Heat/mass transfer and dynamics of bubbles in high-polymer solutions—I. Free oscillations

Z. P. SHULMAN

A. V. Luikov Heat and Mass Transfer Institute, Minsk, 220072, Byelorussia

and

S. P. LEVITSKIY

Voronezh State University, Voronezh, 394693, Russia

Abstract—Free oscillations of bubbles in high-polymer solutions with viscoelastic properties are under investigation. Within the framework of the non-isothermal hereditary model of a liquid phase, an equation for the natural frequency of inclusion was derived, taking into account the effects of the interphase heat and mass transfer, diffusion and temperature non-equilibrium state of the vapour–gas mixture and of the liquid compressibility. A numerical analysis of the damping of free pulsations in a wide temperature range was conducted; the effect and specific features of the rheological factor were investigated.

INTRODUCTION

ONE OF the central problems in the dynamics of vapour- and gas–liquid systems is that of studying thermal, mass and dynamic interactions between bubbles and fluid. Investigation of such interactions under various conditions goes back to Rayleigh who considered the collapse of a spherical cavity in an ideal incompressible fluid. Subsequently, the Rayleigh model of an empty cavity was made more sophisticated due to the involvement of viscosity effects within the scope of the Newton carrier phase model and of other factors such as gas content, fluid compressibility, heat transfer and phase transitions [1]. Far less research has been done on the problems of the thermohydrodynamics of bubbles in rheologically complex media, to which polymer fluids also belong. The first works in this field pertained to the study of the specific features of cavity dynamics in various non-linear and viscoplastic media [2–4]. Later, a similar analysis was extended to viscoelastic fluids described by the Maxwell and Oldroyd equations [5–9]. In these, and some other works, only one of the factors that shows up in the dynamics of bubbles was taken into account, that is the non-Newtonian rheology of the fluid, whereas the relaxation effects, characteristic for polymer systems, were described within the scope of the models with one relaxation time. A more comprehensive analysis of the problem with regard to a wide range of bubble sizes and different temperatures of a polymer carrier phase must be conducted on the basis of hereditary rheological models and must include the effects of interphase heat and mass transfer and of liquid compressibility [10]. Taking into account what has been said above, this paper considers the problem of free pulsations of bubbles in high-polymer

solutions or melts in its general formulation. The use of a linear approximation allows one to obtain an exact solution of this problem and to make a comparative evaluation of the effect of each of the factors considered. Using a similar approach, Part II of the work considers heat/mass transfer and the dynamics of bubbles pulsating under the action of an acoustic field.

EQUATIONS OF TRANSFER IN THE LIQUID PHASE

To describe the rheological behaviour of a polymer fluid, advantage will be taken of the hereditary theory [11]. We augment the governing equations [11] with the terms which take into account the Newtonian properties of the solvent

$$\tau = 2\int_{-\infty}^{t} G_1(t-\tau)s\,d\tau + 2\eta_S s \qquad (1)$$

$$p_2 = p_{20} - \int_{-\infty}^{t} [G_2(t-\tau)tr\,\mathbf{e}$$
$$- G_3(t-\tau)\,\partial\theta_2/\partial\tau]\,d\tau - \rho_{20}\eta_v tr\,\mathbf{e} \qquad (2)$$
$$\theta_2 = T_2 - T_0, \quad tr\,\mathbf{e} = e_{kk}.$$

In the case of the polymer melt it should be assumed that $\eta_S = \eta_v = 0$. Spectral representations of the relaxation functions $G_i(t)$ ($i = 1, 2, 3$) are introduced by the relations

$$G_i = G_{i0} + \int_0^{\infty} F_i(\lambda)\,e^{-t/\lambda}\,d\lambda$$
$$G_{20} = K_T, \quad G_{30} = \alpha K_T \qquad (3)$$

where the distribution function $F_i(\lambda)$ for the discrete

NOMENCLATURE

a_i thermal diffusivity
B individual gas constant
c concentration of polymer in solution; coefficient in equation (25); specific heat
D diffusion coefficient
e tensor of deformation rates
E activation energy of a viscous flow
f natural frequency, $(2\pi)^{-1} \operatorname{Im} \{h\} t_0^{-1}$
$G_{\alpha K}$ partial elasticity modulus
k thermal conductivity coefficient; vapour concentration
k_T isothermal volumetric modulus
l sound wave length in gas (vapour)
L specific heat of vaporization
Le Lewis number, Pe_D/Pe_1
M molecular mass
n numbers of relaxation oscillators in spectrum
p pressure
Pe_D diffusion Peclet number, $D^{-1} R_0 (p_{20}/\rho_{20})^{1/2}$
Pe_i thermal Peclet number $(i = 1, 2)$, $a_i^{-1} R_0 (p_{20}/\rho_{20})^{1/2}$
R_G universal gas constant
R bubble radius
s tensor deviator of deformation rates
t time
T temperature
T_b boiling temperature
u specific internal energy
v velocity vector

$z_{1,2}$ parameter of spectral distribution.

Greek symbols
α coefficient of thermal expansion
Γ_i ratio of heat capacities, c_{iP}/c_{iV}
η_p shear viscosity of solution
η_S shear viscosity of solvent
η_v volumetric viscosity of solvent
κ evaporation coefficient
Λ logarithmic damping constant of bubble oscillation
λ relaxation time
μ molar mass of gas (vapour)
ρ density
σ stress tensor
σ coefficient of surface tension
τ deviator of stress tensor.

Subscripts
1   vapour–gas mixture
2   liquid
g   gas
0   equilibrium state
P heat capacity at constant pressure
V heat capacity in constant volume
v   vapour.

