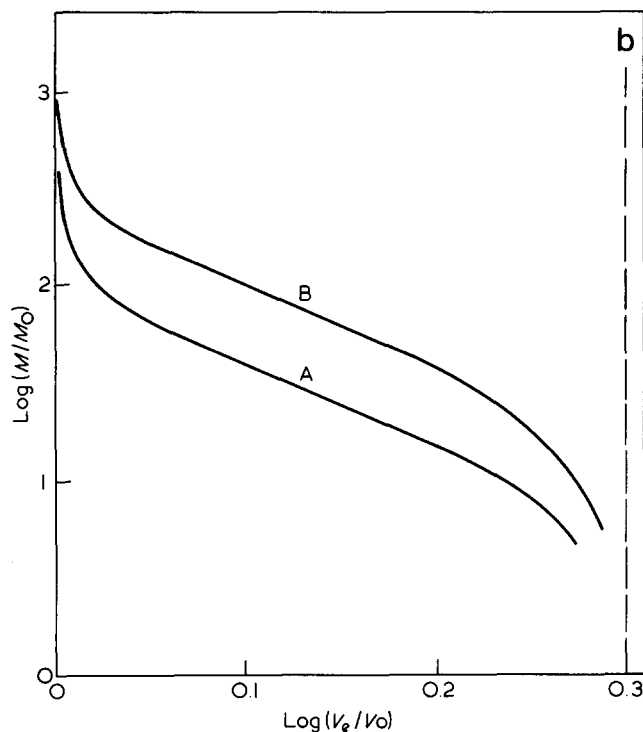
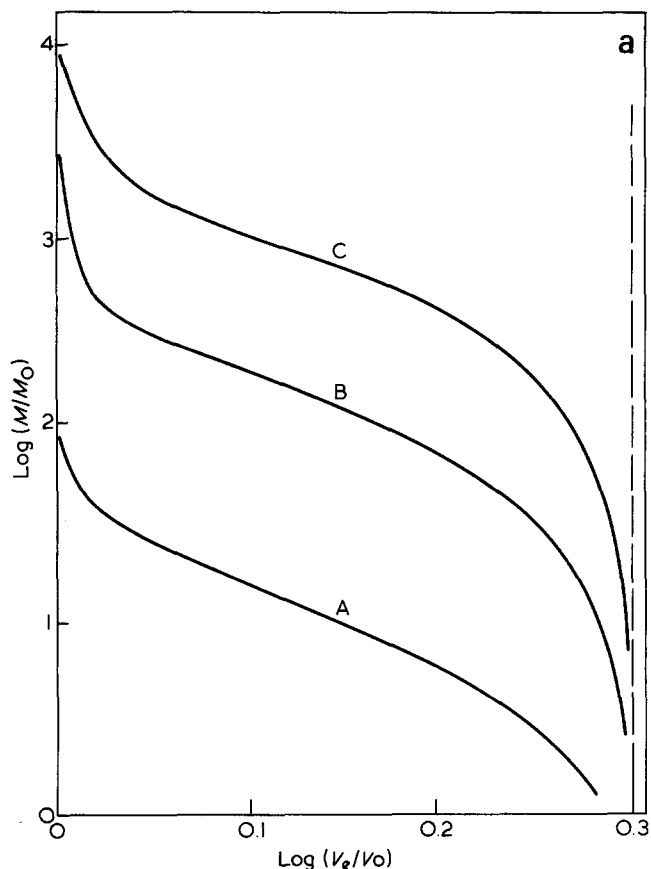


Figure 5 Molecular weight dependence of retention volume (a) for cylindrical pores of width $D = 5$ (A), 20(B) and 50(C) at $-\epsilon = 0$ and (b) for pores of width $D = 9$ at $-\epsilon = 0$ (A) and 0.15(B). $V_0/V_p = 1$

this will lead to an increase in effective pore size, D^* , and hence the probability of the arrival of long chains in the pores will increase and the retention volume will increase correspondingly (Figure 5b). The change in adsorption energy in the pre-critical range makes it possible

to increase the retention volume to $V_e = V_0 + V_p$ without changing the molecular-sieve-type of chromatography.

