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On the Schroeder Paradox for Nonionogenic Polymers

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Abstract—The well-known Schroeder paradox, i.e., the difference in the degrees of swelling of nonionogenic polymers occurring at equilibrium with liquid and vapor phases, has been discussed. A simple example has been presented, which illustrates the unavoidability of different degrees of swelling for a polymer brought into contact with vapor and liquid phases. A simple mechanism has been proposed for the excess swelling of a nonionogenic polymer immersed in a liquid phase, this mechanism being associated with the action of van der Waals and solvation forces at a polymer/solvent interface. The estimation of the contribution from the van der Waals interaction to the "excess" swelling has shown that the predicted values of the "excess" swelling agree with the data of real experiments.

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INTRODUCTION

In [1], we proposed a simple mechanism responsible for the manifestation of the Schroeder effect in ionogenic polymers. This effect, which was discovered nearly 100 years ago [2], remains to be discussed in the literature. It consists in the following. A polymer swells in different manners in vapor and liquid phases, which are at equilibrium with one another, and it is this difference that is the essence of the Schroeder paradox. Polymer swelling is commonly related to the sorption of a solvent (in particular, water). The chemical potentials of solvent molecules in liquid and vapor phases are obviously equal. That is, water molecules having the same chemical potential cause, depending on the phase state of water, different swelling of a polymer, which seems to be paradoxical.

The Schroeder effect plays an essential role in membrane processes, because polymer membranes may simultaneously be in contact with vapor and liquid phases. Therefore, the determination of the mechanism for different swellabilities of polymers is of practical significance. Repeated attempts have been made to explain the paradox theoretically. At the present time, diverse (sometimes, exotic) models have been proposed to explain the Schroeder paradox (a long list of works devoted to its experimental and theoretical study may be found in [3–8]).

In this work, we shall not discuss the previously proposed models. It should only be noted that the Schroeder effect is of a general character; i.e., it is observed in diverse systems. Therefore, its explanation must, in our opinion, be based on fundamental laws rather than on particular models. In [1], we have proposed a universal mechanism for different swellabilities of ionogenic polymers in vapor and liquid phases of water. Therewith, no special models have been used for this purpose. The excess swelling of an ionogenic polymer in a liquid-water phase has been explained by the repulsion between charged groups on the surface of a polymer sample (the shape of a sample is of no significance). Such charged groups result from the passage of mobile ions into water only when a polymer is immersed in its liquid phase. The passage of ions into a vapor phase is known to be impossible at normal temperature.

Estimations have shown that polymer swelling relevant to the electrostatic repulsion agrees with available experimental data. In addition, the proposed mechanism explains the absence of a difference in swelling for some situations. Charge density of surface groups may be low, and the excess swelling may appear to be insufficient to be detected experimentally. In fact, the results obtained in [1] have demonstrated that there is a strong difference in swelling when the Donnan potential at an ion-exchange polymer/water interface is high (nearly 100 mV and above). It is obvious that, the lower the Donnan potential, the smaller the excess swelling of an ionogenic polymer.

The mechanism proposed in [1] is rather universal; however, it is realized only for ionogenic polymers. It is obvious that the swelling of nonionogenic polymers cannot be related to this mechanism. That is, another mechanism must exist that causes the excess swelling of polymers in condensed (in particular, liquid-water) phases as compared with their swelling in vapors, and this mechanism may be of importance for ionogenic polymers as well.

Moreover, work [1] has shown that the Schroeder paradox must indeed be explained on the basis of fundamental laws that are well known, but, for some reason, have not attracted the attention of previous researchers. An important circumstance associated with the Schroeder paradox is the fact that researchers have tried to clarify its mechanism via a change in the state of a solvent in a polymer. In [1], the important fact was, however, noted that the chemical potential of solvent molecules in a polymer may have the same value at completely different states of the latter. Therefore, the explanation for the paradox should be sought through a change in the state of a polymer rather than the state of a solvent. In fact, this approach has been realized in [1] for ionogenic polymers.

In this work, we propose an explanation for the Schroeder paradox in the case of nonionogenic polymers, with this explanation being also based on fundamental laws and having an universal character.

