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# Mathematical modelling of pore formation in polymers using supercritical fluid media in the Ornstein-Zernike approximation

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**Abstract.** The paper studies the process of pore formation using supercritical fluid media. A mathematical model of pore formation in polymers in the process of supercritical carbon dioxide decompression has been developed, taking into account fluctuations in the Ornstein-Zernike approximation based on Patel-Teja cubic equation. Calculations and comparison with experimental data are given on the example of pore formation in polystyrene, which showed satisfactory agreement of the theory with experiment. Parameters of the Lennard-Jones pair interaction potential for carbon dioxide in the carbon dioxide-polystyrene system were obtained. The diffusion coefficient of supercritical carbon dioxide in a polymer takes on a different value than the coefficient of self-diffusion of pure carbon dioxide under the same thermodynamic conditions due to a change in the Lennard-Jones potential profile in a polymeric medium. The obtained values of the parameters of the Lennard-Jones equation, namely, the parameters of the intermolecular interaction potential and the maximum value of the attraction energy, make it possible to adequately estimate the value of the diffusion coefficient under given thermodynamic conditions.

## 1. Introduction

Obtaining materials with a given morphology of the porous structure is an extremely important and relevant area of research in the science and technology of polymers. Currently, most of the processes for obtaining porous structures are associated with the use of significant amounts of toxic chemicals or low-boiling chlorine and fluorine-containing blowing agents. In addition to environmental unpromising, these substances are quite difficult to remove from the polymer at the end of the process. Therefore, much attention is paid to obtaining porous materials using supercritical (SC) CO<sub>2</sub> as active foaming agents. In the last decade, supercritical fluids have found practical application in the processing of a wide class of polymers that can be used in chemistry, pharmaceuticals, surgery, electronics, optics, construction materials, etc. [1]. The processing of polymers using supercritical fluids in comparison with traditional methods is distinguished by a small number of stages of the technological process, moderate operating parameters, which allows to process thermostable polymers, environmental friendliness, easy regeneration and solvent "tunability", and, as a result, low cost of the processing process. Using supercritical fluids, the following polymer processing processes are carried out: plasticization, extraction, impregnation, production of porous structures, crystallization, and viscosity changes in traditional processes (for example, in the extrusion and reflux process). Known methods for modifying polymers can be classified according to several criteria that systematize the accumulated experimental



material. By the nature of the processes, the modification can be divided into two large groups: chemical and physical.

Along with this, interest in this environment is associated with the possibility of changing the morphological and functional properties of polymers as a result of their exposure to supercritical (SC) - CO<sub>2</sub>, as well as the ability of SC-CO<sub>2</sub> to extract low molecular weight substances, including water, residual solvents, monomers from polymers. The process can be adjusted by changing the pressure and temperature in the cuvette. The speed and quantitative characteristics of the diffusion process (plasticization) of SC-CO<sub>2</sub> into polymers can be finely controlled only by simply changing the pressure and/or temperature in the volume where the process is continuing. In this regard, the possibility of directional formation of a porous structure in polymers by varying the pressure and/or temperature of the SC-CO<sub>2</sub> during exposure and decompression is very promising. Obtaining materials with a given morphology of the porous structure is an extremely important and relevant area of research in the science and technology of polymers [2, 3]. Unlike traditional pore production methods (in polymers using low-boiling solvents), supercritical fluid based technologies (SCF) do not require removal of residual solvents from the polymer. Porous polymers obtained in SCF can be used in membranes, medicine, including the creation of implants for bone regeneration, pharmaceuticals, materials science and other industries.

