

# Critical behavior in broad-band dielectric relaxation on approaching the critical consolute point in ethanol-dodecane mixture

S. J. Rzoska,<sup>1</sup> K. Orzechowski,<sup>2</sup> and A. Drozd-Rzoska<sup>1</sup><sup>1</sup>*Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland*<sup>2</sup>*Faculty of Chemistry, University of Wrocław, Ulnika F. Joliot-Curie 14, 50-383 Wrocław, Poland*

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We present a quantitative experimental evidence for the influence of critical fluctuations on the high frequency dielectric relaxation in a binary critical mixture. The analysis clearly shows the presence of critical anomaly both for the maxima ( $\varepsilon_p''$ ) and frequencies ( $f_p$ ) of loss curves peaks. For the temperature evolution of  $\varepsilon_p''$  similar relation as for the static dielectric permittivity was obtained. The temperature dependence of relaxation times can be portrayed by using the Eyring-type equation remote from the critical consolute point and shows the unusual precritical *speeding up*. The obtained behavior resembles that found recently in the isotropic phase of nematic liquid crystals [A. Drozd-Rzoska and S. J. Rzoska, Phys. Rev. E **65**, 041701 (2002)]. Results presented agree also with the recent theoretical suggestion [S. Goodyear and S. C. Tucker, J. Chem. Phys. **111**, 9673 (1999)] that relaxation in supercritical fluids may exhibit glasslike features.

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## I. INTRODUCTION

The broad-band dielectric relaxation is one of the basic methods used for studying dynamics in complex liquids [1–4]. However, for critical mixtures such studies cannot be taken as conclusive. Only preliminary and qualitative statements of the influence of the mesoscopic scale inhomogeneities (critical fluctuations) on the dielectric relaxation exist [5–9]. On the other hand, there is clear evidence for the effect of critical fluctuations on the static dielectric permittivity [9–18]. In the 1980s, after five decades of studies ([9–20] and references therein), the validity of the relation derived by Goulon, Greffe, and Oxtoby [11] and Sengers *et al.* [12] was shown:

$$\varepsilon'(T) = \varepsilon'_{\text{crit}} + a't + A't^\varphi(1 + b't^\Delta + \dots), \quad (1)$$

where  $t = (T - T_C)/T_C$  is the dimensionless distance from the critical consolute temperature  $T_C$ .  $\varphi = 1 - \alpha$ ,  $\alpha$  is the specific heat critical exponent.  $A'$  denotes the critical amplitude, coefficients  $\varepsilon'_{\text{crit}}$ ,  $a'$  and  $b'$  are constants. The expression in brackets describes the first correction-to-scaling term. For the three-dimensional Ising model universality class, to which critical mixtures belong, the exponent  $\alpha \approx 0.115$  and  $\Delta \approx 0.5$ .

It is noteworthy that the theoretical basis of relation (1) was already given by Mistura in 1973 [13]. He concluded that the anomaly of the derivative of dielectric permittivity [ $d\varepsilon'(T)/dT$ ] should resemble that of heat capacity  $C_p \sim t^{-\alpha}$ . The long-standing puzzle of the behavior of the static dielectric permittivity in critical mixtures ([10,14–20] and references therein) can be associated with the low-frequency, critical Maxwell-Wagner (MW) relaxation [14]. Due to its influence the “static” critical effect predicted by relation (1) may appear only for high enough frequencies, i.e., for  $f > 100$  kHz. The contribution from the MW effect is particularly important when taking into account the weakness of  $\varepsilon'(T)$  anomaly [14–20].

This paper presents an experimental evidence of the influence of critical fluctuations on the broad-band dielectric re-

laxation in a critical mixture. The main aim of our studies was to test the temperature behavior of coordinates of loss curve peaks ( $f_p, \varepsilon_p''$ ). Tests were conducted in dodecane-ethanol critical mixture for which dielectric relaxation occurs at a relatively low frequency [5–9]. Recently, Goodyear and Tucker [21] analyzed the influence of precritical inhomogeneities (fluctuations) in the dynamics of a simple supercritical model liquid and suggested that it should resemble the one found in glassy liquids. This paper presents a preliminary discussion of such behavior manifested in dielectric relaxation studies of critical mixtures.