CONSIDERATION OF A SIMPLE MODEL

To clarify the essence of the proposed mechanism, let us, initially, consider the conformational behavior of an isolated macromolecule. This behavior has been described in detail in many monographs; however, we shall partly recollect this description here, because we shall need corresponding data to explain in greater detail the proposed mechanism responsible for the Schroeder effect. It is well known [9] that a freely-jointed polymer chain forms a so-called "Gaussian coil," which is characterized by a linear size R_{g0}. Let us take radius of gyration as this size, which is determined by the following relation:

$$R_{g0}^2 = Anl^2, \tag{1}$$

where A is a coefficient equal to nearly unity, n is the number of segments in a macromolecule, and l is the length of a segment (we do not take into account the fact that Eq. (1) is of an approximate character caused by the ignorance of the effects of the excluded volume, difference between l and the persistent length, etc., because these factors play a secondary role in our consideration). Expression (1) has been derived with no regard to the interactions of segments with each other and with a solvent.

Allowance for diverse interactions leads to changes in the coil size [9]. A change in the macromolecule size is characterized by swelling coefficient α, which is determined as follows:

$$\alpha^2 = \frac{R_g^2}{R_{g0}^2}, \tag{2}$$

where R_g is the radius of gyration of a swollen macromolecule. The swelling coefficient may be either higher or lower than unity [9, 10], depending on the type of a solvent in which a macromolecule occurs. The value of parameter α is determined by intermolecular interactions of components (macromolecule segments and solvent molecules) present in a system [9, 10]. For systems in which the Schroeder paradox has been observed, the swelling coefficient is higher than unity.

Flory has calculated coefficient α and represented it by the following well-known expression [10]:

$$\alpha^5 - \alpha^3 = 2C_M\psi_1\left(1 - \frac{\theta}{T}\right)\sqrt{M}, \tag{3}$$

where C_M is some function (which is of no interest for us); ψ_1 is the entropic parameter of the polymer/solvent interaction; M is the molecular mass of the polymer; and θ is the so-called "θ-temperature," at which the behavior of a polymer molecule is similar to that in an ideal solution. That is, at temperature $T = \theta$, the polymer molecule represents a Gaussian coil. Parameter θ is related to the pair interactions between solvent molecules and macromolecule segments in the following manner [10] (within the framework of the lattice model):

$$\begin{gathered}\theta \propto \left(\Delta u - T\frac{d\Delta u}{dT}\right), \\ \Delta u = u_{ps} - \frac{1}{2}(u_{pp} + u_{ss}),\end{gathered} \tag{4}$$

where u_{ps}, u_{ss}, and u_{pp} are the energies of the interaction between neighboring molecules (segments)—polymer—solvent, solvent—solvent, and polymer—polymer interactions, respectively. Equations (3) and (4) suggest that macromolecule swelling takes place at any temperature, when $\Delta u < 0$ (variation in Δu with temperature is ignored); i.e., when the energy of polymer—solvent "bond" formation is higher than the average rupture energy of the solvent—solvent and polymer—polymer "bonds."

It should be noted that the θ-temperature also corresponds to the curve of the phase separation in a polymer solution and the condition under which the sign of the osmotic pressure is reversed, i.e., the polymer passes from swelling to shrinkage [10].

Now, let us describe the swelling of a macromolecule from a somewhat other point of view. It has been shown [9] that one or another conformational state of a macromolecule may be preset by imposing some external (with respect to the macromolecule) force field. This means that a swollen state of a macromolecule may be created by some force field that stretches it uniformly. It is quite obvious that the set of all possible interactions in a polymer—solvent system creates such stretching force field. In other words, we may believe that a thermodynamically good solvent, in which a polymer coil swells, "stretches" a macromol-