Adsorption range. The adsorption range ($-\epsilon > -\epsilon_c$) is characterized by a decrease in conformational free energy when the macromolecule arrives in the pore (Figure 2): $-\Delta F$ is greater than zero. At $-\epsilon \gg -\epsilon_c$ the free energy per unit of the adsorbed chain is given by:

$$-F \approx -\epsilon + \Delta S_{ads}/k \quad (31)$$

where S_{ads} is the entropy of the adsorbed chain unit. Correspondingly, the probability of arrival of macromolecules into the pore:

$$w \approx 1 - \frac{V_0}{V_p} \cdot \exp\{-N(F_0 + S_{ads}/k)\} \cdot \exp(N\epsilon) \approx 1 \quad (32)$$

is close to unity regardless of the width of the pore.

Comparison of free energies of the macromolecules adsorbed into pores of different shape (Figure 6) shows that in the adsorption range the dependence on the pore shape is also virtually absent.

Hence, in the adsorption range, chromatographic separation depends only slightly on the size and shape of

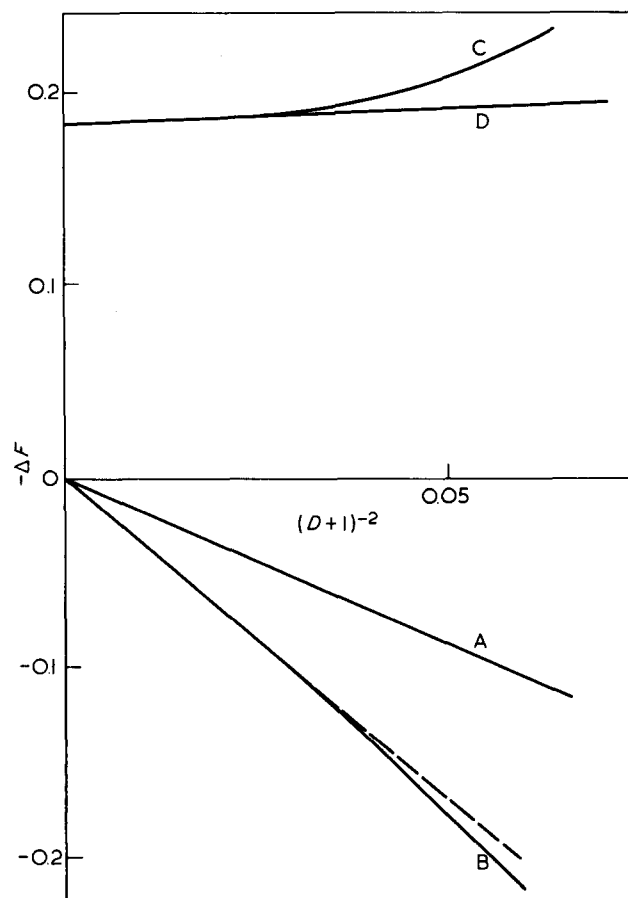


Figure 6 Conformational free energy of the chain vs. pore width in the molecular sieve range at $-\epsilon = 0$ (A, B) and in the adsorption range at $-\epsilon = 0.5$ (C, D) for slit-like (A, C) and cylindrical (B, D) pores

