

Analysis of dynamic light scattering of poly(N-isopropylacrylamide) across the collapse transition

A.V. Gorelov[†], L.N. Vasil'eva[†], A. Du Chesne,
E.G. Timoshenko, Yu.A. Kuznetsov, K.A. Dawson^{*†}

*Complex Fluids and Theory Groups,
Centre for Soft Condensed Matter and Biomaterials,
Department of Chemistry, University College Dublin, Dublin, Ireland
July 30, 2001*

Abstract

We analyse data from the dynamic light scattering of poly(N-isopropylacrylamide) in water solution as we cross the collapse transition. Experimental data are interpreted by the Gaussian self-consistent Zimm model that takes into account two- and three-body excluded volume effects, and Oseen hydrodynamic interactions, as well as by the standard cumulant and Contin analyses. By fitting the dynamic structure factor we extract the temperature dependence of the diffusion coefficient D and the first relaxation time τ_1 across the collapse transition for a range of scattering angles. The relaxation time τ_1 possesses a characteristic peak at about $32.4^\circ C$ due to slowing of the internal motions of the polymer at the theta point, and a minimum at $33.4^\circ C$. We interpret this as a combination of collapse closely followed by the growth of critical correlations. At large scattering angles we reach the universal k^3 regime, and observe that this behaviour vanishes at the onset of the collapse transition.

[†]Also attached to Institute of Theoretical and Experimental Biophysics, Russian Academy of Science

^{*}Author to whom correspondence should be addressed

1 Introduction

We here discuss some recent experimental work on the collapse transition of Poly-N-isopropylacrylamide. This is a part of a program of research aimed at elucidation of the equilibrium and non-equilibrium dynamics in the vicinity of the collapse transition. We have used gel permeation chromatography to isolate selected narrow fractions of polymer and studied the system using dynamic light scattering.

With the systems that we have chosen it is possible to see the effects of collapse prior to critical phase separation at the upper consolute point [1]. As a result it becomes of interest to apply a self-consistent mean-field theory to interpret the result of light scattering, up to the phase separation. Reasonable agreement is achieved between theory and experiment. We find that the Flory coil possesses internal modes that are relatively well fitted by the theory, producing estimates of the size and internal relaxation time of the coil. We also find a universal large momentum regime, and confirm the stretched relaxation law that describes it.

At the collapse point we find anomalously long time-scales that vanish just after collapse, and with slightly increased temperature we again find a long time associated with critical fluctuations.

2 Experimental

The PNIPAM polymer was prepared with ammonium persulphate as initiator in twice-distilled water under Ar . Ferrous sulfate in catalytic amounts was found to produce a polymer of lower molecular weight. The reaction was carried out at $25^{\circ}C$ resulting in a clear solution. Extremely high molecular weights can be prepared without catalyst, but we do not discuss such materials in the present report. The raw product from the reaction consists in all cases of a broad distribution of molecular weights, which we have separated using gel permeation chromatography. Using large 77ml columns filled by Sefacryl SH-500R gel we have found that if the concentration of the sample loaded onto the column is kept sufficiently low, and the elution rate sufficiently slow, the separation is relatively effective. Molecular weights have been estimated from the literature [1],[2]. More details of the procedure are given in reference [3]. Dynamic Light Scattering (DLS) was carried out using a Coherent 5W tunable Ar^{+} laser and Malvern PCS-4700 instrument with

3 Model

The following ideas have been introduced in reference [4] as an approximate means to model the dynamic light scattering of systems across the collapse transition. We intend to test the theory, with the experiments described above, thereby outlining its successes and limitations. We describe the polymer in dilute solutions [5] by the Langevin equation

$$\dot{x}_q^\alpha(t) = \sum_{\alpha', q'} H_{qq'}^{\alpha\alpha'}[x(t)] \left(-k_{q'} x_{q'}^{\alpha'} - \frac{\partial V}{\partial x_{-q'}^{\alpha'}} + \eta_{q'}^{\alpha'}(t) \right), \quad (1)$$

where $H_{qq'}^{\alpha\alpha'}$ is the Oseen hydrodynamic tensor. Here \mathbf{x}_q denote the Fourier transforms of spatial positions of beads

$$\mathbf{x}_q = \frac{1}{N} \sum_{n=0}^{N-1} \exp \frac{i2\pi nq}{N} \mathbf{x}_n. \quad (2)$$

For simplicity we may restrict ourselves by polymers satisfying cyclic boundary conditions $x_{m+N} = x_m$, $m = 0, \dots, N-1$ since open and cyclic polymers are equivalent for sufficiently large degree of polymerization N . Besides the connectivity term proportional to k_q , we take into account the excluded volume interaction potential, V , that includes contributions from two- and three-body effects,

$$V = V_2 + V_3 = u_2 \sum_{mm'} \delta(\mathbf{x}_m - \mathbf{x}_{m'}) + u_3 \sum_{mm'm''} \delta(\mathbf{x}_m - \mathbf{x}_{m'}) \delta(\mathbf{x}_{m'} - \mathbf{x}_{m''}), \quad (3)$$

where u_2 , u_3 are virial coefficients. The noise has the second order correlation function

$$\langle \eta_q^\alpha(t) \eta_{q'}^{\alpha'}(t') \rangle = (H^{-1})_{qq'}^{\alpha\alpha'} 2k_B T \delta(t - t') \delta_{\alpha\alpha'} \delta_{-qq'}. \quad (4)$$