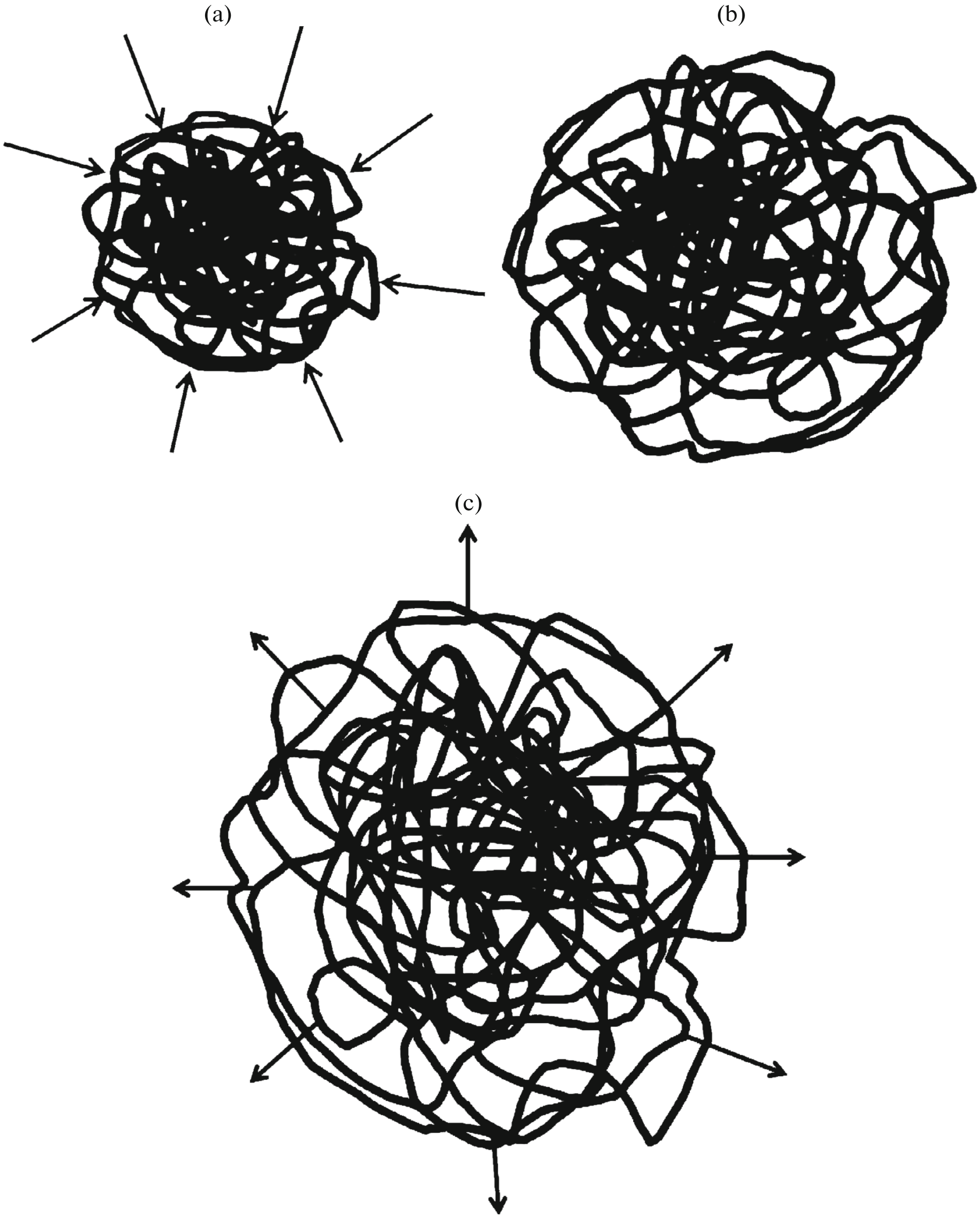

Fig. 1. The structure of a macromolecule and the directions of the forces applied to it in (a) a thermodynamically poor solvent, (b) a θ-solvent, and (c) a thermodynamically good solvent.

ecule (Fig. 1). This stretching is due to the fact that it is more advantageous for macromolecule segments to occur in a region with a larger volume fraction of a solvent. This volume fraction increases while moving away from the coil center, and, accordingly, the segments tend to move away from the center. Drawing an analogy with dissolution, upon the passage through the θ-point to the region of a thermodynamically good solvent, polymer segments begin to behave as if being "dissolved" in it.

In a thermodynamically poor solvent, in which the macromolecule shrinks, the attraction of the segments to each other becomes more advantageous, thus leading to "tightening" of the coil (Fig. 1), so that the macromolecule may pass to the globular state [9, 10]. Langmuir was the first to focus attention on the possibility of coil/globule transition [11]. He suggested that, being suspended in a gas medium (a situation that can hardly be realized in practice), macromolecules must, under the action of van der Waals attraction, roll into balls, the density of which is comparable with the density of a liquid. Since polymer macromolecules do not evaporate (are not dissolved in a gas) at temperatures below the degradation temperature, the gas medium may be considered to be a thermodynamically poor solvent that has no effect on the interaction between segments (because of the low number density of gas phase molecules $\Delta u > 0$). Later, Stockmayer [12] developed Langmuir's idea as applied to macromolecules occurring in thermodynamically poor solvents and described the behavior of macromolecules from the point of view of the interaction between segments and between the segments and a solvent. The quality of a solvent can be regulated by varying its composition. It should, however, be noted that the action of mixed solvents is not purely additive even at the qualitative level. For example, the use of two thermodynamically poor solvents may, in some cases, induce swelling of macromolecules (see, e.g., [13, 14]). We shall not consider such situations, but rather assume that solvent components mixed in a certain proportion act on a polymer in accordance with their thermodynamic characteristics.