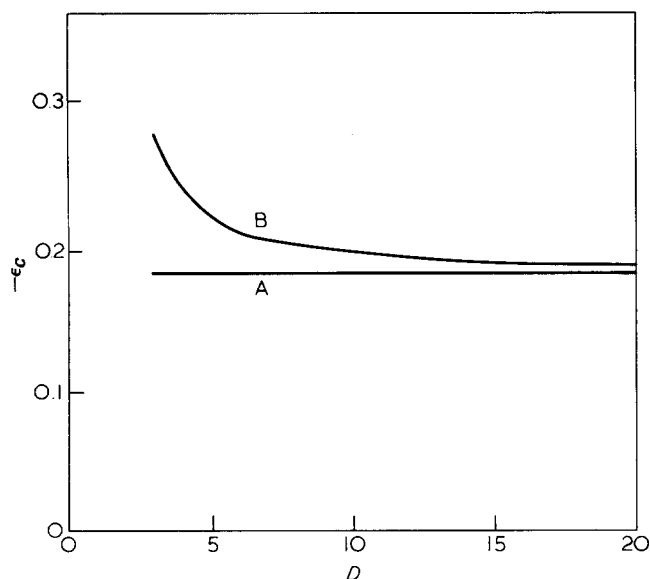


Figure 7 Critical energy vs. width of adsorbent pores for slit-like (A) and cylindrical (B) pores

the pores of the adsorbent and is virtually completely determined by the values of N and ε . According to equation (32), residence in pores is more favourable thermodynamically for longer macromolecules. However, at high adsorption energies, at $-\varepsilon > -\varepsilon_c$, the adsorption of macromolecules in pores is determined by the kinetics of the process rather than by its thermodynamics. More mobile, small polymer molecules penetrate the pores first and are adsorbed there, filling them up. The displacement of short chains by long chains is favourable from the thermodynamic viewpoint but occurs so slowly that equilibrium is not usually attained during the experiment. Hence, adsorption chromatography proceeds reversibly only near the critical point (at $-\varepsilon \gtrsim -\varepsilon_c$).

Critical conditions. The molecular-sieve and the adsorption ranges are separated by the critical point $-\varepsilon = -\varepsilon_c$ at which the conformational free energies of the macromolecule in the mobile and the stationary phases are the same. At the critical point entropy losses of the macromolecule in the pore due to a decrease in the number of chain conformations are completely compensated by the gain in energy caused by the interaction of units with the pore surface.

Consequently, under critical conditions the probability of the arrival of the macromolecule in the pore:

$$w_c = V_p / (V_0 + V_p) \quad (33)$$

no longer depends on the molecular weight of the polymer, and the size and shape of pores and is determined only by the ratio of the free geometrical volume to the pore geometrical volume. The change in retention volume $V_e = V_0 + V_p$ under critical conditions when V_e no longer depends on molecular weight (Figure 5) permits an experimental determination of the extent of porosity V_p/V_0 .

Our investigations show¹⁴ that the molecular-sieve range and the adsorption range and the position of the point of separation between them are retained with finite chains of any length.

For slit-like pores the position of the critical point does

not depend on the pore width and coincides with the energy required for the start of adsorption on a planar surface (for a flexible chain on a cubic lattice $-\varepsilon_c = \ln 6/5 = 0.182$).

For cylindrical pores the dependence of $-\varepsilon_c$ on D is slight (Figure 7) and disappears for adsorbents with wide pores. The reason for this dependence is that in this model 'corners' exist, differing in their properties from the rest of the surface. A chain arriving at a 'corner' cannot leave the sorbing surface at the next step. When the pore width decreases, the relative contribution of 'corner' states, i.e. the degree of surface inhomogeneity, increases and this leads to an increase in the critical energy.

Presumably, in real pores there is no analogy with these 'corners'. However, when the curvature of the pore surface is great (radius is small) the conditions for bonding of the units to the surface can change, altering the critical energy in narrow pores. However, this effect should occur only in very narrow pores.

It should be noted that displacement of the critical point can also occur for other reasons. For example, in narrow pores the volume of the macromolecule itself can be very important.

For adsorbents with wider pores, the critical energies for the passage of the macromolecules into both cylindrical and slit-like pores are equal and are independent of pore size. Consequently, the critical energy is a universal property of the polymer-solvent-adsorbent systems.

It has been shown¹⁵ that:

$$\varepsilon_c = \ln \left(\frac{Z_f + Z_v}{2Z_v} \right) \quad (34)$$

where Z_f and Z_v are the number of possible chain conformations on the adsorbent surface and inside its volume, respectively. Hence, if the statistical sums for a chain unit in the free volume and on the surface are known, it is possible to calculate $-\varepsilon_c$ for any model.