In our self-consistent approach the dynamics of the full Langevin equation (1) is approximated by the Gaussian stochastic ensemble with the Langevin equation,

$$\zeta_q \dot{x}_q^\alpha(t) = -\Delta V_q(t) x_q^\alpha + \eta_q^\alpha(t) \quad (5)$$

and a diagonal correlation function of the form (4) with $H_{qq'}^{\alpha\alpha'} = \zeta_q^{-1} \delta_{qq'}^{\alpha\alpha'}$. Here the potential, $\Delta V_q(t)$ and the friction, ζ_q are unknown functions determined from the self-consistency equation.

This equation is simplified for small q , when we can seek solutions with the properties,

$$\Delta V_q = NA^{-1} \underline{q}^{2\beta}, \quad \underline{q} \equiv \frac{2\pi q}{N}, \quad (6)$$

where A is some unknown constant. Let us define parameters b and ν by the relation

$$\frac{1}{3} \langle (\mathbf{x}_m - \mathbf{x}_{m'})^2 \rangle = b^2 |m - m'|^{2\nu}, \quad (7)$$

then $\nu = \beta - 1/2$ and $b \simeq \sqrt{Ak_B T}$. As we have shown [4], for small \underline{q} the self-consistency equation reduces to the dominant balance equation, from which we may extract three different regimes. When $u_2 > 0$ we find the balance between the order \underline{q}^2 and the u_2 term giving the Flory exponent $\nu = 3/5$ and $b^2 \sim (u_2/k)^{2/5}$. When $u_2 = 0$ we have a balance between \underline{q}^2 and the u_3 term, and so-called θ -point results: $\nu = 1/2$, $b^2 \sim (u_3/k)^{1/4}$. Finally, when $u_2 < 0$, we are in a collapsed state with balance between the two-body and three-body terms giving $\nu = 1/3$ and $b^2 \sim (-u_3/u_2)^{2/3}$. Finally Oseen hydrodynamic interactions lead to the friction of the form

$$\zeta_q \simeq b\eta_s N^\nu q^{1-\nu}. \quad (8)$$

The correlation functions are found to be for $q \neq 0$

$$\langle |\mathbf{x}_q|^2(t) \rangle = \langle |\mathbf{x}_q|^2(0) \rangle = \frac{3k_B T}{\Delta V_q}, \quad (9)$$

$$\langle \mathbf{x}_{-q}(0)\mathbf{x}_q(t) \rangle = \exp\left(-\frac{\Delta V_q t}{\zeta_q}\right) \langle |\mathbf{x}_q|^2(0) \rangle, \quad (10)$$

and for $q = 0$ diffusive component

$$\langle |\mathbf{x}_0(t)|^2 \rangle = \langle |\mathbf{x}_0(0)|^2 \rangle + 6Dt, \quad (11)$$

$$\langle \mathbf{x}_0(t)\mathbf{x}_0(0) \rangle = \langle |\mathbf{x}_0(0)|^2 \rangle, \quad (12)$$

where $D = k_B T/\zeta_0$ is the diffusion constant. Thus the relaxation times are expressed as $\tau_q = \zeta_q/\Delta V_q$ and in this model are

$$1/\tau_q \simeq \frac{k_B T}{b^3 \eta_s} \underline{q}^{3\nu}. \quad (13)$$

By definition the dynamic structure factor is,

$$g(\mathbf{k}, t) = \frac{1}{N} \sum_{nm} \left\langle \exp i\mathbf{k}(\mathbf{x}_n(t) - \mathbf{x}_m(0)) \right\rangle. \quad (14)$$

The wave vector \mathbf{k} is related to the wave length λ , refraction index n and scattering angle θ as follows,

$$|k| = \frac{4\pi n_0}{\lambda} \sin \frac{\theta}{2}$$

In the Gaussian approximation the structure factor takes the form,

$$g(\mathbf{k}, t) = \frac{1}{N} \sum_{nm} \exp \left(-\frac{1}{6} \mathbf{k}^2 \sum_q \left(\langle |\mathbf{x}_q|^2(t) \rangle + \langle |\mathbf{x}_q|^2(0) \rangle - 2 \cos \frac{2\pi q(n-m)}{N} \langle \mathbf{x}_q(0) \mathbf{x}_q(t) \rangle \right) \right). \quad (15)$$

Now we extract the contribution of the zero diffusive mode from the remaining internal modes and substitute the averages,

$$g(\mathbf{k}, t) = g_0(\mathbf{k}, t) g_{int}(\mathbf{k}, t), \quad (16)$$

$$g_0(\mathbf{k}, t) = \exp(-\mathbf{k}^2 D t), \quad (17)$$

$$g_{int}(\mathbf{k}, t) = \frac{1}{N} \sum_{nm} \exp \left(-\mathbf{k}^2 \sum_{q \neq 0} \frac{k_B T}{\Delta V_q} \left(1 - \cos \frac{2\pi q(n-m)}{N} e^{-\frac{\Delta V_q t}{\zeta_q}} \right) \right) \quad (18)$$