Now, let us take a polymer molecule that swells in some solvent. Imagine, that this molecule is transferred into a gas phase. It is obvious that the macromolecule will change its conformation, and, according to Langmuir's notions [9], it will, most probably, pass to a globular state. The formal removal of the solvent due to the transfer of the molecule into the gas phase may be replaced by the introduction of forces compensating for the "stretching" action of solvent molecules. In other words, while the solvent "stretches" the macromolecule, the transfer of the latter into the gas phase is equivalent to the exclusion of the stretching forces or the introduction of compressive forces against the background of the action of the solvent. That is, the transfer of the macromolecule into the gas phase represents the replacement of a thermodynamically good solvent by a poor one. The saturation of the gas medium with a vapor of a good solvent, in which the polymer macromolecule can swell, will have no significant effect. Thus, we obtain a mixture of a thermodynamically poor solvent with a small amount of a good solvent. Polymer molecules will not evaporate into this mixture, because the density of thermodynamically good solvent molecules in the gas phase is low. That is, the gaseous mixture will remain a thermodynamically poor solvent even in the presence of the vapor of the thermodynamically good solvent, and the macromolecule will remain in the globular state. The presence of thermodynamically good solvent molecules only will (possibly) cause some swelling of the globule.

Hence, a polymer chain occurring in a vapor–gas medium is predominantly subjected to compressive forces (the stretching forces are weak because of the low vapor density). The compressive forces are, as has been mentioned above, due to the van der Waals attraction between macromolecule segments. Molecules of the thermodynamically good solvent vapor will be sorbed by the macromolecule and partly suppress this attraction, thereby leading to swelling of the globule. However, this swelling of the polymer molecule will, obviously, be weaker than that in the case of its location in a liquid solvent, because the gas (vapor) phase will remain a thermodynamically poor solvent.

All of the aforementioned shows that the polymer macromolecule will differently swell in a saturated vapor and a liquid solvent. This fact is evident rather than paradoxical.

Let us estimate the value of the compressive forces necessary for the passage of a macromolecule to the globular state. A twofold decrease in the inertia radius of the polymer molecule upon its transition to the globular state seems to be quite real [10]. Hence, the collapse increases the monomer concentration by nearly an order of magnitude. Therefore, the compressive forces must overcome pressure p_s of the segments, this pressure being related to their concentration as follows [9]:

$$p_s = n_s kT \big/ K, \qquad (5)$$

where n_s is the number concentration of the segments in a given volume, k is Boltzmann's constant, K is squared ratio between the size of the region occupied by a polymer and segment length (in our case, it is the ratio between the radius of gyration of a globule and segment length l). The concentration of segments in the Gaussian chain of, e.g., polystyrene with molecular mass $M \approx 10^6$ is nearly 3×10^{20} cm^{-3} ($R_{g0} \approx 20$ nm) [10]. Hence, a pressure of 0.1–1 atm is required for a twofold decrease in the size of a polystyrene molecule. When a macromolecule is placed into a thermodynamically good solvent, stretching stresses relevant to the action of molecular forces arise in it. The stretching stresses are obvious to have the same value, because only the sign of the force is formally changed, while the absolute magnitudes remain the same.

The arising stresses are due to the nonuniformity of the polymer/solvent interface; i.e., it is energetically advantageous for the polymer to pass to a thermodynamically good solvent, because the attraction between polymer segments and the solvent prevails over the attraction between the segments themselves (parameter θ is proportional to the enthalphic component of the free energy for mixing a polymer with a solvent [10]). On the contrary, it is advantageous for the segments to leave a thermodynamically poor solvent, because the intersegment attraction prevails in this case. It is easy to understand that the stresses normal to the polymer/solvent interface are proportional to the gradient of solvent concentration c_s. Indeed, the force acting from the side of solvent molecules on a single segment of a polymer molecule can be approximately expressed as follows:

$$\mathbf{F}(\mathbf{r}_p) = n_0 \int c_s(\mathbf{r}_s) \mathbf{f}(\mathbf{r}_p, \mathbf{r}_s) d\mathbf{r}_s, \qquad (6)$$