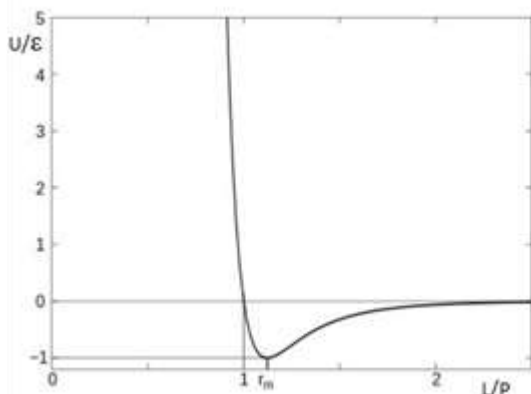
The solution of the problem of mathematical modeling of pore formation process is due to the need to describe the dependence of the size of the resulting pores and the porosity of polymers on the thermodynamic, geometric and kinetic parameters of this process in solving scientific and technical problems of forming porous materials using SCF. Also, when implementing the PGSS process (particles from gas-saturated solutions) using polymers, the obtained particles always have a porous structure [4]. The contribution to the description of particle growth due to pore formation in the PGSS process is absent, which makes it difficult to solve the problem of modeling this process.

An analysis of the literature has shown the absence of a single kinetic mathematical model of the formation and growth of pores. On the other hand, these phenomena and processes are separately described from a theoretical point of view [5, 6], unfortunately, they are not capable of solving specific scientific and technical problems, but they are undoubtedly valuable as a theoretical basis.

To implement the process of pore formation, we have created an experimental installation [3]. The main units of the installation are: high pressure cell ( $V = 600$  ml), a system for creating and maintaining pressure and temperature. The installation allows to process polymers in the form of fibers, granules, and other geometric forms in SCF media. Experiments can be carried out in the pressure range up to 40 MPa and a temperature of 300 ° C. The porosity of the obtained polymers was measured by several methods [3, 5]: by water under high pressure, pycnometrically and by geometric dimensions. The pore size was determined using an optical microscope.

## **2. Modelling of pore formation and pore growth in polymers**

To simulate the process of pore formation a lattice model of the gas will be taken. In accordance with this model, the molecules are located in the lattice sites, and the distance between the lattice sites is the same in all directions. The interaction of individual molecules and clusters is described by Lennard-Jones potential (figure 1), which at the lattice site tends to infinity, and at a distance greater than the size of the lattice site tends to zero. In our case, the supercritical fluid is sorbed by the polymer, therefore, in the lattice points of our model, chains of polymers appear that have their Lennard-Jones potential and affect the interaction energy of molecules and the size of clusters of supercritical fluid - the correlation length. It is proposed to use the potential of pair interaction to describe the interaction of dissimilar molecules in dilute solutions.



**Figure 1.** The potential of Lennard-Jones:  $L$  is the distance between particles,  $\varepsilon$  is the depth of the potential well,  $P$  is the distance at which the interaction energy becomes zero,  $r_m$  is the minimum distance between molecules,  $U$  is the potential.

In accordance with the classical theory of homogeneous nucleation, the most intense pore formation in a polymer is observed in zones with a higher value of supersaturation [6]. In accordance with this theory, the rate of increase in the number of pores per unit volume of the polymer is determined as follows:

$$J = N B \exp(-G) \quad (1)$$

where  $N$  is the concentration of potential nucleation sites in the polymer volume (concentration of  $\text{CO}_2$  molecules);  $B$  - kinetic in the germ or the rate of increase in its size;  $G$  is the Gibbs number determined by the equation:

$$G = W / k_b T \quad (2)$$

where  $k_b$  is the Boltzmann constant;  $T$  is the temperature;  $W$  is the work of the formation of a critical nucleus, which is determined from the equation:

$$W = 16\pi\sigma^3 / 3(\Delta p)^2 \quad (3)$$

where  $\sigma$  is the surface tension at the boundary of the supercritical fluid-polymer;  $\Delta p$  is the pressure difference when crossing this boundary.

To describe the surface tension of individual substances the equation proposed in [7] is used:

$$\sigma = \sigma_0 (1 - \tau)^g (1 + b\tau) \quad (4)$$

where  $\sigma_0$  is the surface tension under normal conditions  $\tau = T / T_{kp}$ ,  $g$  and  $b$  are the dimensionless constants of individual substances.