It is possible to consider two different regimes that result in further simplifications. In the limit $k^2 b^2 N^{2\nu} \ll 1$ one can neglect the contribution of internal modes, and the structure factor will be given entirely by the diffusion part $g_0(\mathbf{k}, t)$. In the opposite case, $k^2 b^2 N^{2\nu} \gg 1$, the contribution of internal modes becomes essential. In fact for large N , their distribution is almost quasi-continuous, so that we may convert the sums into integrals. If we consider sufficiently large times also, the formula takes especially simple form

$$g_{int}(\mathbf{k}, t) = g(\mathbf{k}, 0) \exp(-\mathcal{H}(0)(\Gamma_k t)^{2/3}), \quad (19)$$

$$\Gamma_k \simeq \frac{k_B T}{\eta_s} k^3, \quad (20)$$

where $\mathcal{H}(0) = -2^{2\beta+1} \sqrt{\pi} \Gamma(2\beta) / (2^{3/2} \Gamma(5/3) \nu \Gamma(-\nu))$ and $\Gamma_k t \gg 1$.

Another quantity of interest is the cumulant or logarithmic derivative at zero time. For large k we find by simple differentiation,

$$\mathcal{Q}(\mathbf{k}) \equiv -\left. \frac{d}{dt} \right|_{t=0} g(\mathbf{k}, t) = D k^2 + C(\nu) \frac{k_B T}{\eta_s} k^3. \quad (21)$$

The value $C(\nu)$ may be independently expressed in terms of the static structure factor [6],

$$C(\nu) k^3 = g(\mathbf{k}, 0)^{-1} \int \frac{d\mathbf{q}}{(2\pi)^3} \left(\frac{\mathbf{k}^2 - (\mathbf{k}\hat{\mathbf{q}})^2}{\mathbf{q}^2} \right) g(\mathbf{k} + \mathbf{q}, 0), \quad (22)$$

and we note that it is \mathbf{k} independent if we use the asymptotic formula for $k^2 b^2 N^{2\nu} \gg 1$,

$$g(\mathbf{k}, 0) \simeq (kb)^{-1/\nu}. \quad (23)$$

It is interesting to observe that in this regime $C(\nu)$ does not contain any polymer specific parameters, and it is therefore referred to as the universal k^3 regime.

It is possible to derive another representation for the dynamic structure factor valid for any k . In a previous work [4] we have derived the formula

$$g_{int}(\mathbf{k}, t)/g_{int}(\mathbf{k}, 0) = \sum_{m_1, \dots, m_{N-1} = -\infty}^{\infty} I_{m_1}(\mathbf{k}^2 G_1(t)) \dots I_{m_{N-1}}(\mathbf{k}^2 G_{N-1}(t)), \quad (24)$$

where $G_q(t) = \frac{1}{3} \langle \mathbf{x}_{-q}(0) \mathbf{x}_q(t) \rangle = \frac{k_B T}{\Delta V_q} \exp(-\frac{\Delta V_q}{\zeta_q} t)$, $I_n(z)$ are modified Bessel functions and summation is restricted by the condition

$$m_1 + 2m_2 + \dots + (N-1)m_{N-1} = 0. \quad (25)$$

Such a representation is useful for asymptotics at large t when it is enough to consider only leading terms in the series (24). In the simplest case, we may retain only the contribution of the first internal mode and the formula then reduces to simply,

$$g_{int}(\mathbf{k}, t)/g_{int}(\mathbf{k}, 0) \propto I_0(\mathbf{k}^2 G_1(t)). \quad (26)$$

4 Results and Discussion

To interpret the experimental data and test the theory we have fitted the correlation function by the theoretical formulae for the dynamic structure factor of various samples. Here we shall report only on one case which is somewhat representative of our findings. Thus, the following data are for a polymer of approximate molecular weight $20 * 10^6$. In Fig. 1 we show

the dependence of the apparent hydrodynamic radius R_{app} upon the inverse modulus of scattering vector, $k = \frac{4\pi n_0}{\lambda} \sin(\frac{\theta}{2})$, where λ is the wavelength of the incident light, n_0 the refractive index of solvent, and θ the scattering angle. R_{app} was obtained from the first cumulant of the correlation function [7]. The strong \mathbf{k} dependence of R_{app} at 20°C arises from the internal motions of the polymer, these becoming apparent when $\frac{1}{\mathbf{k}} \leq R_g$ (R_g -radius of gyration). The Contin analysis [8] for this polymer, shown in Fig. 2.a, exhibits a single peak at low angles in the coil state a second peak corresponding to internal modes emerging only at large scattering angles. We note the rather interesting phenomenon illustrated in Fig. 2.b for the collapsed state. Here the assignment is reversed, so that the peak at larger length-scales is interpreted not as diffusion, but correlation between collapsed molecules. It is noted that this peak grows only after some minutes, whilst the collapse of the Flory structure occurs much more rapidly.