where $\mathbf{r}_p$ and $\mathbf{r}_s$ are the coordinates of a segment and a solvent molecule, respectively; $\mathbf{f}(\mathbf{r}_p, \mathbf{r}_s)$ is the force of the interaction between one solvent molecule and one polymer segment; n_0 is the total number of particles (solvent molecules and polymer segments) in unit volume; and $c_s(\mathbf{r}_s)$ is the current (molar) concentration of solvent molecules. If the solvent concentration is constant, the force is obviously equal to zero. A nonzero force arises in a nonuniform solvent. The Taylor expansion of the concentration in the vicinity of point $\mathbf{r}_p$ yields

$$\begin{aligned}\mathbf{F}_s(\mathbf{r}_p) &= n_0 \nabla c_s(\mathbf{r}_p) \\ \times \int (\mathbf{r}_s - \mathbf{r}_p)\mathbf{f}(\mathbf{r}_p, \mathbf{r}_s) d\mathbf{r}_s &= B_s \nabla c_s(\mathbf{r}_p),\end{aligned} \tag{7}$$

where the value and sign of coefficient B_s are determined by the natures of the solvent and segments.

At the same time, the isolated segment undergoes the action of the force from the side of other segments of the macromolecule. The resulting force may, obviously, be represented in the form of Eq. (7); that is,

$$\mathbf{F}_p(\mathbf{r}_p) = B_p \nabla c_p(\mathbf{r}_p), \tag{8}$$

where $c_p(\mathbf{r}_p)$ is the concentration of the segments. Since $\nabla c_p(\mathbf{r}_p) = -\nabla c_s(\mathbf{r}_p)$, the resultant force may be written as

$$\begin{aligned}\mathbf{F}(\mathbf{r}_p) &= \mathbf{F}_s(\mathbf{r}_p) + \mathbf{F}_p(\mathbf{r}_p) \\ &= (B_s - B_p)\nabla c_s(\mathbf{r}_p) = B_0 \nabla c_s(\mathbf{r}_p).\end{aligned} \tag{9}$$

At $B_0 > 0$, the stretching forces prevail, and the macromolecule swells relative to the Gaussian coil, while, at $B_0 < 0$, the macromolecule shrinks.

Let us evaluate coefficient B_0 for a macromolecule in a solvent. This may be done on the basis of the above considerations concerning the pressure of segments. We have shown that, at a concentration gradient of nearly $n_g/(n_0 R_g)$ (concentration n_g of segments in a globule [9] is lower than concentration n_s of molecules in a solvent, so that the concentration gradient may be estimated as $\Delta c_s \approx n_g/n_0$, while outside of the macromolecule, we have pure solvent, and the concentration changes at a distance of nearly R_g), pressure p_s applied by the considered forces to the polymer chain is determined by relation (5). Assuming that the force acts uniformly on all segments to a depth of nearly R_g, we find that $F_s n_g R_g \approx p_0 = 0.01–0.1$ MPa or

$$B_0 \approx \frac{n_0 p_0}{n_g^2}. \tag{10}$$

Thus, it may be concluded that, at the polymer/solvent interface, the segments of polymer molecules undergo the action of force (9), which is proportional to the concentration gradient of the solvent, with the proportionality coefficient in the expression for this force being determined by expression (10). This force may be compressive or stretching depending on the quality of the solvent with respect to a given macromolecule.

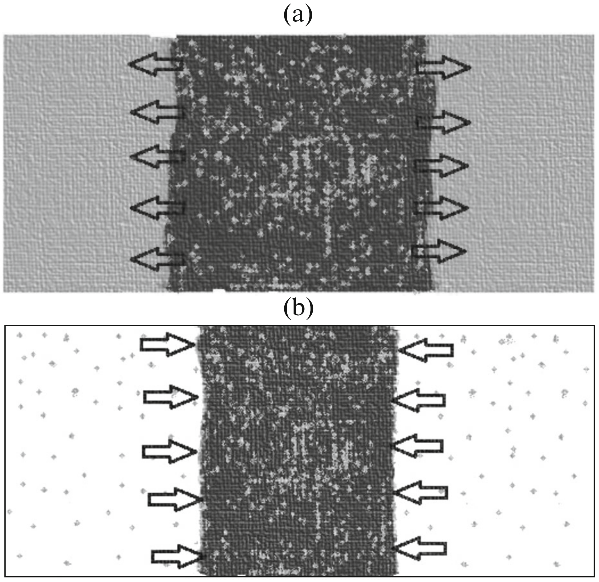

Fig. 2. Toward an explanation of the forces acting at (a) polymer/liquid solvent and (b) polymer/vapor interfaces.