Superscripts
$'$ disturbance of equilibrium
$\hat{\ }$ disturbance amplitude
$*$ non-dimensional quantity.

spectrum of relaxation times is

$$F_i = \sum_{k=1}^{n_1} G_{ik} \delta(\lambda - \lambda_{ik}). \qquad (4)$$

For a viscoelastic fluid G_{1k} and the times λ_{1k} for many polymer systems can be estimated by employing the Rause model [12]:

$$\lambda_{11} = 6\pi^{-2}(\eta_p - \eta_S)G_{11}^{-1}, \quad \lambda_{1k} = \lambda_{1k} k^{-2}$$
$$G_{1k} \equiv G_{11} = cR_G T/M. \qquad (5)$$

In a number of cases, the relaxation spectrum is well described by the Spriggs empirical law [12]:

$$\lambda_{1k} = \lambda_{11} k^{-z_1}, \quad z_1 \geqslant 2.$$

The mass, momentum and energy balance equations for a hereditary medium are [11]

$$d\rho_2/dt = -\rho_2 \nabla_2 v \qquad (6)$$

$$\rho_2 \, dv_2/dt = \nabla \sigma \qquad (7)$$

$$k_2 \nabla^2 \theta_2 - T_0 \,\partial/\partial t \left\{ \int_{-\infty}^{t} [G_3(t-\tau) tr\, e \right.$$
$$\left. - G_4(t-\tau) \,\partial\theta_2/\partial\tau] \, d\tau \right\} = 0$$

$$G_4(t-\tau) = G_{40} - \int_0^{\infty} F_4(\lambda) \, e^{-(t-\tau)/\lambda} \, d\lambda,$$

$$G_{40} = \rho_{20} c_{2v} T_0^{-1}. \qquad (8)$$

EQUATIONS OF TRANSFER IN THE VAPOUR–GAS PHASE

Henceforth, we shall assume that a vapour–gas bubble undergoes spherically symmetric oscillations around the equilibrium radius R_0, with both binary mixture components contained in it obeying the equations of state of an ideal gas:

$$p_{1m} = \rho_{1m} B_m T_1, \quad u_m = c_{Vm} T_1, \quad B_m = R_G/\mu_m$$
$$P_1 = \rho_1 B T_1, \quad B = kB_v + (1-k)B_g,$$
$$\rho_1 = \rho_{1g} + \rho_{1v}, \quad m = v, g. \qquad (9)$$

As the bubble oscillates, the concentrations of vapour and gas change along the radius and in time according to the equations of mass transfer. Introducing the mean mass velocity v_1 and the diffusion velocities w_v and w_g according to the relations

$$v_1 = kv_{1v} + (1-k)v_{1g}, \quad w_m = v_{1m} - v_1 \quad (10)$$

and writing the mass balance equations for each of the components in the spherical coordinate system with the axis r connected with the bubble centre

$$\frac{\partial \rho_{1m}}{\partial t} + r^{-2}\frac{\partial}{\partial r}(\rho_{1m}r^2(v_1 + w_m)) = 0. \quad (11)$$

The diffusion velocities are defined by the Fick law:

$$\rho_{1g}w_g = \rho_1 D\, \partial k/\partial r, \quad \rho_{1v}w_v = -\rho_1 D\, \partial k/\partial r. \quad (12)$$

To close the system of balance equations, it is necessary to add momentum and energy equations. For wide ranges of sizes of bubbles and, consequently, of oscillation frequencies, the relationship $l_m \gg R_0$ is valid and allows an assumption of uniform pressure in the bubble. Taking this into account, the energy equation will be stated as

$$\rho_1 c_{1V}\frac{dT_1}{dt} = \frac{p_1}{\rho_1}\frac{d\rho_1}{dt} + r^{-2}\frac{\partial}{\partial r}\left(k_1 r^2\frac{\partial T_1}{\partial r}\right)$$
$$+ \rho_1 D\frac{\partial k}{\partial r}\frac{\partial(u_v - u_g)}{\partial r}. \quad (13)$$

In this approximation, the momentum equation drops out, whereas the rate of pressure variation $p_1 = p_1(t)$ can be obtained with the aid of the energy integral [1]:

$$\frac{dp_1}{dt} = \left[-p_1 R^2 v_1(R,t) + \int_0^R Gr^2\, dr\right]$$
$$\times \left[R^3/3 - \int_0^R \Phi r^2\, dr\right]^{-1} \quad (14)$$

$$\Phi = B/c_{1P},$$

$$G = c_{1P}^{-1}\left\{(B_v - B_g)c_{1V}T_1 r^{-2}\frac{\partial}{\partial r}(Dr^2\rho_1\,\partial k/\partial r)\right.$$

$$+ B\left[r^{-2}\frac{\partial}{\partial r}\left(k_1 r^2\frac{\partial T_1}{\partial r}\right) + \rho_1 D\frac{\partial k}{\partial r}(c_{Vv} - c_{Vg})\frac{\partial T_1}{\partial r}\right]\right\}$$

$$c_{1P} = kc_{Pv} + (1-k)c_{Pg}, \quad c_{1V} = kc_{Vv} + (1-k)c_{Vg}.$$

BOUNDARY CONDITIONS

In the centre of the cavity $(r = 0)$ the boundary conditions are

$$v_{1m} = 0, \quad \partial T_1/\partial r = \partial k/\partial r = 0. \quad (15)$$