The dependence of R_{app} (here given for large angle) on temperature, shown in Fig. 3, shows that the size of the polymer decreases precipitously at 34.2°C. This rapid decrease of apparent size arises as we cross the so-called θ line where interaction between monomers units changes from being predominantly repulsive to attractive. With further increase of temperature we find bulk phase-separation into the liquid and gas phases of the collapsed globules. In any case, Fig. 3 shows that we first cross the theta line, and then further increase of temperature leads us across the phase-separation. At large angles the increase in apparent size is quite small and Contin analysis produces a single peak (Fig. 2.b), even after many hours. Thus, we believe that for these conditions we have succeeded in crossing the theta line, without crossing the phase-transition.

For small scattering angles (Fig. 3) one can see a similar effect as we cross the θ -point, but here since we probe longer length-scales we may expect to see the remnant of critical scattering from the proximate critical point. Indeed, the apparent size as, determined from the cumulant rises more rapidly beyond the collapse transition. Having discussed the transition using the traditional methods of analysis, we would now like to reanalyse the data using the dynamical mean-field theory discussed earlier.

We shall consider the approximate formula (26) and thereby reduce the number of parameters required for the fit. From this fit we obtain the diffusion, D , and the first relaxation time, τ_1 , at various wave vectors \mathbf{k} and temperatures. We have noted that the χ^2 of the fit for the scattering angles 40°, and 60° is particularly good. The data for smaller angles are quite noisy,

in part due to dust, and gave relatively poor results.

Since the diffusion constant in our model is $D \simeq k_B T / (\eta_s \langle R \rangle)$, where $\langle R \rangle = bN^\nu$ because we consider only isolated molecules. Fig. 4 shows that the average size $\langle R \rangle$ decreases during the collapse transition. However in the model, the inverse first relaxation time is expressed by a similar relation $1/\tau_1 \simeq k_B T / (\eta_s \langle R \rangle^3)$, and this is presented in Fig. 5. In fact, there is a characteristic minimum at a temperature of about $32.4^\circ C$ and a maximum at $33.4^\circ C$. The first feature probably corresponds to the θ -point and we conjecture that the slowing is due to the restriction of internal motions of the polymer. It is possible that one is seeing an enhancement of the Cerf effect [10], but this is difficult to establish without extensive analysis of the chain length dependence.

The maximum in Fig. 5 occurs in the collapsed phase and we assign it to a competition between the reducing size of the globule, and the incipient critical correlations. Neither of these two time-scales is accounted for in the model, but it would be straightforward to incorporate the essential effects of criticality along with collapse [9]. The slowing that we have assigned to internal frictional or increased Cerf effects may be somewhat more difficult to resolve, and remains one of the most uncertain aspects of the dynamics at collapse. We may note that relation $1/\tau_1 \simeq k_B T / (\eta_s R_{app})$, gives us an estimate of the deviation of the apparent radius R_{app} from the Gaussian mean value $\langle R \rangle$ and thereby shows the weaknesses of the simple theory that we have applied. In practice the behaviour of τ_1 is reminiscent of the quantity R_{app} extracted from the Contin analysis and presented in Fig. 3.

At large wave vectors, corresponding to the scattering angles 90° , and 120° , we have observed good agreement (Fig. 6) between the data and the asymptotic formula (19).

The fact that (19) gives a reasonable description of the phenomena indicates that we have reached the universal k^3 regime characterised by the behaviour of the coefficient (20). This agreement is quite good for the Flory coil, worse for the θ -point and still worse for the collapsed globules. The poor agreement for the collapsed state is hardly surprising, given the limitations of the theory in modelling a dense compacted state. However, the deviation in the theta state is probably indicative of an anomalous dynamics at the theta point. Thus, the deviation from the expected exponent $2/3$ in the plot $\log g \propto -t^{2/3}$ near the θ -point and beyond may well be related to the long time-scale at theta conditions that we had earlier noted. From scaling considerations, a change in the t -exponent would correspond to a

change of the $\log g(\mathbf{k})$ dependence, and this is clearly observed in our data. Such a breakdown indicates failure of the Gaussian approximation during the collapse transition, and invites the construction of a more suitable theory.

Briefly then, in conclusion, the theory is fairly satisfactory for a number of questions, but cannot describe the anomalous dynamics at the theta-condition, nor the long-time scale critical behaviour. The former is difficult to improve, but important for development of this field, whilst the latter be resolved by the modification of the theory [11].

5 Acknowledgements

The authors acknowledge the assistance of their colleagues A. Byrne, P. Kieran, Drs. O. Vasil'ev and F. Sicoli. They acknowledge, also, interesting discussion with Prof. A. Khokhlov. The work was supported, in part, by the Higher Education Authority of Ireland, and the University College Dublin. The financial assistance of the Avondale Chemical Company was also instrumental in the work being commenced.

References

- [1] S. Fujishige, K. Kubota, I. Ando, *J.Phys.Chem.*, **93** (1989) 3311.
- [2] J. Rička, M. Meewes, R. Nyffenegger, Th. Binkert, *Phys.Rev.Lett.* **65** (1990) 657.
- [3] A.V. Gorelov, L.A. Vasil'eva, A. Du Chesne, K.A. Dawson, (1994), submitted for publication.
- [4] E.G. Timoshenko, K.A. Dawson, *Phys. Rev. E.* (1994), in press.
- [5] B.H. Zimm, *J. Chem. Phys.* **24**, 269 (1956); B.H. Zimm, G.M. Roe, L.F. Epstein, *J. Chem. Phys.* **37**, 2547 (1962); H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper & Row, New York (1971); S.F. Edwards, K.F. Freed, *J. Chem. Phys.* **61**, 1189 (1974); S.F. Edwards, M. Muthukumar, *Macromolecules* **17**, 586 (1984); A.J. Peterlin, *J. Chem. Phys.* **23**, 2464 (1955); Y. Oono, M. Kohmoto, *J. Chem. Phys.* **78**, 520 (1983).