In the case of a macromolecule occurring in a gas phase, the vapor density is much lower than the density of the segments (the density of molecules in a vapor at normal pressure is lower than 10^{19} cm^{-3}, because a pressure of 1 atm corresponds to this number concentration, while the saturation vapor pressure at room temperature is, commonly, much lower than the atmospheric pressure, and the number concentration of the segments in the macromolecule is higher than 10^{19} cm^{-3}). Therefore, the action of the forces from the side of a gas on a macromolecule occurring in a vapor may be ignored, while attraction forces (9) prevail in accordance with Langmuir's assumptions. That is, coefficient B_0 may, a fortiori, be taken as negative.

MACROSCOPIC POLYMER SAMPLE

Now, let us analyze a situation that arises in experiments on swelling of macroscopic polymer samples. We shall consider a cross-linked polymer sample as a giant macromolecule (this is a rather standard representation) occurring in a solvent or its vapor. The boundaries of the samples swelling in a vapor phase and a liquid solvent are under essentially different conditions, because the concentration of molecules in the vapor phase is substantially lower than that in the liquid phase (Fig. 2).

Solvent-concentration gradients in the situations corresponding to Figs. 2a and 2b may be directed toward the solvent in both cases. However, total molecule number concentration n_0, which enters into Eq. (7), is low for the vapor, thereby leading to a substantial decrease in the absolute value of coefficient B_s as compared to that for the solvent, while, in Eq. (8), B_p comprises the concentration of segments, which is substantially higher than the concentration of vapor molecules. Hence, the polymer undergoes a lower stretching stress from the side of the vapor than from the side of the liquid, while the compressive forces relevant to the attraction between macromolecule segments remain at the same level. Thus, for the polymer/vapor system, the resultant force may appear to be contracting, while the polymer swelling may occur due to entropic effects. As a result, we have a situation similar to the case of a single macromolecule. A polymer occurring in a vapor is compressed by intermolecular forces, while that in a liquid phase is stretched.

Let us assess possible deformations. In this case, the solvent concentration gradient is on the order of $n_{ss}/(n_0 R_g)$, where n_{ss} is the number concentration of segments in a polymer sample. It is assumed that the thickness of the surface layer is on the order of the inertia radius of a macromolecule. Assuming that the forces are applied to segments in the surface layer, we find the value of the stretching stress as follows:

$$\Pi_{nn} = \left(\frac{n_{ss}}{n_g}\right)^2 p_0. \tag{11}$$

Supposing the concentration of segments in a macroscopic sample to be several times higher than their concentration in a polymer globule, we take $\left(\frac{n_{ss}}{n_g}\right)^2 \approx 10$. As a result, we find that the stretching stresses are on the order of $10p_0$, i.e., 0.1–1 MPa. These stresses are quite sufficient for explaining the experimentally observed difference between the degrees of polymer swelling in vapor and liquid phases. Indeed, the elasticity modulus of elastomers is nearly 0.2 Pa [15]. The value of the deformation of a spherical sample with radius r_m is determined by the following expression [16]:

$$\Delta r_m = \Pi_{nn} r_m \frac{1 - 2\sigma_P}{E_Y} \Delta r_m = \Pi_{nn} r_m \frac{1 - 2\sigma_P}{E_Y}, \tag{12}$$

where r_m is the polymer-grain radius, E_Y is the Young modulus of a polymer material, and σ_P is its Poisson modulus. For the determined range of stretching stresses, Eq. (12) shows that the value of the "excess" deformation amounts to 20–100%, which corresponds to the experimental data.

ALTERNATIVE CALCULATION OF STRESS

Stretching and compressive stresses arising in a polymer are, to a substantial extent, determined by molecular (van der Waals) forces. In this section, we shall estimate the values of the stretching (compressive) stresses relevant only to the van der Waals interactions. As has been shown in [17, 18], the contribution of the van der Waals interaction may be calculated via the energy of the fluctuation electromagnetic field.

