

Dynamic Properties of Semidilute Solutions at the Theta Point

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Here we report results obtained by neutron spin echo on semidilute theta solutions of polystyrene in deuterated cyclohexane. It is shown that the pertinent length for the diffusion coefficient is not the correlation length ξ_θ of concentration fluctuations but rather the distance between binary contacts. At length scales smaller than this distance, the dynamics is linked to the local viscosity, which is found to be surprisingly concentration and temperature dependent. [S0031-9007(96)01382-8]

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The theta temperature corresponds to the peculiar thermodynamic situation for polymer solutions where binary interactions vanish. Thus static properties, such as the osmotic bulk modulus K , are only sensitive to ternary interactions. In semidilute solutions, meaning above the overlap concentration C^* , the correlation length ξ_θ of concentration fluctuations decreases as the inverse of the concentration C [1]. However, even if two body thermodynamic interactions vanish, topological interactions remain due to the impossibility for entangled polymers to cross each other. This implies that dynamic properties, such as the shear elastic plateau modulus G , remain sensitive to binary contacts at theta. The two moduli K and G are not proportional: $K = kT/\xi_\theta^3$ while $G = kT/A^2\xi_\theta$. A is the diameter of the tube within which polymers move by reptation and is found to vary as $C^{-2/3}$ if the density of binary contacts is averaged on a volume larger than ξ_θ^3 [2]. In a good solvent, N_e binary contacts are needed to form an entanglement [3], N_e being equal to the number of monomers per entanglement in the melt (for polystyrene PS $N_e = 180$). Polymers become entangled at the concentration C_e at which their radius of gyration is equal to A . This leads to $C_e = C^*N_e^{0.76} = (N/N_e)^{-0.76}$ in a good solvent [3] and to $C_e = (N/N_e)^{-3/4}$ in a theta solvent [4].

Rheological [5] as well as quasielastic light scattering [6] results concerned with length scales larger than ξ_θ are interpreted using A and ξ_θ [2]. At length scales smaller than ξ_θ there is only one chain, and one has to consider the ability of a polymer at theta to perform self-knots [7]. Since the density of binary contacts is proportional to C^2 , the mean distance ls between two successive self-knots varies as $C^{-1/2}$. Two tentative observations by the neutron spin echo technique [8] were performed on 10^6 g/mole linear polymers. In the case of polydimethylsiloxane [9] the range of concentration studied is $0.16 < C < 0.3$ g/cm³, while in the case of labeled deuterated polystyrene [10] ($C = 0.1$ g/cm³) a single polymer was observed using the zero average contrast method [11]. Here we report experimental results ob-

tained with the same technique on semidilute solutions of H-polystyrene in D-cyclohexane for different concentrations ($0.02 < C < 0.12$ g/cm³) and at different temperatures.

Quasielastic scattering experiments allow the measurement of the dynamic structure factor $S(q, t)$, revealing the movement of fluctuating polymers on the scale $1/q$ the inverse transfer vector. Generally, in the case of flexible polymers, for an experiment sensitive to a length L , the time dependence of $S(q, t)$ is of the form

$$S(q, t) = \exp(-t/\tau_c); \tau_c = 1/Dq^2 \text{ for } qL < 1, \quad (1)$$

$$S(q, t) = \exp[-(t/\tau_c)^\beta]; \beta = 1/3 \text{ for } qL > 1. \quad (2)$$

For $qL < 1$, the diffusion coefficient D is q independent but L dependent, while for $qL > 1$, D is q dependent but L independent:

$$D(q) = 1/\tau_c q^2 = kTq/6\pi\eta_{loc}, \quad (3)$$

where η_{loc} is usually taken as the solvent viscosity η_s .

In the case of semidilute solutions at theta $S(q, t)$ is rarely a single exponential even at $q\xi_\theta < 1$. Depending on the relative time scale, two different diffusion coefficients are measured [6]. Let T_r be the longest viscoelastic relaxation time. For $\tau_c/T_r > 1$ a diffusion coefficient is measured, for which $K = C d\pi/dC$ is the only restoring "force" of concentration of fluctuations. For $\tau_c/T_r < 1$, a diffusion coefficient D_{ge1} is measured for which the longitudinal elastic modulus $M_g \propto G$ also plays a role. K and M_g are of the same order of magnitude [12] but are not proportional.