- [6] M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics*, Oxford Science, New York (1989).
- [7] D. Koppel, *J. Chem. Phys.* **57** (1972) 4814.
- [8] S. Provencher, *Comput. Phys. Commun.* **27** (1982) 213.
- [9] E.G. Timoshenko, Yu.A. Kuznetsov, K.A. Dawson, (1994), submitted to *J. Chem. Phys.*
- [10] P.G. de Gennes, *Scaling Concepts in Polymer Physics*. Cornell Univ. Press, Ithaca (1979).
- [11] E.G. Timoshenko, K.A. Dawson, (unpublished).

Figure Captions

Fig. 1. Plot of the apparent radius R_{app} versus the inverse wave vector k^{-1} for the Flory coil at $T = 20^\circ C$ (diamonds), and for the collapsed globule at $T = 33.4^\circ C$ (crosses).

Fig. 2.a. Distribution (in arbitrary units) of the apparent radius R_{app} obtained from the Contin analysis at different angles for Flory coil.

Fig. 2.b. Distribution (in arbitrary units) of the apparent radius R_{app} obtained from the Contin analysis at different angles for collapsed globule.

Fig. 3. Temperature dependence of the apparent radius R_{app} obtained from the Contin analysis for different wave vectors.

Fig. 4. Plot of the diffusion coefficient D versus the temperature T at the scattering angle 40° .

Fig. 5. Plot of the inverse first decay rate $1/\tau_1$ versus the temperature T at the scattering angle 40° .

Fig. 6. Plot of the logarithm of dynamic structure factor $g(\mathbf{k}, t)$ versus the time t for the scattering angles 90° (crosses) and 120° (diamonds) and appropriate theoretical curves in the universal k^3 regime.

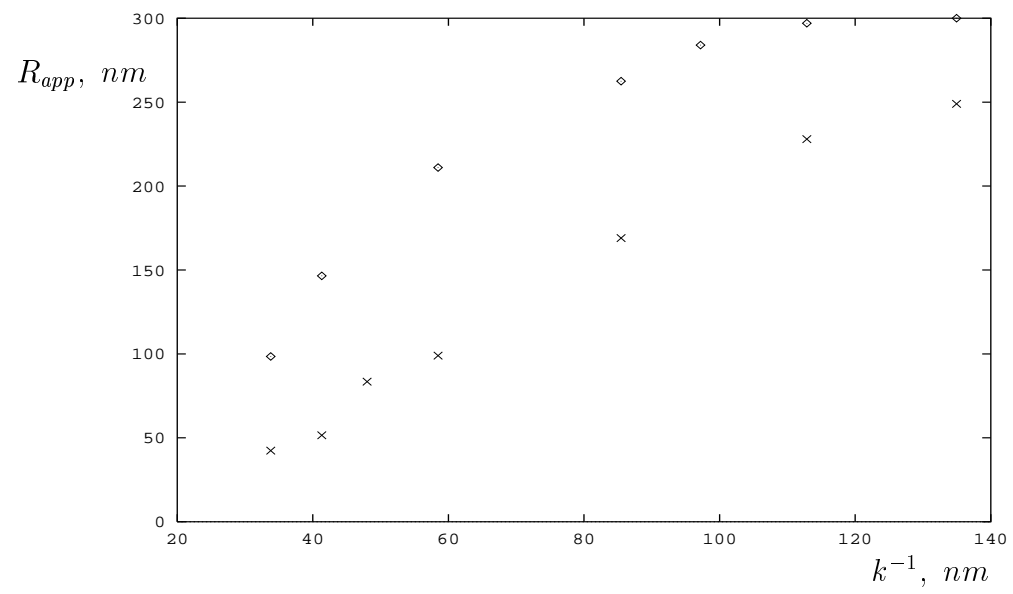


Fig. 1.