Let j denote the rate of phase transitions per unit surface of the bubble. Then, the kinematic condition for the liquid, vapour and gas, the condition for heat fluxes and the equation of kinetics of non-equilibrium phase transitions, with the temperature jump at the phase interphase taken into account, are formulated as [1]:

$$\dot{R} - v_2 = \rho_2^{-1}j, \quad \dot{R} - v_1 - w_v = \rho_{1v}^{-1}j, \quad v_1 + w_g = \dot{R}$$
$$(16)$$

$$k_2\,\partial T_2/\partial r - k_1\,\partial T_1/\partial r = jL \quad (17)$$

$$j = \kappa(2\pi B_v)^{-1/2}[P_s T_2 T_2^{-1/2} - p_{1v}T_1^{-1/2}] \quad (18)$$

$$T_2 - T_1 = 0.32 jT_s(\rho_{1v}(B_v T_s)^{-1/2})^{-1}. \quad (19)$$

Here $T_s = T_s(p_{1v})$ is the saturation temperature, with the following relation being valid along the saturation line:

$$(dp_{1v}/dT_1)_s = L\rho_{1v}T_1^{-1}/(1 - \rho_{1v}/\rho_2). \quad (20)$$

The system of boundary conditions is closed by means of the dynamic condition which determines the balance of forces on the bubble surface:

$$p_1 = p_2 + 2\sigma R^{-1} - \tau_{rr}. \quad (21)$$

All the quantities in equations (16)–(21) are calculated at $r = R(t)$.

GENERAL SOLUTIONS

Within the framework of the earlier formulated complete system of equations, free oscillations of bubbles of variable mass in a polymer solution will be investigated under the assumption that only a low molecular dissolver undergoes phase transitions. The pressure p_2, density ρ_2 and the temperature T_2 in the fluid surrounding the oscillating bubble will be determined from the relations

$$p_{20} = p_2 + p_2', \quad \rho_2 = \rho_{20} + \rho_2', \quad T_2 = T_0 + \theta_2'$$
$$(22)$$

where p_2', ρ_2' and θ_2' stand for the small disturbances of equilibrium parameters. We linearize the equations of transfer in the liquid phase (6)–(8) taking into account the spherical symmetry of the flow and non-dimensionalize them together with rheological relations (1) and (2) using p_{20}, ρ_{20}, T_0 and R_0 as characteristic parameters. The solution of the resulting system of equations is sought in a complex form. Let $h = \mathrm{Re}\{h\} + i\,\mathrm{Im}\{h\}$ be the non-dimensional complex frequency of bubble oscillations and δ be the complex amplitude. We represent the unknown small disturbances of the quantities as

$$\{v_2^*, \rho_2^*, p_2^*, \theta_2^*, \Delta R^*\}$$
$$= \{\tilde{v}_2, \tilde{\rho}_2, \tilde{p}_2, \tilde{\theta}_2, \delta\}\exp(h\tau), \quad (23)$$

$$v_2^* = v_2'/v_0, \quad \rho_2^* = \rho_2/\rho_{20}, \quad p_2^* = p_2'/p_{20},$$

$$\theta_2^* = \theta_2'/T_0, \quad \Delta R^* = (R - R_0)/R_0, \quad \tau = t/t_0,$$

$$t_0 = R_0(\rho_{20}/p_{20})^{1/2}, \quad v_0 = R_0/t_0.$$

After the substitution of equations (23) into the corresponding equations, we find the expressions for the complex amplitudes of disturbances:

$$\tilde{v}_2 = \tilde{v}_{21} + \tilde{v}_{22}, \quad \tilde{\theta}_2 = \tilde{\theta}_{21} + \tilde{\theta}_{22}, \quad \tilde{p}_2 = \tilde{p}_{21} + \tilde{p}_{22},$$
$$(24)$$

$$\tilde{v}_{2k} = -\xi^{-2}(1 + m_k\xi)A_k\, e^{-m_k\xi},$$

$$\tilde{\theta}_{2k} = -G_{5h}(\xi hG_{3h})^{-1}(h^2 G_{5h}^{-1} - m_k^2)A_k\, e^{-m_k\xi},$$

$$\tilde{p}_{2k} = -\xi^{-1}(h - 4/3(\hat{G}_{1h} + \eta_s^*)m_k^2)A_k\, e^{-m_k\xi}$$

$$k = 1, 2, \quad \xi = r/R_0, \quad \eta_s^* = \eta_s/\eta_0,$$

$$\eta_0 = R_0(\rho_{20}p_{20})^{1/2}.$$

Solution (24) is governed by the superposition of the coupled spherical, thermal and sonic waves going off from the oscillating non-isothermal surface of the bubble into the liquid phase. The wave numbers of the sonic and thermal modes, m_1 and m_2 respectively, are the roots of the dispersion equation

$$am^4 - bm^2 + c = 0 \tag{25}$$

$$a = G_{5h}.$$

$$b = h^2 + hG_{3h}^2\, Pe_2\, c_{2P}^{*-1} + hG_{4h}G_{5h}\, Pe_2\, \Gamma_2^{-1},$$

$$c = h^3\, Pe_2\, G_{4h}\Gamma_2^{-1}, \quad c_{2P}^* = c_{2P}\rho_{20}T_0p_{20}^{-1},$$

$$G_{2h} = K_T^* + h\hat{G}_{2h} + h\eta_v^*, \quad G_{3h} = \alpha^*K_T^* + h\hat{G}_{3h},$$

$$G_{4h} = 1 - h\hat{G}_{4h}, \quad G_{5h} = G_{2h} + 4/3h\hat{G}_{1h} + 4/3h\eta_s^*,$$

$$\hat{G}_{kh} = \int_0^r \lambda^*F_k^*(1 + \lambda^*h)^{-1}\, d\lambda^*, \quad k = 1, 2, 3, 4$$

$$K_T^* = K_T p_{20}^{-1}, \quad \alpha^* = \alpha T_0, \quad F_k^* = F_k t_0/p_{20},$$

$$\lambda^* = \lambda/t_0, \quad \eta_v^* = \eta_v/\eta_0.$$

The constants A_1 and A_2 are to be determined from the boundary conditions.

