Rheological Behaviour of Polymer Systems in the Vicinity of Critical Regions

Garry Kerch*

Centre of Science and Engineering EKOTRA, Nicgales str.4-235, LV-1035, Riga, Latvia, E-mail:garry.k@usa.net

SUMMARY:Flow induced phase separation in polymer solutions can be considered taking into account that mechanical motion proceeds in Minkowski space-time. The spinodal temperature shift increasing with increase of the shear rate is interpreted as a result of relativistic effects. Relativistic phenomena can play the important role in processes of flow, especially when velocity of kinetic units on microscopic or mesoscopic level approaches some limiting velocity. The role of the value of limiting velocity in manifestation of relativistic effects was considered and changes of properties of polymers were discussed.

Introduction

A number of phenomena are characterized by drastic changes in mechanical and physical properties during the flow of polymer melts and solutions or during the mechanical deformation of polymer solids. The processes of high-speed melt spinning, flow induced phase separation in polymer solutions, critical coil-stretch transition for flexible molecules, abrupt neck-like deformation of polymers, abrupt shear thickening of the viscosity in the vicinity of critical regions, negative thyxotropy, sharp increase of effective surface energy, stress intensity factor, dynamic fracture toughness during the dynamical fracture of solid polymers are the examples of such phenomena. These phenomena can be considered from a single point of view and drastic changes in mechanical behaviour may be attributed to some general properties of any mechanical motion.

The purpose of this paper is to demonstrate the role of finite limiting velocity and to show how the relativistic approach can be applied to mechanical phenomena in fluids and solids.

 CCC 1022-1360/00/$ 17.50+.50/0

Results and discussions

Let us consider a system of particles arranged in parallel layers which cooperatively slip over each over with some constant velocity[1]. The layer 2 moves with velocity V relative to the layer1 and the layer 3 moves with velocity v relative to the layer 2. If in the framework of the system the relative velocity of mutual displacements is limited and the value of the limiting velocity is equal to some arbitrary constant c, then one can arrive at a conclusion that velocity u of the layer 3 relative to the layer 1 cannot be equal to the sum V + v. In alternative case, when magnitude of velocity is not limited, one can increase step by step the value of velocity of each next layer by certain value Δv until infinity. So the simple arithmetical law of addition of velocities does not stand within the framework of a system provided that the value of velocity of mutual mechanical displacements is limited. The limiting velocity should not by all means be equal to velocity of light. All above mentioned is valid for any other value of limiting velocity. So $u \neq V + v$ and we must assume

$$u = A(V + v) = Av(1+ V/v), \tag{1}$$

$$v = A(u - V) = Au(1 - V/u). \tag{2}$$

As a matter of fact Eqs.(1) and (2) demonstrate viewpoints of two different observers. Combining Eqs.(1) and (2) yields

$$A^2 = \frac{1}{(1+V/v)(1-V/u)}. \tag{3}$$

If A=1, then classical law of addition of velocities u = V + v is valid. Let us denote $A^2 = 1/1-q$ and after simple transformations of Eq.(3) we obtain

$$1 - V/u = (1 - q)/(1 + V/v),$$

$$u = (v + V)/(1 + qv/V). \tag{4}$$

The boundary conditions, due to the existence of limiting velocity c, are

$$c = A\,(V + c),\ A = 1/(1+V/c). \tag{5}$$

According to Eq.(4) we obtain

$$u_{v=c} = (c + V)/(1 + qc/V). \tag{6}$$

Eq.(6) is consistent with boundary conditions (5) provided $q=V^2/c^2$ .Finally, the law of addition of velocities takes the form

$$u = (v+V)/(1 + Vv/c^2). \tag{7}$$

The difference between the relative velocity u of layers 3 and 1 and the arithmetical sum of velocities V+v increases with decreasing the limiting velocity of mechanical displacements c within the system. In the case $c = \infty$ the law u = V+v is valid. So any limitation in the magnitudes of velocities of mutual displacements leads to the law of addition of velocities in the form of Eq.(7). One can assume that infinite velocity is impossible in systems of finite size and the Eq.(7) will be valid in all such systems. The consequence of the limitation of the magnitudes of velocities is that "rigid bodies" and "incompressible fluids" have become impossible objects. For, by definition, they would transmit signals instantaneously. One can conclude that rigidity of a body will increase with increasing the value of speed limit. It is consistent with well known formula

$$E = \rho c^2 \tag{8}$$

where E is the elasticity modulus,ρ is the density and c is the velocity of sound.