At $q\xi_\theta > 1$ and $qls > 1$, one expects to recover the single chain behavior, as in semidilute solutions in a good solvent [Eq. (3)], because at this length scale K and M_g must become independent of C as $D(q)$. At $q\xi_\theta > 1$ and $qls < 1$, the osmotic modulus is only q dependent, and $D(q)$ is expected to be concentration dependent such as the elastic modulus. A $1/q$ dependence of the diffusion coefficient is found theoretically if one supposes that $M_g \gg K$ [13]. Thus, in semidilute theta solutions, for

$q\xi_\theta > 1$, a change in the concentration dependence of $D(q)$ at $qls \approx 1$, is expected.

The neutron spin echo experiments were performed at $0.016 < q < 0.11 \text{ \AA}^{-1}$. The theta temperature for PS in D-cyclohexane is 38.5°C . The temperature stability was better than 0.1°C . The Toyo Soda PS used has a molecular weight of $M = 6.77 \times 10^6 \text{ g/mole}$ for the verification in good solvent (D-benzene) and a molecular weight of $M = 3.84 \times 10^6 \text{ g/mole}$ for the study in theta solvent (D-cyclohexane) (polydispersity 1.14 and 1.04, respectively). For the good solvent study, $C = 0.018$ and 0.072 g/cm^3 correspond to $C/C_e = 1.6$ and 6, respectively. The concentrations at theta ($0.022 < C < 0.12 \text{ g/cm}^3$) were chosen so that $1.2 < C/C_e < 6.5$ and $1.05 < q\xi_\theta < 27$, using $\xi_\theta(\text{\AA}) = 5.5/C$ (C in g/cm^3) established for PS-cyclohexane [1]. One expects to observe dynamics inside the correlation length ξ_θ , whatever the concentration is, but at scale length $1/q$ larger or smaller than ls , depending on the concentration.

All the spectra were analyzed using a stretched exponential [Eq. (2)] with $\beta = 2/3$ [14]. In Fig. 1, the measured diffusion coefficient $D(q) = 1/\tau_c q^2$ is plotted as a function of q for the different concentrations at theta [15], and in the inset for the concentration $C = 0.117 \text{ g/cm}^3$ at a higher temperature $T = 60^\circ\text{C}$. Data at $q = 0$ correspond to the diffusion coefficients D_{gel} deduced from light scattering [6]. Both techniques lead to diffusion coefficients which are in good agreement. At $T = 39.1^\circ\text{C}$, for $q < 0.05 \text{ \AA}^{-1}$ the diffusion coefficient is concentration and q independent (within experimental errors);

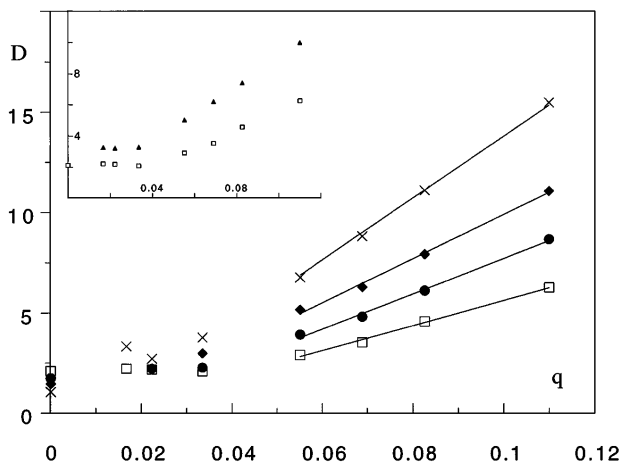


FIG. 1. Diffusion coefficient D (in $10^{-7} \text{ cm}^2/\text{s}$) vs q (in \AA^{-1}) measured near theta ($T = 39.1^\circ\text{C}$) at different concentrations. Crosses, diamonds, circles, squares, correspond to $C = 0.022, 0.057, 0.081, 0.117 \text{ g/cm}^3$, respectively. The inset corresponds to the measurements at $C = 0.117 \text{ g/cm}^3$ in theta (empty squares) and good solvent conditions ($T = 60^\circ\text{C}$, full triangles). The high temperature diffusion coefficient has been multiplied by $\eta_s(T)T_\theta/\eta_s(T_\theta)T$, where $\eta_s(T)$ is the solvent viscosity [19], T_θ and T are in kelvin. Straight lines are guides to the eye. Error bars are of the size of the points except for the two lowest q where they overlap. The $q = 0$ values correspond to D_{gel} measured by light scattering.