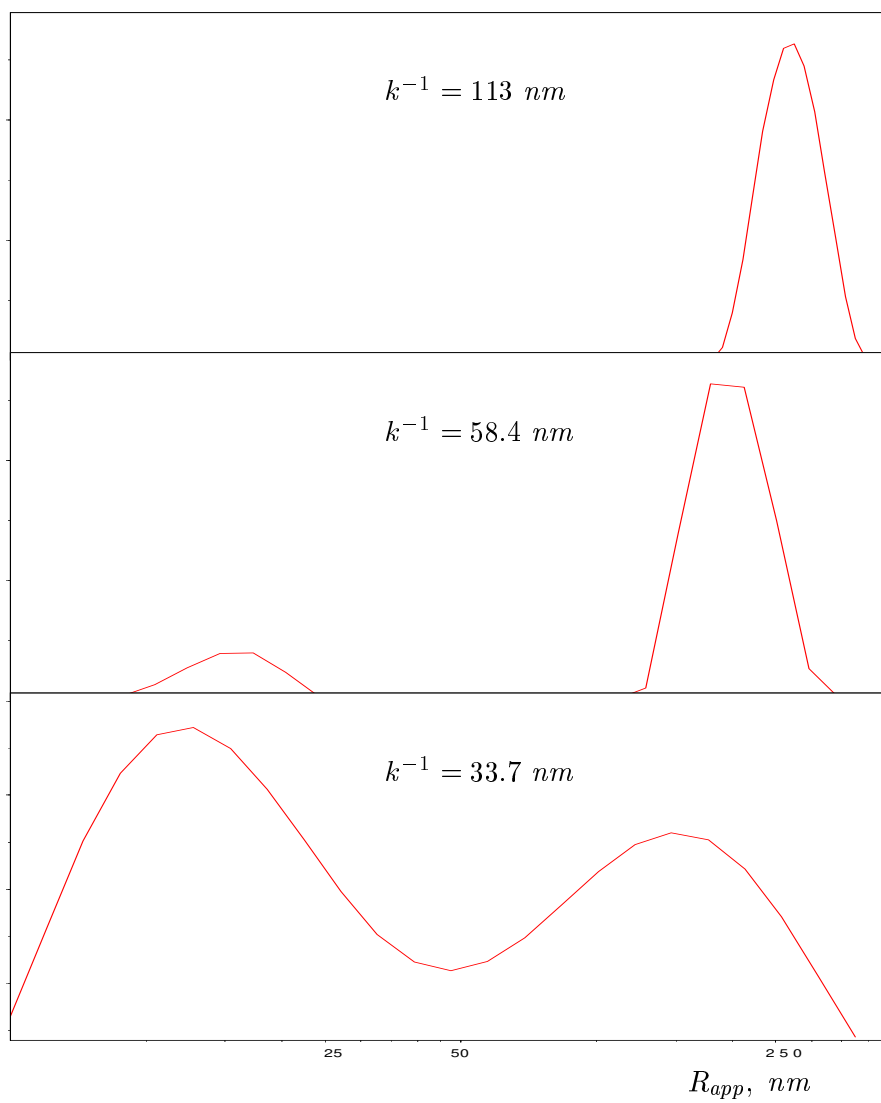


Fig. 2.a.

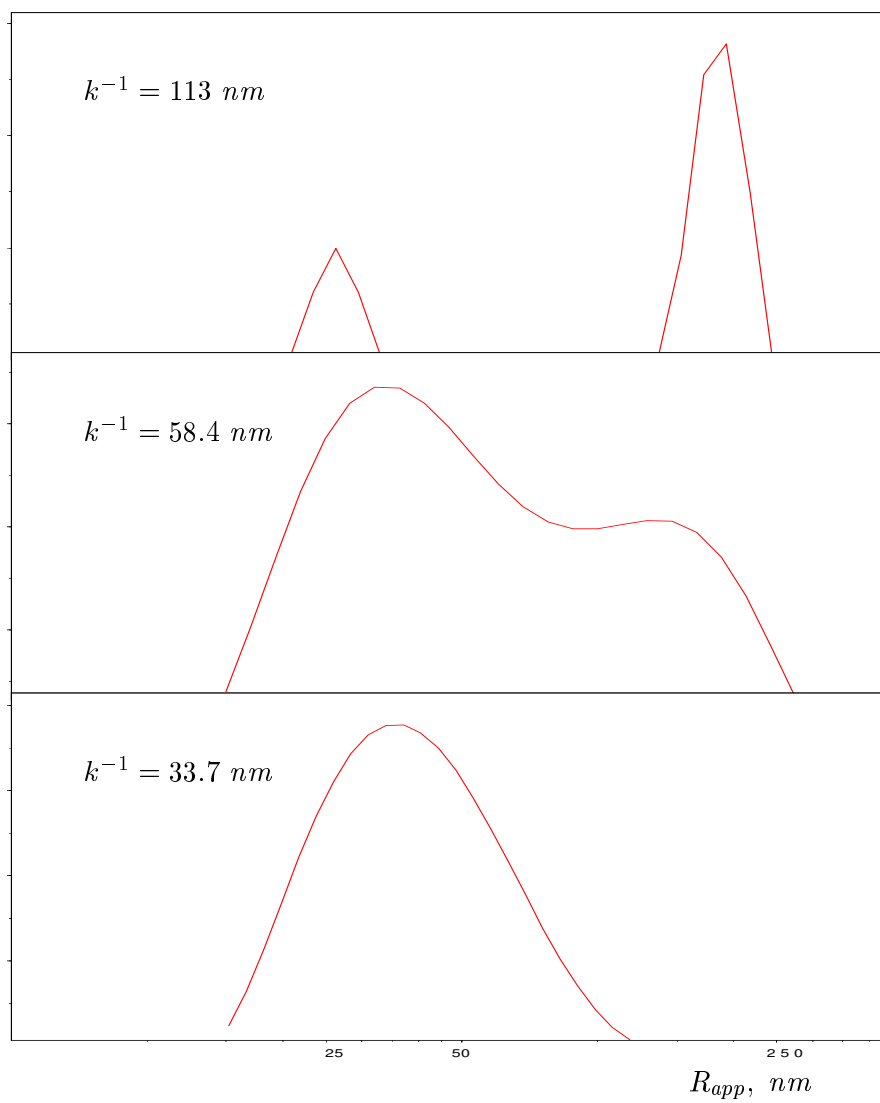


Fig. 2.b.