Eq.(7) can be rewritten as

$$\frac{dx}{dt} = \frac{V + \frac{dx}{dt}}{1 + \frac{dx}{dt}\frac{V}{c^2}} = \frac{dx + V\,dt}{dt + dx\,\frac{V}{c^2}} \tag{9}$$

Hence

$$x' = \gamma(x + Vt),$$

$$t' = \gamma(t + x\frac{V}{C^2}). \qquad (10)$$

By symmetry, we must have

$$x = \gamma(x' - Vt'),$$

$$t = \gamma(t' - x'V/c^2). \qquad (11)$$

Taking into account Eqs.(11), the Eqs.(10) can be written as

$$x' = \gamma[\gamma(x' - Vt') + \gamma V(t' - x'V/c^2)] = \gamma^2 x'(1 - V^2/c^2),$$

$$t' = \gamma[\gamma(t' - x'V/c^2) + \gamma V/c^2 (x' - Vt')] = \gamma^2 t'(1 - V^2/c^2). \qquad (12)$$

Hence

$$\gamma = 1 / (1 - V^2/c^2)^{1/2}, \qquad (13)$$

and Eqs.(10) - (11) are the Lorentz transformations. But instead of velocity of light we must use the limiting velocity c characteristic for the system under consideration. The value of the limiting velocity depends on the nature of interaction between the elements of the system.

Derivations of Lorentz transformations that dispense with postulate of the invariance of speed of the light are known for a long time[2-5] and underline a general character of special relativity as a universal theory describing the structure of space-time. The apparently ad hoc and privileged selection of a specific physical process of the light-signal propagation as a fundamental phenomenon underpinning the basis of special relativity obviously restricts the area of application of the theory. It has been noted [5] that special relativity rules all classes of natural phenomena, not only electromagnetic interactions, which have no privilege other than a

historical one. So, it is a more general approach if the bases of Einsteinian relativity are taken as the special relativity principle and the existence of limiting speed, instead of the relativity principle and some specific experimental observation such as the law of light propagation.

It has been shown[6-8] that equations of motion of crystal dislocations can be brought into a form analogous to those of a particle in special relativity. Dislocations suffer Lorentz contraction in the direction of motion and the total energy is also given by the relativistic equation. But in all equations velocity of light is replaced by velocity of sound. Velocity of elastic waves is the limiting velocity for mechanical displacements in solids. Mott [9] found that the velocity of a crack in solids should asymptotically approach a terminal velocity. It has been shown recently [1,10] that comparatively large weight changes of viscose fibers as a result of fracture can be observed due to relativistic reasons.

We can state that any motion proceeds in Minkowski space-time and that for mechanical displacements of the elements of solids and fluids the limiting velocity obviously differs from velocity of light. As a consequence , if one takes into consideration that motion proceeds in Minkowski space-time, where limiting velocity is not as high as velocity of light, the drastic increase of mechanical characteristics in the vicinity of critical velocity is predictable phenomenon.

Kobayashi et al[11] experimentally demonstrated that cracks in amorphous brittle materials always travel at velocities smaller than the Rayleigh wave speed. Relativistic effects have been observed in a number of works[1,10-21] dealing with dynamical fracture. Yoffe[12] showed that stresses in the neighborhood of the crack adopt a universal form near the tip, and this universal singularity contracts in the direction of motion as the cracks approach the speed of sound and that at around 60% of the Rayleigh wave speed a crack should become unstable, since the maximum tensile stress would no longer be directly ahead of the crack, but would instead be off at an angle. Crack tip instabilities have been discussed recently by Marder and Gross[13] and Marder and Fineberg [14].The energy needed to form a new crack surface increases drastically[15] , the velocity of cracks begins to oscillate[16] and the fracture surface shows periodic structure as the velocity of a crack approaches some characteristic limiting velocity. It has been observed that effective surface energy[17],stress intensity factor[18,19],dynamic fracture toughness[20,21]also increase sharply as the limiting speed is approached.

All the above mentioned theoretical consideration and experimental data support the view that equations of relativistic thermodynamics [22)]

$$T = T_0/(1 - v^2/c^2)^{1/2}$$

$$\Delta Q = \Delta Q_0/(1 - v^2/c^2)^{1/2} \qquad (14)$$

should be valid as well taking into account that the value of limiting velocity c could differ from velocity of light.

Let us consider now the behaviour of fluids. The phenomenon of negative thyxotropy is well known. For example [23)], a several hundred-fold increase in consistency is easily induced by stirring or shaking. A 5% solution of polymethacrylic acid of degree of polymerisation 10000 shows a 350-fold increase in apparent viscosity (from 5 poise to 1750 poise) after subjection, for about one minute, to a rate shear of 10 sec^{-1} The transformations were completely reversible.

The phase-separation behaviour can be greatly influenced by shear flow. As far back as 1952 A.Silberberg and W.Kuhn [24)] reported that for the system polystyrene-ethyl cellulose-benzen a quantitive relationship exists between the number of degrees, ΔT, by which the system is below its critical solution temperature T_c , and the role of shear q which can completely reverse the phase separation at the temperature T_c -ΔT It has been reported that flowing polystyrene solutions with high molecular weights of $2x10^6$ became turbid at temperatures much higher than the spinodal temperature of quiescent solutions [25)] .

We shall take the free energy of mixing n_1 moles of solvent with n_2 moles of polymer to be given by the Flory-Huggins equation [26)]

$$\Delta G_M = RT[n_1 \ln(1 - \varphi) + n_2 \ln \varphi + \chi_1 \varphi (1 - \varphi)N] \qquad (15)$$

where R is the gas constant,T is absolute temperature, φ is the volume fraction of polymer, and N is given by $N = n_1 + m\, n_2$, with m the molar volume of polymer divided by the molar volume of solvent; χ_1 is the interaction parameter, which is assumed to be a constant, independent of concentration.