while for $q > 0.05 \text{ \AA}^{-1}$, $D(q)$ is proportional to q , but is surprisingly strongly concentration dependent. The light scattering diffusion coefficient D_{gel} increases with concentration as is usual for cooperative diffusion. Consequently, an anomaly in the q dependence of the diffusion coefficient should appear between $q = 3.6 \times 10^{-3}$ (highest light scattering) and $1.6 \times 10^{-2} \text{ \AA}^{-1}$ (smallest neutron scattering). This means that the actual q dependence of the diffusion coefficient in the q range $1/\xi_\theta < q < 1/ls$ is not observable within the performance of the different apparatuses presently available. In the following, the value of the pertinent length scale will be determined for one concentration, by comparing good and theta solvent data. Then the concentration dependence will be considered.

The variation of the diffusion coefficient with temperature (inset in Fig. 1) allows us to determine the reduced variable by data superposition. In Fig. 2, the reduced diffusion coefficient D/D_0 is plotted as a function of the reduced transfer vector qL , where D_0 is the mean value of measurements performed at the three lowest and L the length scale we are looking for. At theta, L can be either $\xi_\theta(\text{\AA}) = 5.5/C$ (C in g/cm^3) [1] or $ls = \sqrt{a\xi_\theta}$, the prefactor a being the adjustable parameter. At high temperature, i.e., in good solvent condition, there is only one pertinent length ξ . It decreases with temperature as $\xi/\xi_\theta = 2[(T - \theta)/\theta C]^{-0.23}$, function deduced from the temperature dependence of K [16]. It is evident from the inset in Fig. 2 that $q\xi_\theta$ is not the correct reduced length scale. Taking at theta, $L = ls$ with $a = 20 \text{ \AA}$, the data obtained at the two different temperatures are superimposed. The constant a

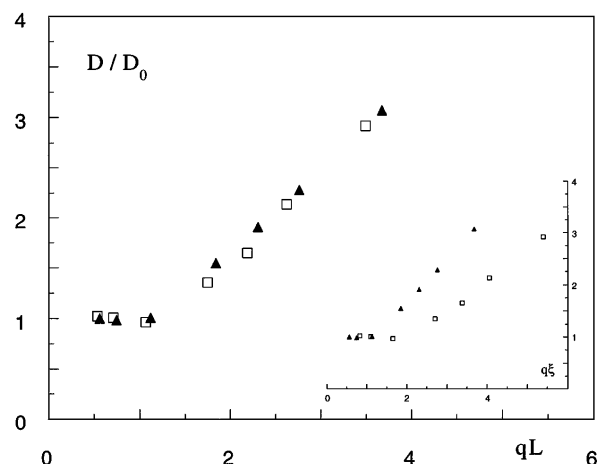


FIG. 2. Reduced diffusion coefficient $D(q)/D_0$ vs the reduced transfer vector qL for measurements near theta at $T = 39.1^\circ\text{C}$ (empty squares) and at $T = 60^\circ\text{C}$ (full triangles) for a given concentration $C = 0.117 \text{ g/cm}^3$. At $T = 60^\circ\text{C}$, L is taken as equal to $\xi = 33.4 \text{ \AA}$; while at $T = 39.1^\circ\text{C}$, L is taken as equal to $\sqrt{a\xi_\theta} = 31.7 \text{ \AA}$ with $\xi_\theta = 49 \text{ \AA}$ and a is found to be equal to 20 \AA . The inset corresponds to a tentative rescaling using L to $L = \xi_\theta = 49 \text{ \AA}$ for $T = 39.1^\circ\text{C}$.

evaluated here is in good agreement with the value [17] given in Ref. [10].