The solution of the internal problem taking account of the temperature and diffusion non-equilibrium state of the vapour gas phase can be obtained by the method of ref. [13]. The equation of transfer in the binary mixture and the boundary conditions are linearized and non-dimensionalized with the use of the same characteristic parameters. The resulting linear system of equations is solved by a substitution similar to equation (23), whereupon the solution, together with equation (24), is introduced into the boundary conditions. As a result, the following equation is obtained for the complex frequency of the natural oscillations of a bubble:

$$\{z_3^2 - 3\alpha_8[1 + \Gamma_1(\alpha_4 - 1)] + n_6^{-1}\Psi(\alpha_4 - Q_{10})\}$$

$$\times [2\sigma^* - 4h(\hat{G}_{1h} + \eta_s^*) - h^2(Q_7 - Q_6)Q_8]$$

$$- p_{10}^*(3\Gamma_1z_3^2 + n_6^{-1}\Psi Q_9h)$$

$$\times [1 + h(n_5 p_{10}^*)^{-1}(m_2 - m_1)(\alpha_4 + n_6 Q_5)Q_8] = 0. \tag{26}$$

The expressions for the quantities α_1–α_9, Q_1–Q_{11}, n_1–n_6 and Ψ are presented in the Appendix. The pressure p_{10}^* satisfies the equilibrium condition

$$p_{10}^* = 1 + 2\sigma^*, \quad p_{10}^* = p_{10}/p_{20}, \quad \sigma^* = \sigma/(p_{20}R_0). \tag{27}$$

Equation (26) is very general and, in the approximation of pressure homogeneity, takes into account all the basic physical factors for free pulsations of bubbles of variable mass in a relaxing non-isothermal hereditary medium. Since the value of the equilibrium

vapour concentration in the bubble, k_0, was considered arbitrary in the derivation of equation (26), this equation can be used for a wide temperature range. With the given temperature of the system T_0, the equation for k_0 follows from equilibrium condition (27), with equation (9) taken into account:

$$k_0 = \{1 + B_v B_g^{-1}[(1 + 2\sigma^*)/p_{v0}^* - 1]\}^{-1},$$

$$p_{v0}^* = p_{v0}/p_{20}. \tag{28}$$

In the case of an incompressible non-Newtonian fluid $(K_T = \infty, \quad \alpha = 0, \quad \hat{G}_{1h} = \hat{G}_{2h} = \hat{G}_{4h} = G_{3h} = \eta_v = 0)$, equation (26) coincides with the characteristic equation of ref. [13] except for the time scale t_0. When $k_0 = 0$ and $\kappa = 0$, equation (26) describes the pulsations of a purely gas bubble. It should be noted that, as follows from equation (28), the condition $k_0 \approx 0$ corresponds to the case $p_{v0}^* \ll 1$, i.e. to low enough temperatures. For this case equation (26) can yield, under certain assumptions, the equation of ref. [14] (the fluid is incompressible and is considered as a thermostat $(z_2 \to \infty)$, the relaxation spectrum $F_2(\lambda)$ is discrete, heat losses in bubble oscillations are absent $(z_3 \to \infty$ or $z_3 \to 0)$ and the pressure in the gas phase follows the polytropic law). The equation of free oscillations of a gas bubble in the Oldroyd fluid [15] can also be considered as a particular case of equation (26) at $k_0 = \kappa = 0, z_2 = \infty$ and $G_{3h} = 0$.

NUMERICAL RESULTS AND DISCUSSION

Equation (26) involves a large number of various physical parameters that characterize the thermophysical and rheological properties of the liquid phase and also the vapour–gas mixture in a bubble. When selecting the values for these parameters it should be taken into account that the greatest interest, from the viewpoint of the joint analysis of heat and mass transfer and rheology effects in the dynamics of bubbles of variable mass, attaches to polymer solutions with highly volatile organic solvents (benzene, toluene, cyclohexane, etc.) which are widely employed in chemical technology. In contrast to polymer fluids, the thermophysical properties of these solutions have been well studied. This is important since the properties of the solutions of low and moderate concentrations are usually close to those of the pertinent solvents. For this reason, we shall first analyse the dynamics of vapour–air bubbles in a pure solvent with a low specific heat of evaporation using toluene as an example $(T_b = 383.7\ \mathrm{K})$. The thermophysical parameters of toluene, its vapours and air were determined with the aid of tabular data and empirical relations within the temperature range $(293\ \mathrm{K}, T_b)$. Consideration was also given to the variants corresponding to the quasi-equilibrium scheme of phase transitions $(\kappa = \infty)$ which has gained great currency in theoretical calculations [1]. The numerical results presented in the plots take into account the relations

$k_0 = k_0(R_0)$ originating under the action of surface tension at $p_{v0} = $ const. in accordance with equation (28). The corresponding curves with $k_0 \neq$ const. are isotherms (IT). Also considered were isoconcentration curves (ICC) along which $k_0 = $ const. and, consequently, the variables were the saturated vapour pressure and the liquid temperature. Curve 7 in Fig. 1 is presented to illustrate the effect of the temperature dependence of thermophysical parameters on the quantity Λ; it corresponds to $T_0 = T_b$ (IT, $\kappa = \infty$), but does not take into account the variation of the liquid and vapour constants within the range (293 K, T_b).