## II. EXPERIMENT

Dielectric relaxation in simple liquids is usually observed at very high frequencies [5–9]. However, in some systems, for instance, solutions of alcohols, it appears at relatively low frequencies. This may be related to the reorientation of large associates depending largely on the local concentration of alcohol molecules and on local viscosity [22,23]. Hence, the influence of critical fluctuations on dielectric relaxation may be particularly effective in alcohol-hydrocarbon mixtures. Results presented below are for the dodecane-ethanol mixture of critical concentration ( $x = 0.687$  mole fraction of ethanol) [24]. The experimental critical temperature was determined as the point of boost in dielectric permittivity on cooling. For the presented analysis the most important was the temperature evolution of loss curves peak coordinates. They could be obtained up to  $T = (T_C + 25)$  K. Measurements were carried out using HP 4191A RF impedance analyzer. The sample was placed at the end of the coaxial line. Absolute precision of the  $\varepsilon'$  and  $\varepsilon''$  was 3% and the resolution was 1% for  $\varepsilon'$  and 3% for  $\varepsilon''$ . Temperature was stabilized using UNIPAN 650 temperature control setup (Unipan Sci. Instrum., Poland) with accuracy  $\pm 0.01$  K. Ethanol and dodecane was purified using the standard procedures [25]. Data were analyzed using ORIGIN 6.1 software (Microcal Inc.). All errors are given as three standard deviations.

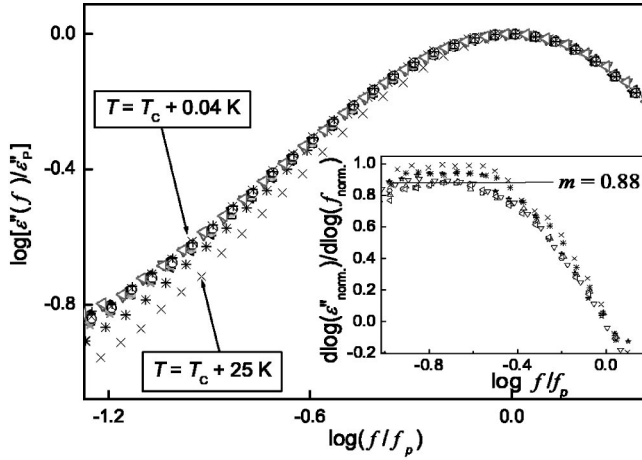


FIG. 1. The time-temperature superposition (TTS) of loss curves in the homogeneous phase of the ethanol-dodecane mixture. The inset shows results of the derivative analysis of chosen data from the main part of the figure showing the validity of relation (2). The horizontal line indicates the value of the power coefficient in relation (2).

### III. RESULTS AND DISCUSSION

Figure 1 shows the superposition of chosen loss curves from the set of 30 tested temperatures, ranging from  $T_C$  up to  $(T_C + 25)$  K. The high-frequency wings were only partially registered in the applied frequency window. Nevertheless, the validity of the power dependence predicted for supercooled liquids and amorphous materials is clearly visible for the low-frequency wing [26–28],

$$\varepsilon''(f)/\varepsilon''_p \propto (f/f_p)^m, \quad (2)$$

where the almost-Debye dependence is related to  $m=1$ .

On cooling, the coefficient  $m$  first decreases and next remains constant at  $m=0.88 \pm 0.02$  for  $T_C < T < (T_C + 20)$  K. This behavior is clearly visible for the derivative analysis of experimental data presented in the inset in Fig. 1. The derivative analysis was also applied to determine the position of peak frequency ( $f_p$ ), which was taken as the frequency at which the condition  $d\varepsilon''(f)/df=0$  is fulfilled. In pure ethanol the evolution of relaxation time can be well parametrized by the simple Arrhenius dependence with activation energy  $E_a = 17.5 \text{ kJ mol}^{-1}$  from room temperature up to 145 K [29]. The obtained evolution of  $\tau(T)$  in ethanol-dodecane critical mixture is clearly non-Arrhenius. A reasonable description of the obtained data, with the exception of the immediate vicinity of  $T_C$ , was possible by applying the Eyring-type [30] dependence (Fig. 2),

$$\tau^{\text{Eyring}} = (A_\tau/T) \exp(B/T), \quad (3)$$

where  $B = (2091 \pm 20)$  K and  $A_\tau = 4.71 \times 10^{-4}$  K. This gives  $17.4 \text{ kJ mol}^{-1}$  as the activation enthalpy.