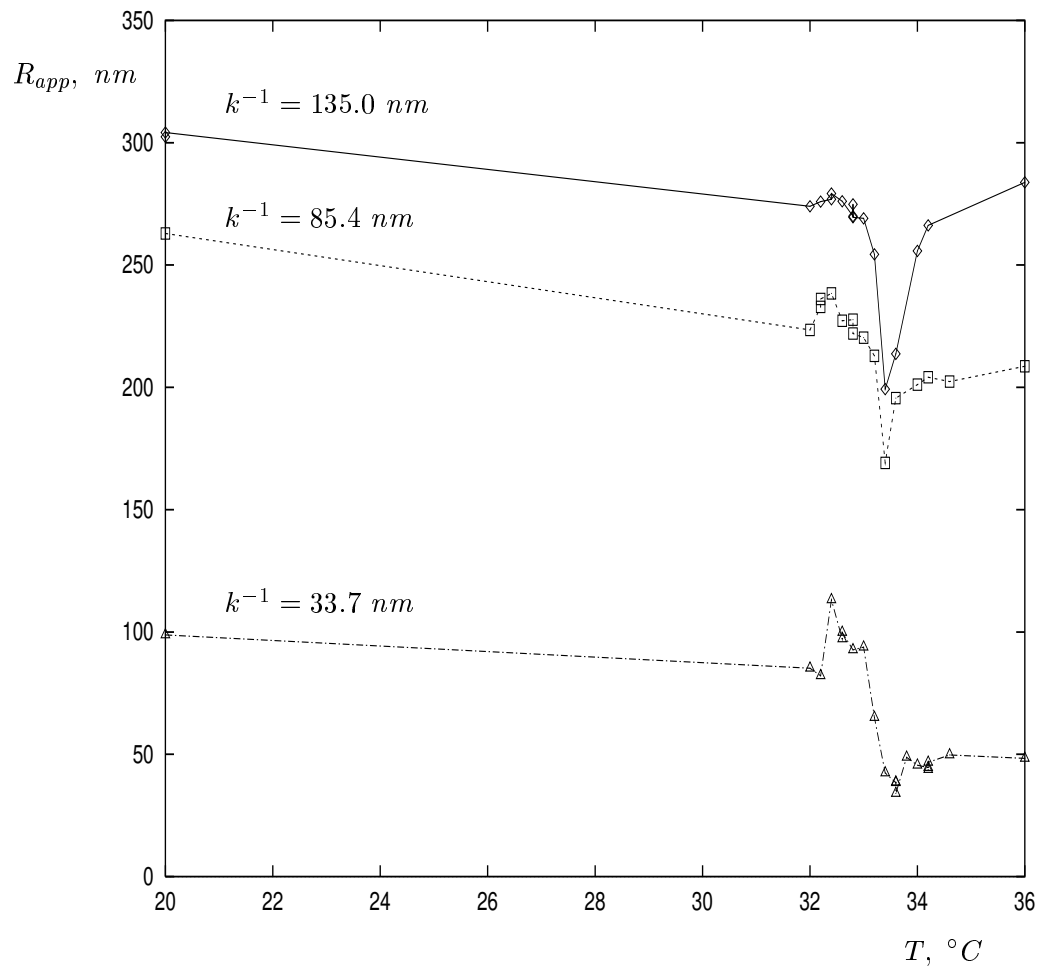


Fig. 3.

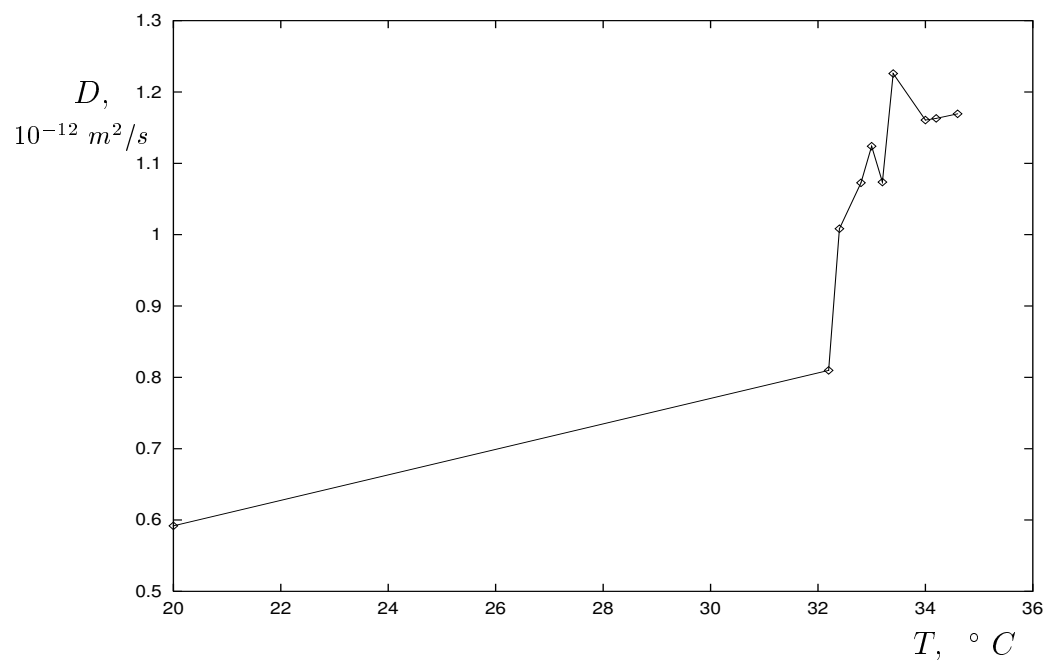


Fig. 4.