In Fig. 3, the diffusion coefficient divided by its interpolated value at $qls = 1$ [18] is plotted as a function of qls with $ls(\text{\AA}) = \sqrt{20.5 \times 5.5/C} = 10.6/\sqrt{C}$. For the measurements performed at theta with samples having three different concentrations, a unique curve is obtained though no adjustable parameter is used. This is an indication that the reduced length for local dynamics is equal to ls .

Let us now consider the behavior of the diffusion coefficient at q larger than 0.05 \AA^{-1} . $D(q)$ is strongly concentration dependent, the higher the concentration, the smaller the slope of the straight line $D(q) = f(q)$ (Fig. 1). Following Eq. (3) this slope corresponds to $kT/6\pi\eta_{loc}$, in which the only quantity concentration dependent is the local viscosity η_{loc} . In Fig. 4, the local viscosity divided by the solvent viscosity [19] $\eta_{loc}/\eta_s = kT\tau_c q^3/6\pi\eta_s$, is plotted as a function of the concentration. This quantity is q independent for $q > 0.05 \text{ \AA}^{-1}$. The local viscosity is a linear function of the concentration:

$$(\eta_{loc}/\eta_s)_\theta = 1.5 + 33C, \quad (4)$$

C being expressed in g/cm^3 . In the same figure we plot $(\eta_{loc}/\eta_s)_{GS}$ measured on PS D-benzene semidilute good solvent solutions at two temperatures $(\eta_{loc}/\eta_s)_{GS}$ is independent of the temperature and of the concentration:

$$(\eta_{loc}/\eta_s)_{GS} = 1.5 \pm 0.1. \quad (5)$$

In doing so, a systematic error is introduced; because, in good solvent condition, τ_c is proportional to $q^{2.9}$ instead of q^3 [20]. On the other hand, data obtained at $q > 0.09 \text{ \AA}^{-1}$ seem to indicate that, in good solvent, the higher the concentration and the lower the temperature, the smaller the q at which the dynamics becomes sensitive to the persistence length [21]. It would be interesting to confirm this by investigation different molecular weight with a wider range of temperature and concentration.

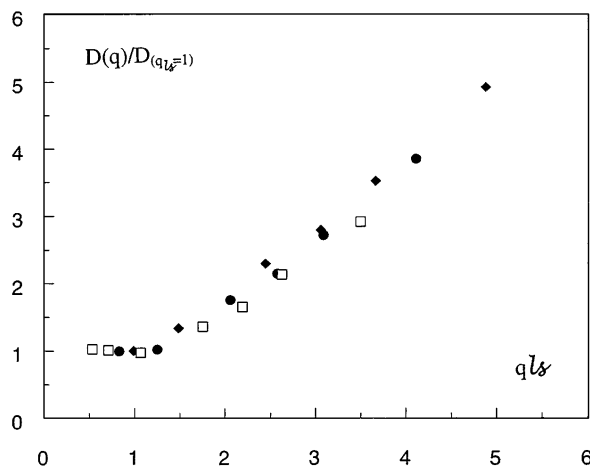


FIG. 3. Reduced diffusion coefficient vs the reduced length qls for the three highest concentrations at $T = 39.1 \text{ }^\circ\text{C}$ (symbols have the same meaning as in Fig. 1). The good superposition indicates that the local diffusion coefficient varies with $ls = \sqrt{a\xi_\theta}$.

In the semidilute theta condition, the zero concentration limit of $(\eta_{loc}/\eta_s)_{\theta, C=0} = 1.5$ comes from our definition of the characteristic decay time τ_c . $S(q, t)$ was fitted using the expression $S(q, t) = \exp[-(t/\tau_c)^{2/3}]$ instead of $S(q, t) = \exp[-1.35(t/\tau_c)^{2/3}]$ [22]. Using this later expression, the local viscosity would have been reduced by the factor $(1.35)^{3/2} = 1.57$, or, in other words, our results confirm the 1.35 prefactor value of Ref. [22].

What is the origin of the concentration dependence of the local viscosity measured at a length scale as small as 50 to 10 \AA and in a concentration range where, in good solvent, $\eta_{loc} = \eta_s$. Theory on the internal viscosity [23] as well as the effective medium approach (Ref. [22], p. 180) cannot explain our results, because, on one hand, the internal viscosity, i.e., the dissipation produced by monomer-monomer friction added to the usual monomer-solvent friction, is predicted to be, in the dilute solutions, molecular weight dependent in good solvents and to be constant at theta. This last point infers that the internal viscosity is independent of the concentration in semidilute theta solutions. On the other hand, the effective medium theory [22] considers that a polymer moves in a medium in which viscosity varies as C^2 , due to the presence of the other polymers.