It is evident from the plots in Fig. 1 that the damping ratio of the pulsations of bubbles increases with temperature due to the greater effect of phase transitions. Calculations show that there occurs a simultaneous decrease in the natural frequency f. The difference between the isotherms and isoconcentration curves increases with the growth of T_0 and becomes

especially significant at $T_0 = T_b$ in the case of quasi-equilibrium character of phase transitions (curves 4″ and 4‴). Especially noteworthy is the qualitatively different character of the behaviour of these curves in the region $R_0 < 10^{-4}$ m. This result emphasizes the importance of the inclusion of capillary effects in calculations of natural pulsations of fine vapour–gas inclusions for temperatures close to T_b. It should be noted, however, that in the case of the non-equilibrium phase transition the difference between the isotherms and isoconcentration curves is less significant (curves 4 and 4′). Calculations showed that the effect of the phase non-equilibrium state in the presence of free oscillations of bubbles in toluene is stronger than in water. Therefore, the correct determination of κ for highly volatile fluids is still more important than for fluids with high heats of vaporization.

The oscillations of bubbles in polymer solutions were calculated for two fluids: 1.46% polyethyleneoxide (PEO) solution in water (at $T_0 = 293$ K) and 2.5% polystyrene (PS) solution in toluene with $M \sim 2 \times 10^6$. The values of the parameters for the first solution were taken from ref. [16], whereas for the second solution they were determined taking account of the available experimental data on the basis of the perature–frequency superposition principle [12] at 15 kJ mol^{-1}. They are presented in Tables 1 and 2. The relaxation parts of the moduli $G_{3,4}$, the influence of which is usually significant only for temperatures (or frequencies) close to the glass transition zone, were not taken into account. In calculations, account was taken of the fact that there was a difference between the partial pressure of solvent vapours above the solution $\bar{p}_{vo}^*$ and the pressure p_{vo}^* above the pure solvent ($\bar{p}_{vo}^* = a p_{vo}^*$). The parameters of spectral distribution $z_{1,2}$ (it was assumed that $\lambda_{2p} = \lambda_{21} p^{-z_2}$) varied over the range (2,3); the activity factor a changed over the range (0.85, 1). According to ref. [16], for the PEO solution $\eta_p = 6.9$ Pa s and $z_1 = 3.4$. The values $n_1 = n_1^*$ and $n_2 = n_2^*$ correspond to the limiting curves on the plots, the position of which does not change with a further increase in $n_{1,2}$ [14].

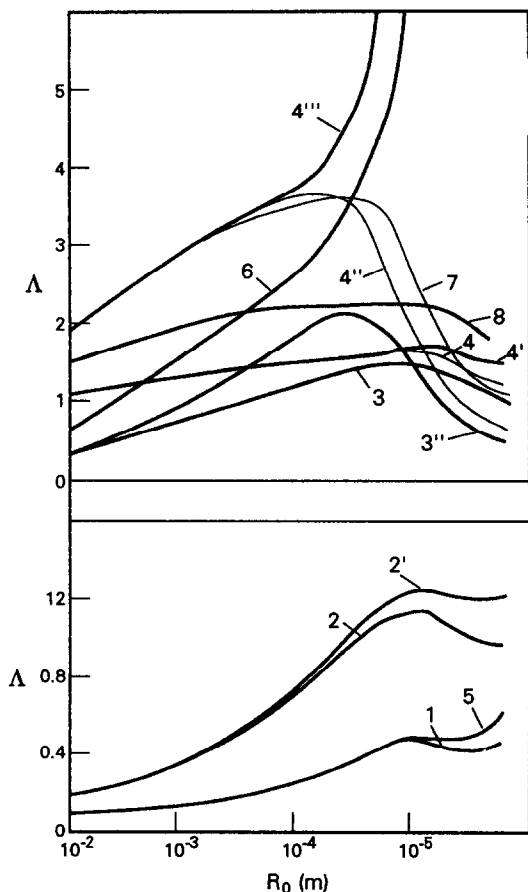Free pulsations of air bubbles in polymer PEO and PS solutions at T_0 293 K are characterized by the plots

FIG. 1. Damping constants of vapour–gas bubble oscillations in toluene. 1, 2, 3, 3″, 4, 4″, 5, 8, IT; 2′, 4′, 4″, 4‴, 6, ICC; 3, 3″, III, κ is equal to 0.02 and ∞, respectively; 4, 4′, IV, $\kappa = 0.018$; 4, 4′, IV, $\kappa = \infty$; 8, IV, $\kappa = 0.027$; 6, water, $T_0 = 373$ K, $\kappa = \infty$; 1, I; 2, 2′, II; 5, I, water. Roman figures I–IV correspond to $T_0 = 293, 363, 378$ and 383.7 K respectively.