Generally, in critical mixtures a precritical *slowing down* is expected [19]. The strong *slowing down* was found in the time-resolved birefringence [electro-optic Kerr effect (EKE)]

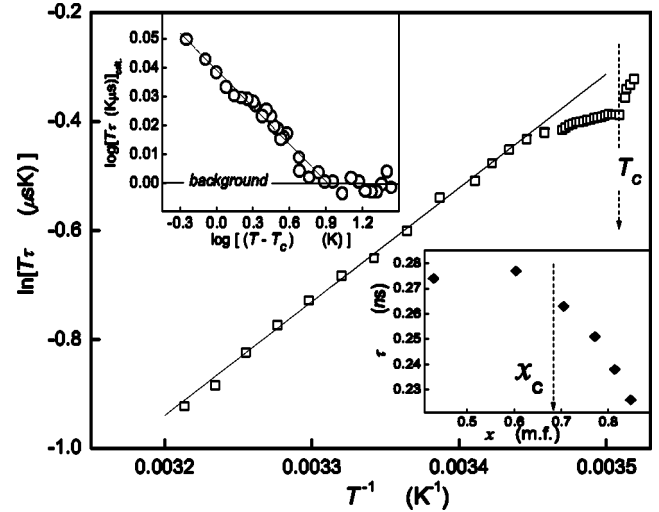


FIG. 2. The Eyring plot of the temperature dependence of dielectric relaxation times. The solid line is parametrized by Eq. (3). The upper inset shows the pretransitional effect analyzed using Eq. (4). The lower inset presents the influence of the alcohol concentration on dielectric relaxation time [ $T = (T_C + 5)$  K]. Concentrations are given in mole fractions of ethanol. Arrows indicate position of critical temperature and concentration.

[31], in the nonlinear dielectric effect (NDE) [32], and in the sound attenuation (SA) [19,24] studies:

$$\tau \propto 1/(T - T_C)^y, \quad (4)$$

where  $y \approx 1.9$  (SA) ([24] and references therein) or  $y = 1.1 - 1.3$  (time-resolved EKE and EKE) [19,31,32]. The latter was associated with the appearance of the quasinematic anisotropic structure induced by a strong electric field [32]. This precritical *slowing down* is accompanied by the precritical increase of shear viscosity [33–36],

$$\eta(T) = \eta_B A_\eta t^{-\phi}, \quad (5)$$

where  $\eta_B$  is the noncritical background term, most often given by the Arrhenius dependence.  $A_\eta$  and  $\phi = z_\eta \nu$  are the critical amplitude and the critical exponent, respectively. The mode-coupling theory predicts  $z_\eta \approx 0.054$  as the shear viscosity exponent whereas in the renormalization group analysis  $z_\eta \approx 0.065$  [19,33–36]. Taking the value  $\nu \approx 0.63$  one gets  $\phi \approx 0.033$  and  $\phi \approx 0.042$ , respectively.

However, results presented in Fig. 2 show that for the tested mixture the precritical *speeding up* occurs. To explain this behavior the results given in the lower inset in Fig. 2 are worth noting. They show that for a given temperature the increase of the alcohol concentration results in a strong nonlinear decrease of the relaxation time. In the tested mixtures alcohol-poor and alcohol-rich critical fluctuations on approaching  $T_C$  appear. The registered dielectric response is the average from the *background*, *normal liquid* and from critical fluctuations. However, the “weight” of contributions from alcohol-rich and alcohol-poor fluctuations is different as it is shown in the lower inset in Fig. 2. On approaching  $T_C$ , where the size of fluctuations increases, the influence of alcohol-rich fluctuations dominates resulting in pretransi-

tional *speeding up*. One may expect that the Debye-Stokes-Einstein (DSE) relation is fulfilled for processes associated with the reorientation of alcohol molecules in a nonpolar solvent within fluctuations. This is an essentially different situation than the one described in Eqs. (4) and (5) showing the direct response from mesoscopic-scale critical fluctuations. At present, there is no theory that describes the critical behavior of dielectric relaxation time. The upper inset in Fig. 2 shows that the obtained critical effect can be portrayed by

$$\tau(T) = \tau^{\text{Eyring}} A_C t^{-\phi'}, \quad (6)$$

where  $A_C = 1.09 \pm 0.01$ ,  $\phi' = 0.042 \pm 0.005$ ,  $T_C = 284.86 \text{ K} \pm 0.03$ .

The form of Eq. (6) agrees well with relation (5), assuming the validity of the DSE relation for the tested mixture. We also tried to test the possible validity of two other equations to portray this critical effect. The first was analogous to Eq. (1). The second contained the additional ‘‘Eyring’’-type background term. Similar relations were recently successfully applied to describe the anomaly of electric conductivity in a critical mixture [37]. However, for  $\tau(T)$  the satisfactory fit was obtained only with unreasonable values of fitted parameters.