Critical conditions have been found experimentally for polystyrene on silica gel^{11,16}. They are achieved in a mixed solvent, cyclohexane-benzene-acetone at a volume concentration of acetone, x , of 0.031. By varying the value of x ¹⁶ or the temperature¹¹ it is possible to pass reversibly and continuously from the molecular-sieve range into the adsorption range.

For copolymers consisting of two components, one of which exhibits high sorption capacity, the value of $-\varepsilon_c$ depends on copolymer composition. This makes it possible to use adsorption chromatography to determine the compositional inhomogeneity of heteropolymers¹⁷.

Structure in restricted volumes and the nature of the transition of polymer chains from solution into pores

The structure of the macromolecule inside the pore will be characterized by the degree of adsorption, i.e. by the average fraction of chain units θ in contact with the inner surface of the pore. It has been shown² that the structure of long macromolecules inside slit-like pores can be of three types depending on the energy of interaction between the polymer and the pore surface. In the pre-critical (molecular-sieve) range at $-\varepsilon < -\varepsilon_c$ the macromolecule is a coil more or less flattened by the pore walls. The degree of chain bonding to the pore walls is not high and decreases rapidly with increasing pore width D ($\theta_s = 4\pi^2 D^{-3}$). θ_s is

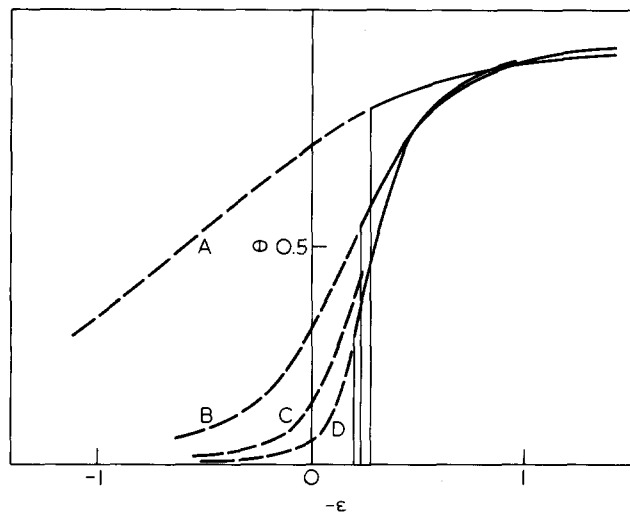


Figure 8 Degree of chain bonding vs. adsorption energy in cylindrical pores of width $D = 3$ (A), 5 (B), 7 (C) and 11 (D). Broken line represents chain behaviour in closed pores; a discontinuity in the full lines reflects the possibility of passage of the macromolecule from the pore into the solvent volume. $V_0/V_p = 1$

the degree of adsorption in slit-like pores. In contrast, in the adsorption range at $-\varepsilon > -\varepsilon_c$ the long parts of the macromolecule are located along the pore walls and alternate with more or less short loops. In this range the degree of sorption does not depend on the pore size ($\theta \sim D^0$) and is determined only by the adsorption energy.

At the critical point the chain units are distributed in the pore volume regularly and $\theta_s = 5D^{-1}/3$. Figure 8 shows the function $\theta(\varepsilon)$ for macromolecules in cylindrical pores with different diameters (Figure 8 refers to molecules unable to leave the pore, e.g. molecules bound to the pore surface by one unit).

The dependence of θ on $-\varepsilon$ and D in the pre-critical range can easily be determined by equations (27) and (28), valid virtually over the entire range $-\varepsilon < -\varepsilon_c$ with the exception of $-\varepsilon = -\varepsilon_c$. Since θ is equal to $\partial F/\partial \varepsilon$, it follows from equations (27) and (28) that:

$$\theta = \frac{\pi^2}{6} K \cdot \frac{4(1 - e^{\varepsilon_c})e^{\varepsilon}}{(D^*)^3(e^{\varepsilon} - e^{\varepsilon_c})^2} \quad (35)$$

Equation (35) shows that in the pre-critical range the degree of bonding is inversely proportional to the cube of the effective width of the pores regardless of their shape.