Table 1. Thermophysical parameters of the solution and solvent

Parameter	Dimension	Value
ρ_{20}	kg m^{-3}	850
η_s	Pa s	0.5×10^{-3}
η_v	Pa s	5×10^{-3}
α	K^{-1}	10^{-3}
L	J kg^{-1}	4×10^5
c_{2P}	J kg^{-1} K^{-1}	1.7×10^3
Γ_2	—	1.4
k_2	W m^{-1} K^{-1}	0.125
σ	N m^{-1}	0.022
D	m^2 s^{-1}	10^{-5}

Table 2. Rheological parameters of the solution and the pressure of saturated vapour

Parameter	Dimension	Value		
T_0	K	293	378	383.7
η_p	Pa s	0.5	0.125	0.117
η_b	Pa s	1	0.25	0.23
λ_{11}	s	10^{-2}	2×10^{-3}	1.5×10^{-3}
λ_{21}	s	2×10^{-2}	4×10^{-3}	3×10^{-3}
p_{s0}	Pa	0.287×10^{-4}	0.85×10^5	10^5
K_T	Pa	1.15×10^9	0.63×10^9	0.6×10^9

in Fig. 2. They indicate that the viscoelastic properties of the fluid are responsible for the reduction of dissipative losses in the presence of bubble pulsations as compared to a similar Newtonian fluid. The growth of the spectral distribution parameter z_1 leads to the strengthening of relaxation effects (curves 2 and 3), being attributable to the broadening of the relaxation spectrum. Note that the values of Λ for the PEO solution are very close to the values corresponding to pure water. This is due to the large molecular weight, relaxation time and the value of the parameter z_1 for the fluid. The result agrees with the experimental data on the damping of free oscillations of air bubbles in polyox aqueous solution presented in ref. [17].

The main conclusions resulting from the analysis of free oscillations of vapour–air inclusions are as follows. The effect of the relaxation properties of the fluid on pulsations of variable-mass bubbles, for which the phase change-induced dissipation is large, turns out to be somewhat smaller than in the case of gas inclusions and is important only for $R_0 < 10^{-3}$ m (Fig. 3). The effects of viscoelasticity are especially significant for quasi-equilibrium vapour–gas bubbles (isotherms 1″ and 2″). In this case a qualitatively different character of the variation of Λ on the decrease of R_0 is observed for a viscous fluid with $\eta_S = \eta_p$ and for a viscoelastic solution due to the following two reasons: the reduction of dissipative losses in the course of the pulsations of bubbles due to visco-

elasticity and the growth of the role of this factor along isotherm 2″ against the background of the reduction in heat dissipation due to a decrease in vapour concentration in the bubbles.

When the viscoelasticity of the fluid is taken into account, the natural frequency of small vapour–gas bubbles increases, but in the given polymer solution this effect turns out to be less significant than, for example, in the systems considered in ref. [14]. This result is explained by the difference in molecular weights of the polymers: the variants presented in Table 2 correspond to values of M which are almost an order of magnitude higher than those adopted in ref. [14]. Calculations showed that with the growth of
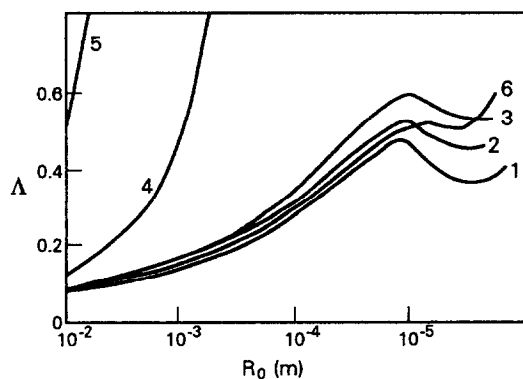

FIG. 2. Damping constant of free oscillations of bubbles in a polymer solution at $T_0 = 293$ K. 1, $z_1 = 2$, $n_1 = 1$; 2, $z_1 = 2.5$, $n_1 = n_1^*$; 3, $z_1 = 2$, $n_1 = n_1^*$; 4, 5, viscous fluid with $\eta = 0.5$, 6.9 Pa s; 1–3, polystyrene solution in toluene; 6, 1.46% polyethyleneoxide solution in water.
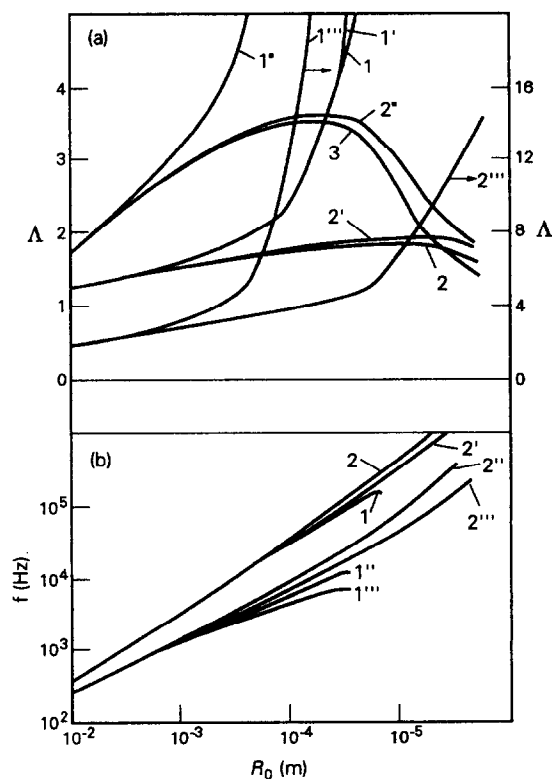
FIG. 3. Damping constant and natural frequency of vapour and vapour–gas bubble in a polymer solution at $T_0 = 383.7$ K, $a = 1$: 1, 1″, 2, 2″, 3. ICC; 1′, 1‴, 2, 2, IT; 2, 2′, 2″, 2‴, 3, $n_1 = n_1^*$; 1, 1′, 1″, 1‴, $\eta_p = \eta_S = 0.117$ Pa s; 1, 1′, $\kappa = 0.02$; 1″, 1‴, $\kappa = \infty$; 2, 2′, $\kappa = 0.02$, $z_1 = 2$; 2″, 2‴, $\kappa = \infty$, $z_1 = 2.5$.

the activity coefficient a the value of Λ decreases due to the reduction of heat dissipation caused by the decrease of vapour content in the bubbles.