Figure 3 shows that the evolution of the maxima of the loss curves is described by the same relation as static permittivity,

$$\varepsilon_p''(T) = \varepsilon_{p,\text{crit}}'' + a''t + A''t^\varphi(1 + b''t^{0.5}), \quad (7)$$

where  $\varepsilon_p'' = 2.15$ ,  $a'' = -19.2$ ,  $A'' = 9.86$ ,  $b'' = 1480$ , and  $\varphi = 1 - \alpha = 0.88 \pm 0.1$  for  $40 \text{ MHz} < f_p < 700 \text{ MHz}$ .

The behavior of the static dielectric permittivity is presented in the upper inset in Fig. 2. The obtained dependence is well portrayed by relation (1) with  $\varepsilon'_{\text{crit}} = 7.55$ ,  $a' = -38$ ,  $A' = 2$ ,  $b' = 1660$ , and  $\varphi = 1 - \alpha = 0.9 \pm 0.3$  for the constant frequency  $f = 10 \text{ MHz}$ . For the chosen value of frequency both the dielectric relaxation the MW relaxation did not influence the anomaly of the static dielectric permittivity. It is noteworthy that by omitting the correction-to-scaling term it was possible to describe data for  $T - T_C < 4 \text{ K}$ , with approximately the same values of the critical exponent  $\varphi$ . All fits gave the same value of  $T_C = (284.85 \pm 0.06) \text{ K}$  in fair agreement with the experimental value  $T_C = (284.88 \pm 0.02) \text{ K}$ . Concluding, the experimental dependences of  $\varepsilon_p''(T)$  and  $\varepsilon'(T)$  are described by isomorphic relations, with the same universal critical exponent  $\varphi = 1 - \alpha$ . The existence of the above anomalies and their similar forms are supported by the distortion-sensitive derivative analysis. They are presented in the lower inset in Fig. 3. It also directly shows the validity of the dependence predicted by Mistura for  $d\varepsilon'(T)/dT$  is valid also for  $d\varepsilon_p''(T)/dT$ . The applied scale in the inset reduces the analysis to the linear regression and shows the relationship of discussed anomalies with the exponent  $\alpha \approx 0.12$ . This inset made it possible to estimate the temperatures  $\Delta T_{\text{max}} = T_{\text{max}} - T_C$  at which the inversion of temperature dependences of  $\varepsilon_p''(T)$  and  $\varepsilon'(T)$  occur, i.e., at which  $d\varepsilon'/dT = 0$  and  $d\varepsilon_p''/dT = 0$ . They are  $\Delta T_{\text{max}} \approx 0.1 \text{ K}$  for  $\varepsilon'(T)$  and  $\Delta T_{\text{max}} \approx 0.32 \text{ K}$  for  $\varepsilon_p''(T)$ . It is noteworthy that

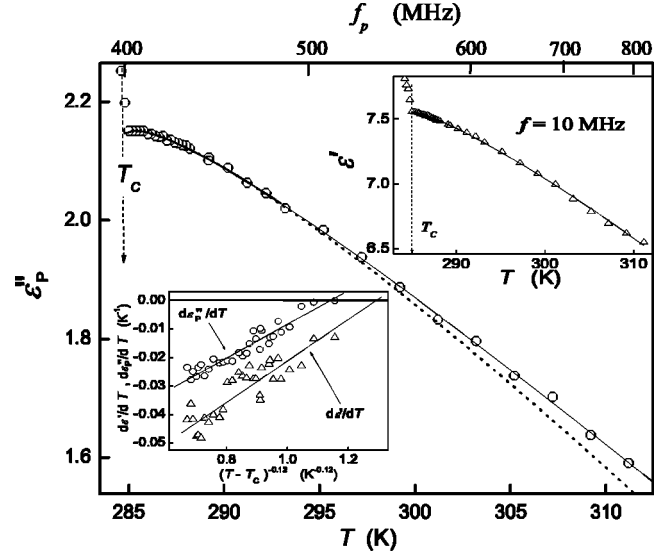


FIG. 3. The temperature evolution of the height of dielectric loss curves. The solid curve is portrayed by relation (7). The dotted curve shows the behavior when the correction-to-scaling term is neglected. Both curves superpose on approaching  $T_C$ . The upper scale shows values of peak frequencies associated with presented values of  $\varepsilon_p''(T)$ . The upper inset presents the behavior of the static dielectric permittivity where the solid line is parametrized by relation (1). The lower inset presents results of the derivative analysis of  $\varepsilon'(T)$  and  $\varepsilon_p''(T)$  experimental data. The applied scale shows that  $d\varepsilon'(T)/dT$ ,  $d\varepsilon_p''(T)/dT \propto t^{-\alpha}$  with  $\alpha \approx 0.12$ .