At the critical point equations (27) and (28) do not hold. Figure 9 shows that in this case θ_c is proportional to D^{-1} (if the value of D is not too low) and the slope of this straight line is steeper for a cylindrical pore than for a slit-like pore. Analysis shows that for cylindrical pores:

$$(\theta_c)_{\text{cyl}} = 3D^{-1} \quad (36)$$

In the sorption range ($-\varepsilon > -\varepsilon_c$) the degree of bonding is determined virtually only by the sorption energy $-\varepsilon$ regardless of the size and shape of the pores.

We now consider the case of a macromolecule which can pass from the pore into the solvent and vice versa. This occurs in chromatography. The passage of a long Gaussian chain from an unrestricted volume into a slit-like pore takes place by a first-order phase transition³. In the mobile phase the energy of the Gaussian chain is zero.

The average energy for an ensemble of chains coexisting as mobile and stationary phases is then given by:

$$E(\varepsilon) = N \cdot \theta(\varepsilon) \cdot \varepsilon \cdot w(\varepsilon) \quad (37)$$

Using equations (25), (32) and (33) at the limit $N \rightarrow \infty$ we obtain:

$$w(\varepsilon) = \begin{cases} 0 & -\varepsilon < -\varepsilon_c \\ (1 + V_0/V_p)^{-1} & -\varepsilon = -\varepsilon_c \\ 1 & -\varepsilon > -\varepsilon_c \end{cases} \quad (38)$$

Hence, the energy of the adsorbed chain is changed abruptly with the evolution of latent heat of adsorption ΔE , under critical conditions:

$$\Delta E = -N \cdot \varepsilon_c \cdot \Delta \theta_c \quad (39)$$

which is equal to $-5N \cdot \varepsilon_c / 3D$ for slit-like pores and $-3N \cdot \varepsilon_c / D$ for cylindrical pores.

For finite chains the average energy changes abruptly in the vicinity of the transition point and the energy distribution function has a bimodal shape³ characteristic of a first-order phase transition in a finite system.

Adsorption on a cylindrical surface

The results of our theory of adsorption of a polymer chain onto the outer surface of a cylinder will now be considered. As mentioned before, one of the chain ends is assumed to be bound to the surface of the adsorbent.

Figure 10 shows the degree of chain bonding to the surface, θ , versus adsorption energy, $-\varepsilon$, at different values of the diameter of the sorbing cylinder D . Curve A representing adsorption on a thread ($D=1$) has been obtained previously¹³ and curve D representing adsorption on a plane ($D=\infty$) is calculated according to the theory¹². Figure 10 shows that the macromolecule is more highly sorbed on a surface with smaller curvature $\rho \sim D^{-1}$. However, with even a slight increase in the thickness of the adsorbing cylinder, functions $\theta(\varepsilon)$ for a cylinder and for a planar surface become similar. Hence, it

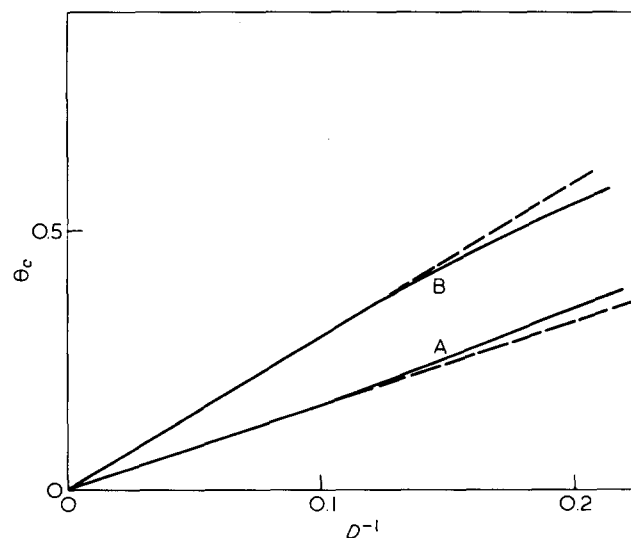


Figure 9 Degree of chain bonding vs. width of slit-like (A) and cylindrical (B) pores under critical conditions. Broken lines represent asymptotic dependences at high D , equation (36)