If we take into account equations (14) the eq.15 must be written in the form

$$\Delta G_M = RT[n_1 \ln(1 - \varphi) + n_2 \ln \varphi + \chi_1 \varphi (1 - \varphi)N]/(1 - v^2/c^2)^{1/2} \qquad (16)$$

We may assume, as it was done in paper of Rangel-Nafaile et al [25], that generalized Gibbs free energy of mixing consists of the ordinary Flory-Huggins mixing free energy and an elastic free energy stored in the system due to chain deformations

$$\Delta G_M/RT = n_1 \ln(1 - \varphi) + n_2 \ln \varphi + \chi_1 \varphi (1 - \varphi)N + \hat{w}N \, tr\mathbf{P}/2RT \qquad (17)$$

Where tr**P** is the trace of the stress tensor, $\hat{w}$ is themolar volume of solvent
Then we must rewrite eq.17 in the form

$$\Delta G_M = RT[n_1 \ln(1 - \varphi) + n_2 \ln \varphi + \chi_1 \varphi (1 - \varphi)N]/(1 - v^2/c^2)^{1/2} + \hat{w}N \, \mathbf{tr}P/2 \qquad (18)$$

where the trace of the deviatoric stress tensor **P** is also equivalent to the first normal stress difference if we have a steady laminar shearing flow.
Eq.(16) and (18) show that when velocity of flow approaches some limiting velocity c the temperature of phase separation will increase.
All above consideration is qualitative: we have not made attempts to calculate exactly the numerical coefficients involved, and to predict precisely the shapes of experimental curves. Our aim is only to draw attention to the possibility that new effects may show up in some measurements in the vicinity of critical velocities.

Conclusions

The realization of the significance of the limiting velocity and relativistic ideas about interrelation between energy and inertia of the processes and their sharp increase in the neighborhood of the limiting velocity gives the opportunity to develop a new approach to consideration of mechanical deformation and fracture of solids and to understanding of drastic changes in properties during the flow of polymer melts and solutions. Manifestation of relativistic effects is more pronounced in polymers which are characterized by comparatively

low value of the velocity of elastic waves. Flow induced shift of phase separation temperature to higher temperatures can be interpreted from the relativistic point of view.

References

1.G.M.Kerch,in:*Trends in Continuum Physics*,B.Maruszewski,W.Muschik and A.Radowicz (Eds.), World Scientific Publishing, Singapore 1999, p.195

2. N.Umov in *Selected Works*,(Gosizdat,Moscow,1950).
3. Y.Terletskii in *Paradoxes in the Theory of Relativity*,(Plenum,NY, 1968).
4. W.Rindler in *Essential Relativity*,(Springer-Verlag,New York,1979).
5. J-M.Levy-Leblond,*Am.J.Phys.* **44**,271 (1976).
6. J.I.Frenkel in *Vvedenie v teoriju metalov*, (Nauka, Leningrad, 1972).
7. F.C Frank, *Proc. Phys. Soc.* **62**, 131(1949).
8. J. D.Eshelby, *Proc. Phys. Soc.* **62**, 307 (1949).
9. N. Mott,*Engineering* **165**,16 (1947).
10. G.Kerch, *Int.J.Fracture* **83**, L33 (1997).
11. A.Kobayashi *et al,J.Appl.Pol.Sci.***18**,1625 (1974).
12. E.Yoffe,*Phil.Mag.* **42**,739 (1951).
13. M.Marder and S.Gross,*J.Mech.Phys.Solids* **43**,1(1995).
14. M.Marder and J.Fineberg,*Physics Today*,N9,24 (1996).
15. A.Green and P.Pratt, *Eng.Fracture Mech.* **6**,71(1974).
16. J.Fineberg *et al,Phys.Rev.* B **45**,5146 (1992).
17. L.Rose,*Int.J.Fracture* **12**,799 (1976).
18. J.Dally *et al,Int.J.Fracture* **27**,159 (1985).
19. W.Knauss and K.Ravi-Chandar, *Int.J.Fracture* **27**,127 (1985).
20 . T.Kanazawa *et al,Exp.Mech.* **21**,76.
21. Rosakis.and A. Zehnder,*Int.J.Fracture* **27**,169 (1985).
22. C.Moller,*Det.Kong.Danske Videnskab.Selskab. Mat.-fys.Medd.*,**36,**N1,Kobenhavn,(1967)
23. J.Elissaf, A.Silberberg, A.Katchalsky,*Nature* **176**,Nr.4493, p.1119 (1955)
24. A.Silberberg,W.Kuhn, *Nature*, **170**, Nr4324,450 (1952)
25. C.Rangel-Nafaile, A.Metzner, K.F.Wissbrun, *Macromolecules*, **17**,1187 (1984)
26. P.J.Flory,*Principles of Polymer Chemistry*,Cornell University Press, Ithaca, NY,1953