the pretransitional *bending down* for the static dielectric permittivity is observed in all mixtures with the upper critical consolute point tested so far [9–17]. Molecular origins of such behavior are still unexplained only the dependence on such thermodynamic factors as  $dT_C/dE^2$  (strong-electric-field-induced shift of  $T_C$ ), enthalpy, and volume excesses have been established [12,17,20].

#### IV. CONCLUSIONS

Results presented show that the appearance of critical fluctuations on approaching the critical consolute point significantly influence the behavior of the high-frequency dielectric relaxation. The form of loss curves is non-Debye. The low-frequency wing is described by the same exponent  $m \approx 0.88$  for  $T - T_C < 20 \text{ K}$ . The evolution of the maxima of loss curves (for  $400 < f_p < 800 \text{ MHz}$ ) and the static dielectric permittivity (for  $f = 10 \text{ MHz}$ ) are described by analogous relations, associated with the same critical exponent  $\varphi = 1 - \alpha$ . This similarity may be considered as a result of the validity of Kramers-Kronig relations [30]. It is noteworthy that similar pretransitional behavior of  $\tau(T)$ ,  $\varepsilon'(T)$ , and  $\varepsilon_p''(T)$  was recently found in the isotropic phase of a nematic liquid crystal [38]. This agrees with the *fluidlike* hypothesis suggesting a common description of the homogeneous phase of critical mixtures and isotropic phase of nematogens [39–41]. Regarding the temperature evolution of the dielectric relaxation time, the precritical *speeding up* was observed. This behavior is unlike the precritical *slowing down* observed for fluctuation-sensitive methods [19,24,31,32].

Worth recalling here is the fact that for linear spectroscopies homogeneous (from “normal” liquid) and inhomogeneous (from critical fluctuations) contributions are inseparable. This is the case of dielectric relaxation discussed in this paper. On the other hand, nonlinear spectroscopies, including nonlinear dielectric relaxation [32], extract the contribution from inhomogeneities. For dielectric relaxation the pretransitional *speeding up* may be associated with intermolecular interactions dominating in alcohol-poor and alcohol-rich fluctuations. The significance of this factor is indicated by recent studies of vibrational relaxation in supercritical ethane and carbon dioxide [42]. In both cases, the pretransitional *speeding up* was found but only for ethane, a clear inversion of temperature behavior occurred. Worth mentioning are also dielectric relaxation studies in poly(vinylmethylether)-water mixture with a lower critical consolute point [43]. For this mixture the critical point is reached on heating and hence the relaxation time decreases on approaching  $T_C$ , in the immediate vicinity of  $T_C$  an additional, precritical, decrease of  $\tau(T)$  was observed. Although in Ref. [43] the quantitative

temperature dependence of  $\tau(T)$  was not discussed yet the basic influence of critical fluctuation on the form of the  $\alpha$  relaxation loss curve was clearly demonstrated.

Recently, Goodyear and Tucker [21] numerically analyzed a model supercritical liquid and concluded that its dynamics should exhibit glasslike features. The non-Debye and non-Arrhenius behaviors are basic features of glass-forming liquids appearing in dielectric relaxation studies [1–4]. Results discussed above show that such behavior also occurs in critical mixtures. The glasslike behavior is even more visible in nonlinear dielectric relaxation studies. In Refs. [31,32] the validity of the stretched-exponential decay was demonstrated for nitrobenzene-dodecane mixture. Moreover, at early stages of decay the possible validity of von-Schweindler-type dependence was found [44].