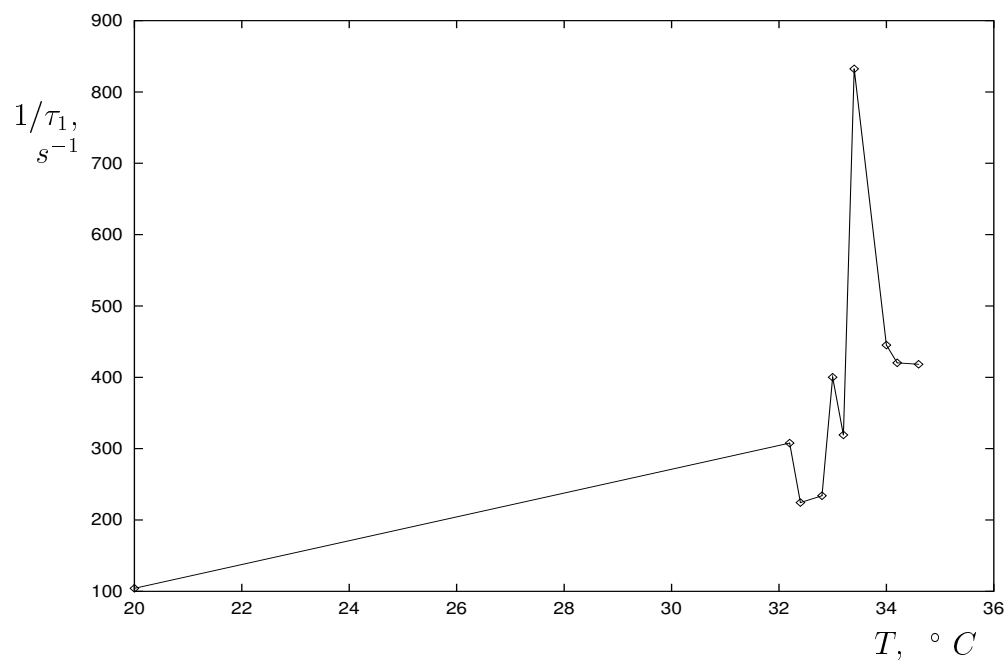


Fig. 5.

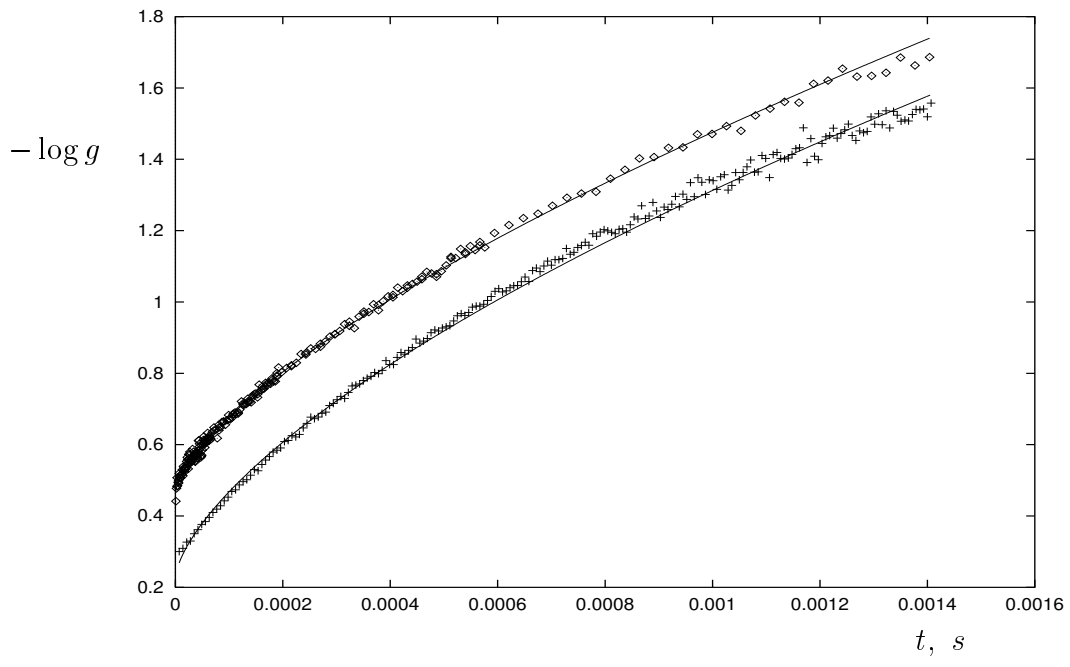


Fig. 6.