The contribution of the fluctuation electromagnetic field (the energy of the fluctuation electromagnetic field) to the thermodynamic characteristics is expressed via the so-called "Green function" [18] $D_{ik}(\mathbf{r}, \mathbf{r}', \omega)$, with the component (which we are interested in) of this function for a uniform medium with complex dielectric permittivity $\varepsilon(\omega)$, where ω is the electromagnetic-field frequency, may be presented as follows [18, 19]:

$$D_{ik}(\mathbf{r} - \mathbf{r}', \omega) = -\hbar \left[\delta_{ik} + \frac{c^2}{\omega^2 \varepsilon} \frac{\partial^2}{\partial x_i \partial x_k} \right] \times \frac{1}{|\mathbf{r} - \mathbf{r}'|} \exp\left(i \frac{\omega}{c} \sqrt{\varepsilon} |\mathbf{r} - \mathbf{r}'| \right), \tag{13}$$

where $\hbar$ is the Planck constant, c is the speed of light, δ_{ik} is the Kronecker symbol, $\mathbf{r}$ and $\mathbf{r}'$ are the vectors of spatial coordinates, and x_i denotes the spatial coordinates. Moreover, expression (13) may approximately be applied to slightly nonuniform media [19], if we take the dielectric permittivity to be dependent on the spatial coordinates. In the case of highly nonuniform media, a corresponding solution must, naturally, be found for the Green function. Here, we shall use an approximate approach, in which, when calculating the Green function, the dielectric permittivity is considered to be constant, because, for the considered systems, it weakly varies in the space.

If we have a nonuniform medium with dielectric permittivity varying in space, forces arise that are induced by the fluctuation electromagnetic field and related to the nonuniformity of the dielectric permittivity. The density of this force (per unit volume) may be represented as follows [18, 19] (we have confined ourselves to allowance for only one term, because this work is mainly devoted to the estimation of corresponding values):

$$f = \frac{kT}{4\pi\hbar c^2} \sum_l{}' (\nabla \varepsilon(\mathbf{r}, i\zeta_l)) D^E_{kk}(\mathbf{r}, \mathbf{r}, i\zeta_n), \tag{14}$$

where the "frequencies" are $\zeta_l = 2\pi l kT/\hbar$, the prime symbol at the sum denotes that the term comprising $l = 0$ is taken with a weight of 1/2, and repeated index k indicates the summation over the indices; after the implementation each of them, the following may be obtained from (13):

$$D_{kk}^{E}(\mathbf{r},\mathbf{r},\zeta_l) = 2\hbar\zeta_l^2\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right.$$
$$\times\exp\left(-\frac{\zeta_l}{c}\sqrt{\varepsilon(\mathbf{r},i\zeta_l)}|\mathbf{r}-\mathbf{r}'|\right) \tag{15}$$
$$\left.-\,2\pi\frac{c^2}{\varepsilon(\mathbf{r},i\zeta_l)\zeta_l^2}\delta(\mathbf{r}-\mathbf{r}')\right]_{\mathbf{r}=\mathbf{r}'}.$$

The $\varepsilon(\mathbf{r},i\zeta_n)$ function of the imaginary frequency is, at real frequencies, related to the imaginary component of the dielectric permittivity by the following relation [18]:

$$\varepsilon(\mathbf{r},i\zeta) = 1+\frac{2}{\pi}\int_0^\infty\frac{\omega\,\mathrm{Im}\,\varepsilon(\omega)d\omega}{\omega^2+\zeta^2}. \tag{16}$$

The function in Eq. (15) is clearly seen to have a peculiarity at $\mathbf{r} = \mathbf{r}'$. This is related to the inapplicability of the Green-function equation at small distances (when the condensed phase cannot be considered as a continuous medium). In some cases, this peculiarity may be excluded using special techniques [18]. We, following [20, 21], use the procedure of the cutoff at small distances. Namely, take $|\mathbf{r}-\mathbf{r}'| = a$, where the value of a is about ten atomic sizes. In this scale, the condensed medium may already be considered as a continuous one; therefore,

$$D_{kk}^{E}(\mathbf{r},\mathbf{r},\zeta_l) = 2\hbar\frac{\zeta_l^2}{a}\exp\left(-\frac{i\zeta_l}{c}\sqrt{-\varepsilon(\mathbf{r},i\zeta_l)}a\right). \tag{17}$$