The evaluation of the surface tension at the “germ – solvent” boundary for nano- and submicron particles was made according to [5]:

$$\sigma = (\sigma_1^2 + \sigma_2^2 - 2\sigma_1\sigma_2 \cos \alpha_s)^{0.5} \quad (5)$$

where  $\alpha_s$  is pore wetting angle with supercritical carbon dioxide solvent.

To calculate the size of the critical nucleus, we use the equation [6]:

$$(4/3)\pi r_{kp}^3 = -k_b T (\partial G / \partial p)_T \quad (6)$$

The calculation of pore size at time  $t$  can be estimated by the equation [6]

$$\ln \left( \frac{r}{r_{cr}} \right) = (\Delta p / 4\eta) t \quad (7)$$

where  $\eta$  is polymer viscosity, and  $\Delta p = 2\sigma / r_{cr}$  is external pore pressure.

The partial derivative in equation (6) can be determined by the equation:

$$(\partial G / \partial p) = \frac{C(t)}{N(T, p)} g(T, p) \quad (8)$$

where  $C(t)$  – concentration of supercritical fluid molecules in a polymer at a time  $t$ ,  $N(T,p)$  – the absolute concentration of fluid molecules at given  $T$  and  $P$ ,  $\vartheta(T,p)$  – specific (molar) volume.

The kinetics of the release of gases from solids is described by the diffusion equation (Fick's second law), which for the Cartesian coordinate system has the following form [8]:

$$\frac{\partial C}{\partial t} = D \Delta C \quad (9)$$

where  $C$  is concentration;  $D$  is diffusion coefficient;  $t$  is time;  $\Delta$  is Laplace operator.

Due to the physical analogy of thermal conductivity and diffusion under supercritical conditions in the present work, the diffusion coefficient of supercritical fluid in the regular region is in the Ornstein-Zernick approximation in the form of the Kawasaki equation [9]:

$$D = \frac{k_b T}{6\pi\eta_g \xi} \quad (10)$$

where  $\eta_g$  is carbon dioxide viscosity;  $\xi$  is correlation length.

The viscosity of carbon dioxide is calculated using the equations presented in [10]:

$$\eta_g = \eta_{id}^* \exp(\ln \eta^*) \quad (11)$$

where  $\eta_{id}$  is the viscosity of the ideal gas,

$$\ln \eta^* = \sum_{i=1}^4 \left( \sum_{j=0}^1 \frac{a_{ij}}{\tau^j} \right) \omega^i \quad (12)$$

where  $\{a_{ij}\}$  are coefficients presented in [10],  $\omega = \rho/\rho_c$  is reduced density.

Correlation length is found by the equation [9]:

$$\xi = R_D \sqrt{nk_b T k_t} \quad (13)$$

Here  $n$  is concentration,  $k_t$  is isothermal compressibility factor,  $R_D$  is Debye attenuation length, which is found from the equation [9]:

$$R_D^2 = \frac{2\pi}{3} \frac{n^*}{T^*} r_m^2 \left( c + \frac{\gamma_0}{3} \right) \quad (14)$$

where  $n^* = n^3 r_m$ ;  $T^* = k_b T / \varepsilon$ ;  $c = (m - \gamma_0(m - 8)) / (m - 6)$ . In particular, for carbon dioxide:  $\varepsilon/k_b = 600$  K;  $m = 6$ ;  $\gamma_0 = 1.24$ ;  $r_m = 2.928 \cdot 10^{-10}$  m. Here  $\varepsilon$  – maximum value of the energy of attraction (depth of the potential well);  $m$ ,  $\gamma_0$  are parameters of intermolecular interaction potential.