In Fig. 5, we plot as a function of the temperature the relative local viscosity, η_{loc}/η_s . As the temperature is increased from theta, the higher the concentration, the larger the decrease in the local viscosity. In the same figure we plot η_{loc}/η_s for the two PS benzene solutions, a quantity which is concentration and temperature independent. The most striking result is the variation of the relative macroscopic viscosity, η_m/η_s , measured some ten years ago [5] with the magnetorheometer on a sample ($M = 6.77 \times 10^6 \text{ g/mole}$, $C = 0.083 \text{ g/cm}^3$). The variation of local and macroscopic viscosities, are identical within ex-

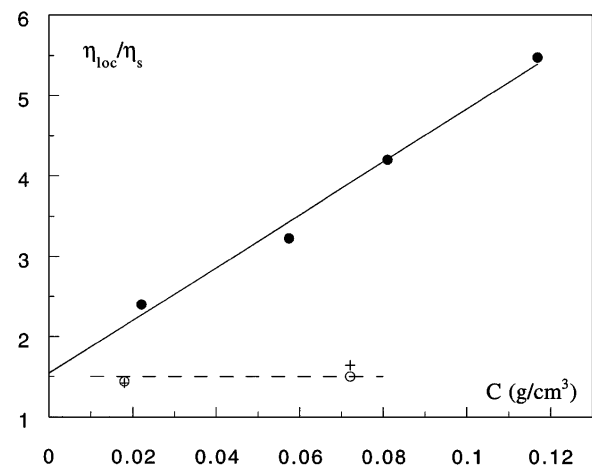


FIG. 4. Relative local viscosity $\eta_{loc}/\eta_s = (kT\tau_c q^3)/(6\pi\eta_s)$ vs the concentration for PS cyclohexane at theta (full circles) and PS benzene at two temperatures $T(^{\circ}\text{C}) = 30.6$ (empty circles) and 65 (crosses). The full line corresponds to Eq. (4) and the dotted line corresponds to Eq. (5).

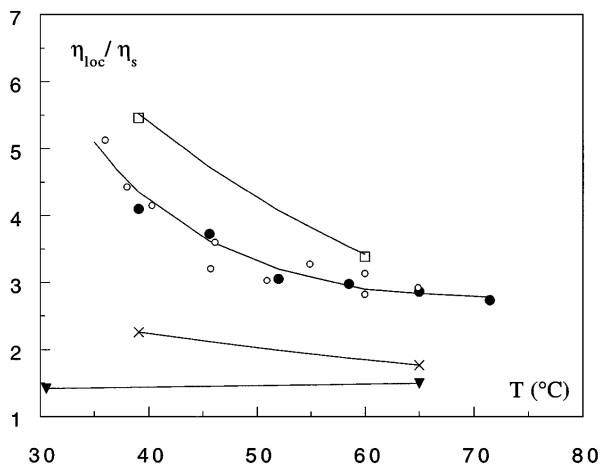


FIG. 5. Relative local viscosity η_{loc}/η_s vs the temperature T . The symbols have the same meaning as in Fig. 1, the others correspond to PS/benzene solutions (full triangles) and to the relative macroscopic viscosity [5] multiplied by 5×10^{-6} (open circles). The full lines are guides to the eyes.

perimental errors. This decrease of the macroscopic viscosity as the temperature increases just above theta, which remains theoretically unexplained, is due to the local viscosity. Thus we switch from a macroscopic to a local problem awaiting an explanation. However, taking into account the local viscosity behavior, one may wonder if the increase of the macroscopic viscosity predicted theoretically [24] with solvent quality can be observed.

