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# EFFECTS OF RELAXATIONAL DIFFUSION IN FILM BOILING OF A POLYMER SOLUTION

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*Effects of relaxational diffusion during rapid evaporation of a solvent from a polymer solution taking place as a result of a thermal shock from the side of the free surface of the liquid are investigated. It is shown that, as a result of diffusional resistance to evaporation, a polymer-enriched layer is formed in the vicinity of the phase interface that can stabilize substantially the shape of the phase interface.*

Diffusional transfer in polymer systems depends substantially on the temperature and concentration conditions, the quality of the solvent, and the hereditary factor. The contribution of the latter can be characterized by the Deborah number $\mathrm{De} = \lambda/t_D$, where $t_D$ is the characteristic diffusion time. When $\mathrm{De} >> 1$, the system has no possibility of rearranging in the process of diffusional transport, and the solvent diffuses practically through the macromolecular matrix. If $\mathrm{De} << 1$, processes of macromolecular relaxation in the solution occur on a much shorter time scale than diffusional transport, and calculation of the concentration field can be carried out on the basis of the classical diffusion equation. In the case where $\mathrm{De} \sim 1$ rearrangement of polymer chains takes place on a time scale comparable to the characteristic time of concentration equilibration in the solution. The instantaneous macromolecular conformation is not equilibrium, and therefore one should expect the diffusional transfer to have a relaxational character. According to [1], the diffusional flux $\mathbf{n}$ is defined in this case as

$$\mathbf{n} = -\rho_2 \int_0^t \mu\,(t - t')\,\nabla k\,(t', x)\,dt'\,, \quad \mu\,(t) = D_i\,\delta\,(t) + \frac{D_0 - D_i}{\lambda} \exp\left(-\frac{t}{\lambda}\right), \tag{1}$$

where $\mu$ is the memory kernel for a single relaxation time.

Conditions favorable for manifestation of relaxational processes are difficult to create in traditional diffusion experiments due to high values of the time scale $t_D$. The reverse situation is observed during rapid evaporation of a solvent from a polymer solution under the action of a thermal shock from the side of the evaporation surface. In this case, diffusional resistance to the evaporation process can turn out to be attributable to the value of not only the equilibrium transfer coefficient $D_0$, but also the nonclassical parameters $\lambda$ and $D_i$.

The objective of the present work was modeling of the processes under consideration during nonstationary evaporation of the solvent from the surface of the solution with rapid heat supply.

1. Let us consider a horizontal layer of a polymeric liquid heated uniformly to the temperature $T_{20} = T_s(p_0, k_0)$. The initial layer thickness is $L$. The space over the layer is occupied by the saturated vapor at the same temperature. At the initial instant, a constant heat flux $q$ is applied to the surface. It is assumed that the process takes place at a constant vapor pressure $p_0$ and transfer of the evaporating component to the phase transition interface in the liquid is effected by means of a diffusional mechanism. Let us direct the $0x$ axis from the bottom ($x = 0$) to the free surface ($x = h(t)$).

The heat flux fed to the evaporation surface goes into evaporation of the solvent and heating of the liquid $q = jl + k_2 dT/dx$. We derive the equation of motion for the boundary based on the assumption that the densities

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of the substances comprising the solution are additive and vary negligibly during evaporation and diffusion. For $h(t)$ we obtain

$$l\rho_2 \frac{dh}{dt} = q - k_2 \frac{dT}{dx}, \quad x = h(t). \tag{2}$$

The temperature and concentration fields are obtained from the equations

$$\frac{dT}{dt} = a_2 \frac{d^2T}{dx^2}, \quad a_2 = \frac{k_2}{\rho_2 c_{p2}}, \tag{3}$$

$$\frac{dk}{dt} = D_i \frac{d^2k}{dx^2} + \frac{D_0 - D_i}{\lambda} \int_0^t \exp\left(-\frac{t-\tau}{\lambda}\right) \frac{d^2k}{dx^2}\, d\tau. \tag{4}$$

The initial and boundary conditions are as follows:

$$h(0) = L; \quad T(0, x) = T_0; \quad k(0, x) = k_0; \quad \left.\frac{dk}{dx}\right|_{x=0} = 0; \tag{5}$$

$$\text{at } x = h(t): \quad T(t, 0) = T_0; \quad n = -(1 - k_h)\frac{dM}{dt}; \quad l\frac{dM}{dt} = q - k_2 \frac{dT}{dx}; \tag{6}$$

$$n = -\rho_2 D_i \frac{dk}{dx} - \rho_2 \frac{D_0 - D_i}{\lambda} \int_0^t \exp\left(-\frac{t-\tau}{\lambda}\right) \frac{dk}{dx}\, d\tau; \tag{7}$$

$$P_s = \bar{P}_s \Phi_1 \exp\left[1 - \Phi_1 + \chi(1 - \Phi_1)^2\right] \equiv P_0,$$

$$\Phi_1 = k_h\left[k_h + (1 - k_h)\Psi\right]^{-1}; \quad \Psi = v_p/v_{sol}; \quad \bar{P}_s = A\exp(-B/T_h). \tag{8}$$

Equation (8) characterizes the phase equilibrium $p_s = p_s(T_h, k_h)$, for which the Flory–Huggins relationship [2] was used.