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- [1] W. Goetze and L. Sjoegren, Rep. Prog. Phys. **55**, 241 (1992).  
 [2] C. A. Angell, Science **267**, 1924 (1995).  
 [3] A. K. Jonscher, *Universal Scaling Law* (Chelsea Dielectric, London, 1996).  
 [4] *The Physics of Complex Liquids*, Proceedings of the International Symposium on Complex Liquids, Nagoya, Japan, 1997, edited by F. Yonezawa, K. Tsuji, K. Kaji, M. Doi, and F. Fujiwara (World Scientific, Singapore, 1998).  
 [5] R. G. Quinn and E. P. Smyth, Can. J. Chem. **51**, 545 (1973).  
 [6] M. Hollecker and J. Goulon, Chem. Phys. **11**, 99 (1975).  
 [7] U. Kaatze and D. Woermann, Ber. Bunsenges. Phys. Chem. **86**, 81 (1982).  
 [8] U. Kaatze and D. Woermann, J. Chem. Phys. **88**, 284 (1984).  
 [9] J. Hamelin *et al.*, Phys. Rev. E **53**, 779 (1996).  
 [10] A. Piekara, Phys. Rev. **42**, 445 (1932).  
 [11] J. Goulon *et al.*, J. Chem. Phys. **70**, 4742 (1979).  
 [12] J. V. Sengers, D. Bedeaux, P. Mazur, and S. C. Greer, Physica A **105**, 574 (1980).  
 [13] L. Mistura, J. Chem. Phys. **59**, 4563 (1974).  
 [14] J. Thoen, R. Kindt *et al.*, Physica A **192**, (1989).  
 [15] J. Hamelin *et al.*, Phys. Rev. A **42**, 4735 (1990).  
 [16] K. Orzechowski, J. Chem. Soc., Faraday Trans. **90**, 2757 (1994).  
 [17] J. Hamelin *et al.*, Phys. Rev. Lett. **74**, 2733 (1997).  
 [18] S. J. Rzoska, P. Urbanowicz, A. Drozd-Rzoska, M. Paluch, and P. Haddas, Europhys. Lett. **45**, 334 (1999).  
 [19] A. Drozd-Rzoska *et al.*, IEEE Trans. Dielectr. Insul. **9**, 112 (2002). The paper contains a review of results up to 1 September 2000.  
 [20] S. J. Rzoska *et al.*, Phys. Rev. E **64**, 061104 (2001).  
 [21] S. Goodyear *et al.*, J. Chem. Phys. **111**, 9673 (1999).  
 [22] E. Jakusek and L. Sobczyk, in *Dielectric and Related Molecular Processes*, edited by M. Davies (Chemical Society, London, 1977), Vol. 3, pp. 108–142.  
 [23] L. Glasser and J. Crossley, J. Chem. Phys. **57**, 3977 (1972).  
 [24] U. Duerr *et al.*, J. Phys. Chem. A **104**, 8855 (2000).  
 [25] A. Weissberger and E. S. Proskauer, *Organic Solvents. Physical Properties and Methods of Purification* (Interscience, New York, 1955).  
 [26] A. K. Jonscher, Nature (London) **267**, 673 (1977).  
 [27] I. A. Dissado and R. Hill, Proc. R. Soc. London, Ser. A **340**, 131 (1983).  
 [28] E. Schlosser *et al.*, Colloid Polym. Sci. **267**, 133 (1989).  
 [29] S. Benkhof, A. Kudlik, T. Blochowicz, and E. Roessler, J. Phys.: Condens. Matter **10**, 8155 (1998).  
 [30] A. Chelkowski, *Dielectric Physics* (PWN-Elsevier, Warsaw, 1980).  
 [31] S. J. Rzoska *et al.*, Phys. Rev. E **49**, 3093 (1994).  
 [32] S. J. Rzoska *et al.*, Phys. Rev. E **61**, 960 (2000).  
 [33] R. F. Berg *et al.*, J. Chem. Phys. **93**, 1926 (1990).  
 [34] J. F. Douglas, Macromolecules **25**, 1468 (1992).  
 [35] R. F. Berg *et al.*, Phys. Rev. Lett. **82**, 920 (1999).  
 [36] A. Drozd-Rzoska, Phys. Rev. E **62**, 8071 (2000).  
 [37] A. Oleinikova and M. Bonetti, Phys. Rev. Lett. **83**, 2985 (1999).  
 [38] A. Drozd-Rzoska and S. J. Rzoska, Phys. Rev. E **65**, 041701 (2002).  
 [39] P. K. Mukherjee, J. Phys.: Condens. Matter **10**, 9191 (1998).  
 [40] A. Drozd-Rzoska, Phys. Rev. E **59**, 5556 (1999).  
 [41] A. Drozd-Rzoska, S. J. Rzoska, and J. Ziolo, Acta Phys. Pol. A **98**, 637 (2000).  
 [42] D. J. Myers *et al.*, J. Chem. Phys. **109**, 5971 (1998).  
 [43] N. Shinyashiki *et al.*, J. Chem. Phys. **104**, 6877 (1996).  
 [44] S. J. Rzoska *et al.*, Phys. Rev. E **56**, 2578 (1997).