In order to find  $\vartheta(T, p)$  one can use the equation of state. To take into account fluctuations in our calculations, a combined equation of state was chosen, which includes the regular and crossover parts based on the Patel-Tei cubic equation of state:

$$\frac{P}{P_{cr}} = (1 - Y) \frac{P_{clas}}{P_{cr}} + Y \frac{P_{cros}}{P_{cr}} \quad (15)$$

where  $P$  is pressure;  $Y$  is quenching (occurrence) function of temperature and density fluctuations;  $cr$  – critical;  $clas$  – classic;  $cros$  – crossover.

The Patel-Teja cubic equation of state in the classical form is presented in [11].

To describe the crossover region, the Helmholtz free energy is written in a dimensionless form:

$$\bar{A}(T, V) = \frac{A(T, V)}{RT} = \Delta \bar{A}(\Delta T, \Delta V) - \frac{V}{V_{0c}} \bar{P}_0(T) + \bar{\mu}_0(T) \quad (16)$$

where  $A(T, V)$  – Helmholtz energy for one moth substance,  $\bar{A}(T, V)$  – Helmholtz energy in the critical region,  $\bar{\mu}_0(T)$  – analytical function of temperature,  $\Delta T = T_r - 1$  – temperature deviation in dimensionless form from temperature  $T_{0c}$ ,  $\bar{P}_0(T) = P(V_{0c}, T) V_{0c} / RT$   $\bar{P}_0$  – dimensionless pressure at

critical isochore  $V=V_{0c}$ , а так же  $\Delta V = V/V_{0c} - 1$  - specific volume deviation in dimensionless form from volume  $V_{0c}$ .

The dimensionless temperature and dimensionless specific volume in the renormalized form for the crossover region is written in the following form:

$$\bar{\tau} = \tau \cdot Y^{-\frac{\alpha}{2\Delta_1}} + (1 + \tau) \Delta \tau_c \cdot Y^{\frac{2(2-\alpha)}{3\Delta_1}} \quad (17)$$

$$\text{where} \quad \Delta \bar{\eta} = \Delta \eta \cdot Y^{\frac{(\gamma-2\beta)}{4\Delta_1}} + (1 + \Delta \eta) \Delta \eta_c \cdot Y^{\frac{(2-\alpha)}{2\Delta_1}} \quad (18)$$

$$\Delta \eta = \frac{V}{V_c} - 1, \quad \Delta \tau_c = \frac{\Delta T_c}{T_{0c}}, \quad \Delta \eta_c = \frac{\Delta V_c}{V_{0c}}, \quad \Delta T_c = T_c - T_{0c}, \quad \Delta V_c = V_c - V_{0c}, \quad \tau = \frac{T}{T_c} - 1$$

Critical indices are equal to:

$$\gamma = 1,24, \beta = 0,325, \alpha = 2 - \gamma - 2\beta = 0,110, \Delta_1 = 0,51$$

The crossover function Y is written as follows:

$$Y(q) = \left[ \frac{q^2}{R(q)} \right]^{\Delta_1} \quad (19)$$

The function R(q) described in equation [19] is:

$$R(q) = \left( 1 + \frac{q^2}{1+q} \right)^2 \quad (20)$$

A parametric variable q having meaning of a renormalized measure of distance from a critical point can be found by solving the equation:

$$q^2 = \frac{\tau}{Gi} + b_{LM}^2 \left( \frac{\Delta \eta + d_1 \tau + d_2 \tau^2}{Gi^\beta} \right)^2 \cdot Y^{\frac{(1-2\beta)}{\Delta_1}}(q) \quad (21)$$

where Gi is Ginzburg criterion, d1 and d2 are individual parameters of substances, and the universal parameter of the linear model is found by the equation:

$$b_{LM}^2 = \frac{(\gamma - 2\beta)}{\gamma(1 - 2\beta)} = 1.359 \quad (22)$$

Taking into account the new variables introduced, the Helmholtz free energy for the crossover region is written in the following form:

$$\bar{A}(T, V) = \Delta \bar{A}(\bar{\tau}, \Delta \bar{\eta}) - \frac{V}{V_{0c}} \bar{P}_0(T) + \bar{\mu}_0(T) - K(\tau^2) \quad (23)$$