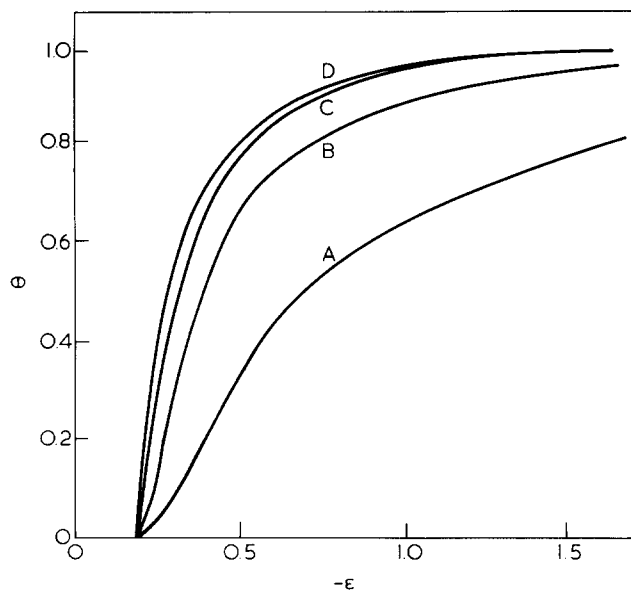


Figure 10 Degree of chain bonding vs. interaction energy $-\epsilon$ for adsorption on a plane (D) and on cylindrical surfaces of diameter $D = 1$ (A), 3(B) and 7(C)

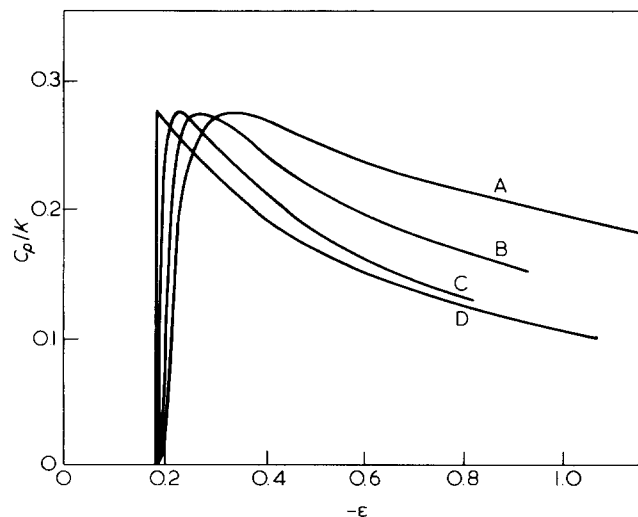


Figure 11 Specific heat calculated per chain unit vs. interaction energy $-\epsilon$ for adsorption on a plane (D) and cylindrical surfaces of diameter $D = 1$ (A), 3(B) and 7(C)

might be expected that the adsorption of macromolecules on a linear surface, e.g. on a polymer matrix, will occur in the same manner as adsorption on a planar surface.

Figure 11 shows the difference in specific heats $C_p/k = \epsilon^2 \partial \theta / \partial \epsilon$ versus adsorption energy $-\epsilon$. It is clear that as the diameter of the adsorbing cylinder increases, the curves of specific heat become steeper and their maxima shift towards $-\epsilon_c = \ln 6/5 \approx 0.182$. In the limit $D \rightarrow \infty$ (planar surface) the specific heat exhibits a discontinuity at the critical point indicating a second-order phase transition. In other cases the maximum specific heat value remains constant and equal to:

$$\left(\frac{C_p}{K}\right)_{\max} = \frac{25}{3} \epsilon_c^2 \quad (40)$$

but a discontinuity in $C_p(\epsilon)$ is absent. Figure 11 shows that $\theta(-\epsilon_c)$ is zero. Analysis shows that in this case all

derivatives also become equal to zero: $\partial^k \theta / \partial \epsilon^k = 0$, $k = 1, 2, \dots, \infty$; this corresponds to an 'infinite-order phase transition'¹⁸.