At normal temperatures, we may pass [18] in (14) from summation to integration over $dl = \dfrac{\hbar}{2\pi kT}d\zeta$; so, for the force normal to the surface, we obtain the following expression:

$$f \approx c_{\mathrm{ss}}\frac{\hbar}{\pi}\int_0^\infty\frac{(\varepsilon_{\mathrm{i}}(i\zeta)-\varepsilon_{\mathrm{e}}(i\zeta))}{R_{\mathrm{g}}}\frac{\zeta^2}{c^2a}$$
$$\times\exp\left(-\frac{\zeta}{c}\sqrt{\varepsilon(i\zeta)}a\right)d\zeta, \tag{18}$$

where we have again taken that the thickness of the boundary layer is equal to R_{g}; subscripts i and e attribute the parameters to the polymer and an external medium, respectively; ε may be considered as some average value; and we have taken into account that $\varepsilon(\mathbf{r},i\zeta)$ is a real positive value (imaginary component $\mathrm{Im}\,\varepsilon(\omega)$ is always positive [22]). In addition, we have introduced concentration c_{ss} of polymer molecule segments, because we are interested in the force applied namely to the polymer (we introduce this concentration using a simplified scheme, because these calculations are of an approximate character). The $\varepsilon(i\zeta)$value may be represented approximately in the following form [23, 24]:

$$\varepsilon(i\zeta) = 1+\frac{n_{\mathrm{r}}^2-1}{1+\zeta^2/\nu_{\mathrm{e}}^2}, \tag{19}$$

where n_{r} is the refractive index of a medium, while $\nu_{\mathrm{e}} \approx 3\times10^{15}\ \mathrm{s}^{-1}$ is the frequency corresponding to the band of electron absorption.

Since, for gases (vapors), $n_{\mathrm{r}} \approx 1$, while, for organic liquids, $n_{\mathrm{r}} = 1.5-2$, Eq. (19) shows that the compressive force for a polymer occurring in a vapor is stronger than that for a polymer occurring in a liquid solvent (or, vice versa, the stretching force for the case of a liquid solvent is stronger). Thus, combining expressions (19) for the polymer/liquid solvent and polymer/vapor systems, we may conclude that a polymer occurring in a liquid solvent undergoes the action of excess stretching stress (we suppose that the forces are applied to segments in a surface layer with thickness R_{g})

$$\Pi_{nn} \approx c_{\mathrm{ss}}\frac{\hbar}{\pi}\int_0^\infty(\varepsilon_{\mathrm{s}}(i\zeta)-1)\frac{\zeta^2}{c^2a}\exp\left(-\frac{\zeta}{c}\sqrt{\varepsilon(i\zeta)}a\right)d\zeta, \tag{20}$$

where we have, for simplicity, taken that that, for vapor, $\varepsilon(i\zeta) = 1$ and $\varepsilon_{\mathrm{s}}(i\zeta)$ is a characteristic of a solvent. Let us estimate this value. Assuming that $a = 1$ nm, we obtain that

$$\Pi_{nn} \approx c_{\mathrm{ps}}\frac{\hbar}{\pi}(n_{\mathrm{r}}^2-1)\nu_{\mathrm{e}}^2\frac{1}{ca^2}$$
$$= \frac{\hbar c}{\pi}(n_{\mathrm{r}}^2-1)\nu_{\mathrm{e}}^2\frac{1}{c^2a^2} \approx 10^6\ \mathrm{Pa}. \tag{21}$$

This value is close to that found above in another way; hence, it may be stated that it corresponds to a real situation.

CONCLUSIONS

Using two different methods, we have obtained close values of an excess stress stretching a polymer sample immersed in a condensed phase (liquid solvent). This indicates the adequacy of the results obtained.

Note that the physical reason for the excess swelling of a polymer in a liquid solvent relative to the swelling in its vapor is quite obvious. A peculiar “extraction” of polymer units from the polymer or their “dissolution” take place. It is known that extraction in a liquid is substantially more efficient than that in a vapor. As has been noted in [9], the behavior of polymer molecules may be described by considering the behavior of isolated segments taking into account their joining into a chain. The existence of this joining predetermines the fact that the “extraction” or “dissolution” does not transfer the segments into a solvent but rather is reduced to the excess swelling. It should, once more, be noted that the θ-conditions (i.e., the conditions of macromolecule swelling) correspond to the line of polymer dissolution and the transition from the swelling to the shrinking of a polymer chain.

Note that, in the latter case, we have taken into account only the van der Waals forces, which represent only part of the solvation forces. Allowance for all other contributions may, naturally, lead to an enhancement of the effect. A well-known effect is the dissolution of salts, when the solvation forces overcome a strong Coulomb interionic interaction.

It should also be noted that swelling of a polymer network leads to a decrease in its elasticity modulus [25], which also may substantially enhance the effect in the course of sample swelling.

Thus, the Schroeder effect may be rather simply explained as applied to both ionogenic [1] and nonionogenic polymers. The explanation does not require the use of any artificial models. The paradox is explained within the framework of simple fundamental laws.

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