Let us consider the initial stage of evaporation, when the relationship $h \approx L$ is fulfilled. For simplicity, we consider phase transitions as taking place according to an equilibrium scheme, and we make Eqs. (2)-(8) dimensionless. We choose $k_0$, $T_{20}$, $L$, and $\rho_2$ as scaling factors. Assuming that $k_h^* = 1 + K$, $M^* = 1 + m$, and $T^* = 1 + \Theta$, where $K$, $m$, and $\Theta$ are small perturbations of the equilibrium quantities, we obtain upon linearization a system of equations whose solution is sought using the Laplace transform. After passing to the image space, we find an asymptotic expression for the dimensionless mass perturbation at $s \to \infty$:

$$\hat{m} = k_0 \sqrt{\alpha_D}\, K (1 - k_0)^{-1} s^{-1/2}; \quad \alpha_D = D_i/D_0 \tag{9}$$

(here and in what follows we drop the asterisk in dimensionlees quantities).

As is shown in [3], in a system with the small parameter $D_i$, manifestation of diffusional slowing down of the evaporation process can be expected at higher values of $k_0$ than would follow from results obtained without taking into account relaxation effects. Let us consider the limiting situation $\alpha_D \to 0$ $(D_i \to 0)$ at finite $\lambda$. Upon coming back to the inverse transform space we find

$$m = 4t^{3/2} qLk_0\, a_2^{1/2} (1 - k_0)^{-1} (\pi\lambda)^{-1/2} (3k_2T_0T_{sk})^{-1},$$

$$K = 2t^{1/2} qLa_2^{1/2} (\pi D_0)^{-1/2} (k_2 T_0 T_{sk})^{-1} ; \quad \Theta = 2t^{1/2} qL (k_2 B)^{-1} . \tag{10}$$

It follows from (10) that relaxational phenomena in diffusion of the evaporating component to the phase interface can reduce substantially the evaporation rate $(m \sim \lambda^{-1/2})$.

The problem under consideration was also solved numerically on a finite time interval using a grid algorithm [4] generalized to the case of relaxational diffusion transfer. The results obtained bear witness to the possibility of substantial concentration of the solution in the vicinity of the phase interface, which leads to redistribution of the heat fluxes going into evaporation of the solvent and heating of the layer.

2. Let us consider the more complex situation when the heat fluxes coming to the phase interface are time-dependent. Let us assume that a high-temperature spherical particle with radius $a$ is submerged instantaneously in a polymer solution with temperature $T_{20}$ and concentration $k_{20}$. We assume that a microscopic vapor layer with thickness $\delta_0 = (R_0 - a) << a$ is formed initially at the solid surface. Assuming the initial temperature of the solid particle to be $T_{\text{s.p}} >> T_{20}$, we investigate the evaporation dynamics of the low-molecular component. We consider the expansion process of the vapor film to be spherically symmetric, and we neglect convective transfer in the vapor. The considered model formulation of the problem is directly related to the problem of utilization of polymeric liquids for hardening cooling of metals and preventing vapor explosions [5].

We determine the temperature profile in the vapor phase by the method of heat balance assuming that $a_1 \approx$ const, the pressure is uniform, and the temperature jump in the Knudsen vapor layer is negligible. For thin layers, the assumption of small thermal losses in the vapor is valid, which leads to an equation for the temperature of the interphase surface in the following form [6]

$$\frac{dT_{1h}}{dt} = \frac{1}{M} \frac{dM}{dt} (T_{1h} - T_{\text{s.p}}) .$$

In this case the heat flux can be defined by the expression

$$q_1 = \rho_1 k_1 (T_{\text{s.p}} - T_{2h})/M ; \quad p_1 h = B_{\text{v}} M T_{\text{av}} ; \quad T_{\text{av}} = (T_{\text{s.p}} + T_{2h})/2 .$$

We write the equation of film surface dynamics within the quasi-acoustic Kirkwood–Bethe approximation [3]:

$$R (1 - V_{2h}/C_2) \frac{dV_{2h}}{dt} + 3 (1 - V_{2h}/(3C_2)) V_{2h}^2/2 =$$

$$= (1 + V_{2h}/C_2) (P_{2h} - P_{20})/\rho_2 + (1 - V_{2h}/C_2) R/(\rho_2 C_2) \frac{dP_{2h}}{dt} , \tag{11}$$

$$R = a + h(t) ; \quad P_{2h} = p_1 + \tau_{2h} ,$$

where $\tau_{2h}$ is the normal component of the tensor of excess stress $T$ of the polymeric liquid at the interphase surface. For a qualitative analysis of the effect of rheological nonlinearity on the evaporation dynamics of the polymer solution it is sufficient to use the equation of state of a hereditary liquid with a single relaxation time [3]

$$\mathbf{T} = \mathbf{T}^{(1)} + \mathbf{T}^{(2)} ; \quad \mathbf{T}^{(2)} = 2\eta (1 - \beta) \mathbf{E} ; \quad \mathbf{T}^{(1)} + \lambda_1 \left[ \frac{D\mathbf{T}^{(1)}}{Dt} - \alpha (\mathbf{T}^{(1)}\mathbf{E} + \mathbf{E}\mathbf{T}^{(1)}) \right] = 2\eta\beta \mathbf{E} . \tag{12}$$