It should be noted in conclusion that since a new equilibrium state is impossible for purely vapour bubbles after the change in pressure, equation (26) at $k_0 = 1$ also has a positive real root in addition in the complex root. Due to the effect of capillary pressure, a similar situation is also possible for small enough vapour–gas inclusions with $1 > k_0 > k_*$ where $k_* = \varphi(1+\varphi)^{-1}$, $\varphi = B_g B_v^{-1}[2+3/2\sigma^*]$ [18]. In this case the damping radius fluctuations determined by the complex root of equation (26) are accompanied by an exponential growth or collapse of a bubble. It is important, however, that if the equilibrium vapour content k_0 at $T_0 = T_b$ is determined from formula (28), which takes into account the existing relation $k_0 = k_0(R_0)$, then we shall have $k_0 < k_*$ at all R_0 values. This means that the existence of bubbles with the critical vapour concentration k_* requires the superheating of fluid, whereas the isotherms presented in the plots for $T_0 = T_b$ always correspond to steady free oscillations of inclusions.

CONCLUSIONS

Numerical analysis of the characteristic equa for the complex natural frequency of a vapour bubble in a polymer solution showed that in contrast to the heat and mass transfer processes the relaxation properties of the carrier phase are responsible for the reduction of losses in pulsation as compared to a similar viscous fluid. The effect increases with a decrease in the bubble radius, increase in the relaxation time and with broadening of the relaxation spectrum. For polymer solutions with a high molecular weight this can lead, according to experimental data, to a decrease in the damping constant down to values close to those corresponding to a pure solvent. The effect of the viscoelastic properties of the fluid on damping of oscillations of variable-mass bubbles, for which the phase change-induced dissipation is large, is expressed to a lesser extent than in the case of gas bubbles. The natural frequency of bubbles in a relaxing medium is higher than in a similar viscous fluid.

REFERENCES

1. R. I. Nigmatulin, *Dynamics of Multiphase Media*. Izd. Nauka, Moscow (1987).
2. W. J. Yang and H. C. Yeh, Approximate method for determining bubble dynamics in non-Newtonian fluids, *Physics Fluids* **8**, 758–760 (1965).
3. A. Shima, The natural frequency of a bubble oscillating in Bingham liquids, *Proc. 13th Congr. Int. Assoc. Hydraul. Res.*, Kyoto, Vol. 2, pp. 55–62 (1969).
4. S. P. Levitskiy, V. B. Yevchenko and A. T. Listrov, On the oscillations of a gas-filled spherical cavity in. pseudoplastic and dilatant fluids, *Izv. AN SSSR Mekh. Zhidk. Gaza* **1**, 146–148 (1975).
5. J. R. Street, The rheology of phase growth in elastic liquids, *Trans. Soc. Rheol.* **12**, 103–131 (1968).
6. H. S. Fogler and J. D. Goddard, Collapse of cavities in viscoelastic fluids, *Physics Fluids* **13**, 1135–1141 (1970).
7. I. Tanasawa and W.-J. Yang, Dynamic behaviour of a gas bubble in viscoelastic liquids, *J. Appl. Phys.* **41**, 4526–4531 (1970).
8. S. P. Levitskiy and A. T. Listrov, Small oscillations of a gas-filled spherical cavity in viscoelastic polymer media, *Zh. Prikl. Mekh. Tekh. Fiz.* **1**, 137–142 (1974).
9. S. P. Levitskiy and A. T. Listrov, The effect of viscoelastic properties of liquid on the dynamics of small oscillations of a gas bubble, *Zh. Prikl. Mekh. Tekh. Fiz.* **3**, 82–87 (1976).
10. Z. P. Shulman and S. P. Levitskiy, Dynamics of a gas–vapour bubble in a hereditary medium with account for heat and mass transfer, *Dokl. Akad. Nauk BSSR* **24**, 1088–1091 (1980).
11. R. M. Christensen, *Introduction in the Theory of Viscoelasticity*. Wiley, New York (1969).
12. G. V. Vinogradov and A. Ya. Malkin, *Polymer Rheology*. Izd. Khimiya, Moscow (1977).
13. F. B. Nagiyev and N. S. Khabeyev, The effects of heat transfer and phase transitions in oscillations of vapour–gas bubbles, *Akust. Zh.* **25**, 271–279 (1979).
14. S. P. Levitskiy and A. T. Listrov, Investigation of the effect of dissipation, thermophysical and rheological factors on free oscillations of gas bubbles. In *Heat and Mass Transfer*—VI (Minsk), Vol. 6, Part 2, pp. 80–88 (1980).
15. S. P. Levitskiy, Dissipative effects in pulsations of gas bubbles in viscoelastic polymer fluids, *Zh. Prikl. Mekh. Tekh. Fiz.* **1**, 98–105 (1979).
16. T. W. Spriggs, A four-constant model for viscoelastic fluids, *Chem. Engng Sci.* **20**, 931–940 (1965).
17. W. D. McComb and S. Ayyash, The production, pulsation and damping of small air bubbles in dilute polymer solutions, *J. Phys.* **13**, 773–787 (1980).
18. N. S. Khabeyev and V. Sh. Shagapov, Oscillations of vapour–gas bubbles in an acoustic field, *Izv. AN SSSR Mekh. Zhidk. Gaza* **3**, 79–83 (1986).