It should be noted that this situation corresponds to Landau's conclusion¹⁸ that only first-, second- and 'infinite'-order phase transitions exist.

Adsorption on surrounding cylinders

Gels are often used in polymer chromatography as porous adsorbents (stationary phase). Parallel threads (cylinders) randomly located on a cubic lattice at a concentration C can serve as the simplest model for a gel.

Murakami¹⁹ has obtained an expression for the free energy of a long flexible macromolecule located among these cylinders:

$$\frac{F}{N} = \ln \left\{ \frac{1}{2} \left[1 - \frac{2C}{3} + \left(\frac{1}{3} + \frac{2C}{3} \right) q + \sqrt{\left(1 - \frac{2C}{3} \right)^2 + 2 \left(1 - \frac{2C}{3} \right) \left(1 + \frac{2C}{3} \right) q + \left(\frac{1}{3} + \frac{2C}{3} \right)^2 q^2 - \frac{4}{3} q} \right] \right\} \quad (41)$$

where $q = e^{-\epsilon}$ and $-\epsilon$ is the energy of a chain unit arriving at the cylinder surface (the thickness of the cylinder itself is assumed to be zero).

The dependence of $-F/N$ on $-\epsilon$ is shown in Figure 12. It is clear that the behaviour of the macromolecule among the adsorbing cylinders (threads) is qualitatively similar to that of the chain in a slit-like or cylindrical pore. At $-\epsilon < 0$ the residence of the chain among the threads is thermodynamically unfavourable: this range corresponds to molecular-sieving (gel chromatography). For infinitely high forces ($-\epsilon \rightarrow -\infty$) when the threads become impermeable for the polymer chain:

$$-F/N = \ln \left(1 - \frac{2}{3} C \right) \approx \frac{2}{3} C \quad (42)$$

and, hence, the 'gel' behaves as a porous system with effective pore width:

$$\tilde{D} = \frac{\pi}{2} C^{-1/2} \quad (43)$$

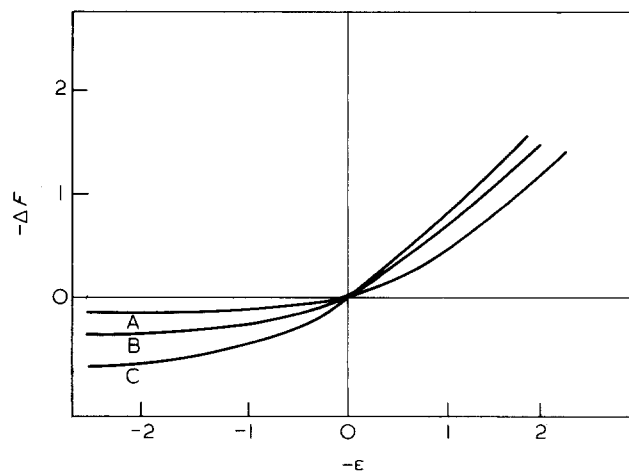


Figure 12 Conformational free energy of the chain (per unit) vs. the interaction energy, $-\epsilon$, among parallel threads of different concentration: $C = 0.2$ (A), 0.5(B), 0.75(C)

At $-\varepsilon > 0$

$$-F/N \approx -\varepsilon + \ln \frac{1+2C}{3} \quad (44)$$

and the residence of the macromolecule among the cylinders is more advantageous than in the free volume.

The point $-\varepsilon = 0$ corresponds to critical behaviour. In this case the probability of the passage of a chain from the free volume into the 'gel' is determined only by the ratio of the volumes:

$$w_c^g \approx \frac{V_{\text{gel}}}{V_0} \quad (45)$$

and the degree of chain bonding abruptly becomes:

$$\theta_c = \frac{1}{6} + \frac{2}{3}C \quad (46)$$

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