Here the parameter $\alpha$ determines the contribution of nonlinear terms to the total stress $(1/2 \le \alpha \le 1)$. Integrodifferential equation (11) can be reduced to one or two ordinary differential equations for $\alpha = 1/2$ or $\alpha = 1$ [3], which makes it possible to simplify the problem substantially.

The boundary conditions on the surface of the phase transition and the transfer equations in the liquid are formulated similarly to the preceding problem. The system of equations obtained was solved numerically after converting to the Lagrange coordinate $\eta = r/R(t)$ that follows the position of the moving evaporation surface. After reduction to dimensionless form with the use of $R_0$, $\rho_0$, $\rho_2$, and the equilibrium time of the temperature in the liquid $t_{\text{lev}} = R_0^2/a_2$ as scaling factors, we obtain the following equations for $k$ and $T_2$ in the coordinates $\eta$, $\tau$:

$$\frac{dT_2}{d\tau} + \frac{v_R\eta^{-2} - \dot{R}\eta}{R}\frac{dT_2}{d\eta} = \frac{1}{R^2\eta^2}\frac{d}{d\eta}\left(\eta^2\frac{dT_2}{d\eta}\right);$$

$$\frac{dk}{d\tau} + \frac{v_R\eta^{-2} - \dot{R}\eta}{R}\frac{dk}{d\eta} = \frac{\alpha_{\text{D}}}{\text{Le}R^2\eta^2}\frac{d}{d\eta}\left(\eta^2\frac{dk}{d\eta}\right) + \tag{13}$$

$$+ \frac{1-\alpha_D}{\text{Le}\,\lambda}\int_0^t \exp\left(-\frac{\tau-u}{\lambda}\right)\frac{1}{R^2\eta^2}\frac{d}{d\eta}\left(\eta^2\frac{dk}{d\eta}\right)du\,.$$

The results of calculations by the elimination method with a conservative difference scheme revealed characteristic regularities of evolution of the vapor film formed as a result of rapid evaporation of the liquid. In particular, we have revealed a substantial decrease in the surface concentration of the solvent in the nonlinear stage of the process and a decrease in the thermal response as a result of an increase in $T_{2\text{R}}$. Manifestation of relaxational phenomena in diffusion can enhance substantially the result observed and thus contribute noticeably to stabilization of film boiling of the solution.

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## NOTATION

$\rho$, density; $t$, time; $\lambda$, relaxation time; $D_i$, $D_0$, instantaneous and equilibrium diffusion coefficients; $T$, temperature; $p$, pressure; $k$, solvent concentration; $l$, specific heat of evaporation; $j$, phase transition rate per unit area of the phase interface surface; $k_{1,2}$, thermal conductivity coefficients of the vapor and the liquid; $c_p$, specific heat at constant pressure; $M$, mass of the liquid (vapor) in the layer per unit area; $A$, $B$, parameters of the phase equilibrium equation; $\chi$, Flory–Huggins constant; $v_{\text{p}}$, $v_{\text{sol}}$, specific volumes of the polymer and the solvent; $T_{sk}$, derivative of the saturation temperature with respect to the solvent concentration calculated at $k = k_0$; $R$, phase interface radius; $B_{\text{v}}$, individual gas constant for the vapor; $\eta$, Newton viscosity of the solution; $\beta$, model parameter; $\text{Le} = a_2/D_0$, Lewis number; $v_{\text{R}}$, radial component of the velocity at the phase interface. Subscripts: 1, 2, vapor, liquid; 0, initial state; s, saturation; $h$, liquid–vapor interface; *, dimensionlees quantity; av, averaged; lev, levelling; s.p, solid particle; v, vapor.

## REFERENCES

1. P. Neogi, AIChE J., **29**, No. 5, 829-833 (1983).
2. V. P. Budtov and V. V. Konsetov, Heat and Mass Transfer in Polymerization Processes [in Russian], Leningrad (1975).
3. S. P. Levitskiy and Z. P. Shulman, Bubbles in Polymeric Liquids. Dynamics and Heat-Mass Transfer, Lancaster-Basel (1995).
4. N. I. Nikitenko, Conjugate and Inverse Problems of Heat and Mass Transfer [in Russian], Kiev (1988).
5. Z. P. Shul'man, Z. A. Shabunina, and S. P. Levitskii, in: Heat and Mass Transfer-VII [in Russian], Vol. 5, Pt. 2, Minsk (1984), pp. 167-172.
6. A. Inoue, A. Ganguli, et al., J. Heat Mass Transfer, **103**, No. 3, 465-471 (1981).