APPENDIX: NON-DIMENSIONAL QUANTITIES IN EQUATION (26)

$$\alpha_1 = (B_v - B_g)c_{1P}^{-1}, \quad \alpha_2 = 1/3\chi(p_{20}/(\rho_{20}B_v T_0))^{1/2},$$

$$\chi = 0.32, \quad \alpha_3 = L(\rho_{20}/(2\pi p_{20}B_v T_0)^{1/2}),$$

$$\alpha_4 = B_v T_0 L^{-1}, \quad \alpha_5 = (B_v - B_g)B_0^{-1},$$

$$B_0 = k_0 B_v + (1-k_0)B_g, \quad \alpha_6 = k_1/k_2,$$

$$\alpha_7 = L(3c_{1P}T_0)^{-1}, \quad \alpha_8 = z_3 \coth z_3 - 1,$$

$$\alpha_9 = z_1 \coth z_1 - 1, \quad z_1^2 = h Pe_D,$$

$$z_2^2 = h Pe_2, \quad z_3^2 = h Pe_1, \quad Q_1 = (1-k_0)(3\alpha_9)^{-1},$$

$$Q_2 = \alpha_2(Le-1) + \alpha_1 k_0 Q_1 Pe_D,$$

$$Q_3 = 1 + 3\kappa\alpha_3\alpha_4 B_9 B_0^{-1}Q_1 Pe_D + 3/2\kappa\alpha_2\alpha_3\alpha_4,$$

$$Q_4 = 3\kappa\alpha_3\alpha_8 Q_2 - (Le-1)(\alpha_8 Q_3 + 3\kappa\alpha_3 k_0\alpha_7 Pe_1)$$
$$- \kappa\alpha_1\alpha_3 k_0(1-k_0)Pe_D,$$

$$Q_5 = \alpha_6\alpha_8(\alpha_4 - 1 + \Gamma_1^{-1}), \quad Q_6 = n_1(1 - n_3 n_6),$$

$$Q_7 = n_2(1 - n_4 n_6), \quad Q_8 = (n_3 Q_7 - n_4 Q_6)^{-1},$$

$$Q_9 = n_1 n_2 n_5 n_6(n_4 - n_3)Q_8, \quad Q_{10} = Q_{11}(\alpha_4 + n_6 Q_5),$$

$$Q_{11} = (n_1 n_4 - n_2 n_3)Q_8,$$

$$\Psi = 3\Gamma_1(\alpha_6 Q_4)^{-1}(\kappa\alpha_3 k_0 Pe_1)[\alpha_5(1-k_0)(Le-1)\Gamma_1^{-1}$$
$$+ \alpha_1(1-k_0)Le + Le - 1] + \alpha_8 Q_3(Le-1) - 3\kappa\alpha_3\alpha_8 Q_2,$$

$$n_1 = -m_1^2 + h^2 G_5^{-1}, \quad n_2 = -m_2^2 + h^2 G_5^{-1}, \quad n_3 = 1 + m_1,$$

$$n_4 = 1 + m_2, \quad n_5 = G_5(hG_3)^{-1}, \quad n_6 = Q_3(Le-1)(\alpha_6 Q_4)^{-1}.$$

TRANSFERT THERMIQUE/MASSIQUE ET DYNAMIQUE DES BULLES DANS DES SOLUTIONS DE HAUTS POLYMERES—I. OSCILLATIONS LIBRES

Résumé—On étudie les oscillations libres de bulles dans des solutions d'un haut polymère à propriété viscoélastique. Dans le cadre d'un modèle héréditaire non isotherme d'une phase liquide, une équation pour la fréquence naturelle d'inclusion est obtenue, prenant en compte les effets du transfert de chaleur et de masse entre phases, du non équilibre de diffusion et de température du mélange vapeur–gaz et de la compressibilité du liquide. Une analyse numérique de l'amortissement des pulsations libres est conduite dans un large domaine de température; on étudie les configurations spécifiques et l'effet du facteur rhéologique.

WÄRME- UND STOFFÜBERTRAGUNG UND BLASENDYNAMIK IN HOCHPOLYMEREN LÖSUNGEN—I. FREIE OSZILLATIONEN

Zusammenfassung—Freie Oszillationen von Blasen in hochpolymeren Lösungen mit viskoelastischen Eigenschaften werden untersucht. Im Rahmen des nichtisothermen "Vererbungsmodells" einer Flüssigphase wird eine Gleichung für die natürliche Frequenz entwickelt. Dabei werden folgende Einflüsse berücksichtigt: Wärme- und Stoffübertragung über die Phasengranze, Nichtgleichgewichtszustand des Dampf-Gasgemisches im Hinblick auf Diffusion und Temperatur sowie Kompressibilität der Flüssigkeit. Die Dämpfung der freien Schwingungen wird in einem weiten Temperaturbereich numerisch analysiert. Die Auswirkung und die spezifischen Merkmale des reologischen Faktors werden ebenfalls untersucht.

ТПЛОМАССООБМЕН И ДИНАМИКА ПУЗЫРЬКОВ В РАСТВОРАХ ВЫСОКОПОЛИМЕРОВ—I. СВОБОДНЫЕ КОЛЕБАНИЯ

Аннотация—Исследуются свободные колебания пузырьков в растворе высокополимера с упруго-ваязкими свойствами. В рамках неизотермической наследственной модели жидкой фазы получено уравнение для собственной частоты включения, учитывающее эффекты межфазного тепломассо-переноса, диффузионной и температуоной неравновесности парогазовой смеси, сжимаемости жидкости. Проведен численный анализ затухания свободных пульсаций в широком диапазоне температур, изучено влияние и особенности проявления реологического фактора.