In this paper we have shown that the pertinent length for the local dynamics is not the correlation length ξ_θ but rather the distance between two successive self-knots $ls = \sqrt{a\xi_\theta}$ with $a = 20 \text{ \AA}$. At the highest concentration studied, the diffusion coefficient is independent of q for $qls < 1$. This result contradicts previous spin-echo neutron scattering experiments [9,10] and confirms that for polystyrene semidilute theta solutions the longitudinal and osmotic moduli are of the same order of magnitude [6]. We have shown that the local dynamics is influenced by a viscosity which is concentration and temperature dependent. This last dependence, which cannot be understood within the framework of current theory, allows us to account for the variation of the macroscopic viscosity with temperature.

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- [1] J.P. Cotton, B. Farnoux, G. Jannink, *J. Chem. Phys.* **57**, 290 (1972); P. Wiltzius, H.R. Haller, D.S. Cannell, and D.W. Shaeffer, *Phys. Rev. Lett.* **51**, 1183 (1983).
- [2] M. Rubinstein and R.H. Colby, *Macromolecules* **23**, 2753 (1990).
- [3] E. Raspaud, D. Lairez, and M. Adam, *Macromolecules* **28**, 927 (1995).
- [4] E. Raspaud, D. Lairez, and M. Adam (to be published).
- [5] M. Adam and M. Delsanti, *J. Phys. (Paris)* **45**, 1513 (1984).
- [6] M. Adam and M. Delsanti, *Macromolecules* **18**, 1760 (1985).
- [7] F. Brochard and P.G. de Gennes, *Macromolecules* **10**, 1157 (1977); P.G. De Gennes, *Scaling Concept in Polymers Physics* (Cornell University Press, Ithaca, 1979).
- [8] F. Mezei, *Neutron Spin Echo Spectroscopy* (Springer, Berlin, 1980).
- [9] B. Ewen, D. Richter, B. Farago, and B. Stuhn, *J. Non-Cryst. Solids* **172**, 1023 (1994).
- [10] A. Brulet, J.P. Cotton, A. Lapp, and G. Jannink, *J. Phys. (Paris)* **6**, 331 (1996).
- [11] These experiments were performed at $q\xi_\theta > 1$, i.e., a condition where the self and total $S(q,t)$ are identical, as only one polymer exists in the volume ξ_θ^3 .
- [12] It was shown [5,6] that in the case of PS, for $0.02 < C < 0.12 \text{ g/cm}^3$, $2.7 < M_g/K < 0.5$, a ratio which decreases as the concentration increases.
- [13] F. Brochard, *J. Phys. (Paris)* **44**, 39 (1983).
- [14] This exponent was fitted on one spectrum ($q = 0.11 \text{ \AA}^{-1}$, $C = 0.057 \text{ g/cm}^3$) and was found equal to 0.72. Taking β equal to 2/3 or to 0.72 introduces an error of 5% in the τ_c determination.
- [15] The temperature was fixed 0.6 °C above the theta temperature in order to avoid proximity to the demixing curve.
- [16] P. Stepanek, R. Perzynski, M. Delsanti, and M. Adam, *Macromolecules* **17**, 2340 (1984).
- [17] G. Jannink (private communication).
- [18] For $C = 0.022 \text{ g/cm}^3$, $qls = 1$ is not in the range of neutron scattering. If $D_{(qls=1)}$ is determined by extrapolation, results obtained on the four samples lie on a single curve.
- [19] The viscosities of deuterated solvent are $\eta_{benzD}(P) = 1.12 \times 10^{-4} \exp(1204/T)$ and $\eta_{cycloD}(P) = 6.54 \times 10^{-5} \exp(1482/T)$, where T is in kelvin; c.f. J.A. Dixon and R.W. Schiessler, *J. Phys. Chem.* **58**, 430 (1954).
- [20] M. Adam and M. Delsanti, *Macromolecules* **10**, 1229 (1977).
- [21] L.K. Nicholson, J.S. Higgins, and J.B. Hayter, *Macromolecules* **14**, 836 (1981).
- [22] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986), p. 135.
- [23] Y. Rabin and H.C. Ottinger, *Europhys. Lett.* **13**, 423 (1990).
- [24] R.H. Colby, M. Rubinstein, and M. Daoud, *J. Phys. II (Paris)* **4**, 1299 (1994).

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Equation (2) should read as follows:

$$S(q, t) = \exp[-(t/\tau_c)^\beta]; \quad \beta = 2/3 \quad \text{for} \quad qL > 1. \quad (2)$$