The function K, which ensures the correct scaling behaviour of the isochoric heat capacity in asymptotically close to the critical point, is found from the following equation:

$$K(\tau^2) = \frac{1}{2} a_{20} \tau^2 (Y^{-\frac{\alpha}{\Delta_1}} - 1) \quad (24)$$

where  $a_{20}$  - individual substance parameter.

The dimensionless pressure on the critical isochore is written as:

$$\bar{P}_0(T) = \frac{1}{b_1} - \frac{T_{0c}}{T} \cdot \frac{\Omega_a a_0(T)}{Z_{0c} b_2 b_3} \quad (25)$$

Critical function part  $\Delta \bar{A}$  is written in the following form:

$$\Delta \bar{A}(\bar{\tau}, \Delta \bar{\eta}) = -\ln \left( \frac{\Delta \bar{\eta}}{b_1} + 1 \right) + \frac{T_{0c}}{T} \cdot \frac{\Omega_a a_0(\bar{\tau})}{\Omega} \ln \left( \frac{\Delta \bar{\eta} / b_2 + 1}{\Delta \bar{\eta} / b_3 + 1} \right) + \frac{\Delta \bar{\eta}}{b_1} - \frac{T_{0c}}{T} \frac{\Omega_a a_0(\bar{\tau}) \Delta \bar{\eta}}{Z_{0c} b_2 b_3} \quad (26)$$

$$\text{where } b_1 = 1 - \frac{\Omega_b}{Z_{0c}}, \quad b_2 = 1 + \frac{\Omega_b + \Omega_c - \Omega}{2Z_{0c}}, \quad b_3 = 1 + \frac{\Omega_b + \Omega_c + \Omega}{2 \cdot Z_{0c}}$$

where  $\Omega_a, \Omega_b, \Omega_c$  - functions of the critical compressibility factor  $Z_{0c}$ , which are found from the equations:

$$\Omega_c = 1 - 3Z_{0c} \quad (27)$$

$$\Omega_a = 3Z_{0c}^2 + 3(1 - 2Z_{0c})\Omega_b + \Omega_b^2 + \Omega_c \quad (28)$$

$$\Omega_b^3 + (2 - 3Z_{0c})\Omega_b^2 + 3Z_{0c}\Omega_b - Z_{0c}^3 = 0 \quad (29)$$

Taking into consideration equation (22), the crossover equation of state is written as

$$P_{cros}(T, V) = - \left( \frac{\partial A}{\partial V} \right)_T = \frac{RT}{V_{0c}} \left[ - \frac{V_{0c}}{V_c} \left( \frac{\partial \Delta \bar{A}}{\partial \Delta \eta} \right)_T + \bar{P}_0(T) + \frac{V_{0c}}{V_c} \left( \frac{\partial K}{\partial \Delta \eta} \right)_T \right] \quad (30)$$

The sample porosity using our mathematical model is found by the equation:

$$W = \frac{V_{o\phi p}}{\rho(V_{o\phi p} - V_{nop})} \quad (31)$$

where  $\rho$  is polymer density,  $V_{sam}$  – the total sample;  $V_{por}$  – the total volume of all pores in the sample, which is found by the equation:

$$V_{por} = V_{sam} J \frac{4}{3} r^3 \quad (32)$$

To describe the process of pore formation, the concept of “apparent density” was introduced, the definition of which is given in GOST 18898-89. Apparent density is the ratio of the mass of a powder or porous material to the volume it occupies, which in our case is found by the equation:

$$\rho_{\text{как}} = \frac{1}{W} \quad (33)$$

In our experiments carried out in [3], carbon dioxide was used as a supercritical medium, the classical and crossover parameters of which are listed in table 1.

**Table 1.** Classic and crossover carbon dioxide parameters.

Classic critical parameters		Critical offsets		Classical parameters of the equation of state		Crossover options	
$P_{0c}(\text{MPa})$	7.3830	$\Delta T_c(\text{K})$	$1.5500 \times 10^{-1}$	$c_1$	0.63199	$G_i$	$6.18200 \times 10^{-2}$
a)	304.210	$\Delta V_c(\text{l mol}^{-1})$	-	$c_2$	-2.69935	$d_1$	0
$T_{0c}(\text{K})$	0.31330	<sup>1)</sup>	$1.3213 \times 10^{-2}$	$c_3$	0	$d_2$	-2.69935
$Z_{0c}$				N	0		

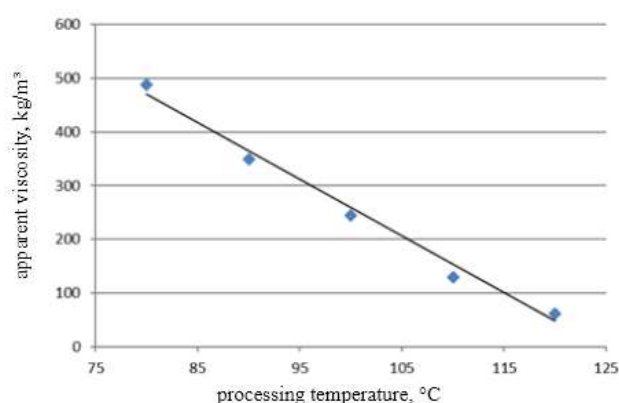
To find the porosity, equations (1) - (7) are solved together. Equation (9) has an analytical solution for C ( $x = [0, l_x]$ ,  $y = [0, l_y]$ ,  $z = [0, l_z]$ ,  $t = 0$ ) = const. The diffusion coefficient D is found by finding the minimum of the error function.

$$F = \sqrt{\frac{\sum_{i=1}^N (W^{pacq} - W^{acc})^2}{N}} \quad (34)$$

In this case, the optimal parameters of the Lennard-Jones pair interaction potential are selected. The specific volume from the equation of state (15) and the value of  $q$  from equation (21) are found numerically by the half-division method.

### 3. Modelling results

The results of the modelling of pore formation in comparison with experimental data are shown in figure 2.



**Figure 2.** The change in the apparent density of polystyrene at  $P = 25$  MPa:  $\diamond$  - experimental results obtained in this work; line - calculation.

Analysis of the obtained data in the form of apparent density makes it possible to estimate how much the sample has changed in density and, as a consequence, its volume in comparison with the initial one. Under normal conditions, the density of our polystyrene was  $1049 \text{ kg/m}^3$ . The increase in porosity (or decrease in density) in figure 2 with an increase in processing temperature is primarily due to a decrease in viscosity  $\eta$  with increasing temperature, but on the other hand,  $\Delta p$  in equation (7), which depends on surface tension, increases. With an increase in temperature, the surface tension decreases and, as we see from the results, the influence and change in the viscosity of the polymer are more significant than the surface tension at the “polymer – SCF” boundary. Consequently, the processing of polymeric materials in order to obtain high porosity should be carried out in the viscous region of the current state of the polymer, where the viscosity varies significantly, rather than in other areas. In further calculations, we can use the parameters of the Lennard-Jones potential for carbon dioxide in the carbon dioxide-polystyrene system found in this work (table 2).

**Table 2.** Parameters of Lennard-Jones pair interaction potential for carbon dioxide in the carbon dioxide-polystyrene system.

$\epsilon/k_b$	$m$	$\gamma_0$	$r_m$
600 K	6	1.24	$2.928 \cdot 10^{-10} \text{ m}$

### 4. Conclusion

A mathematical model of pore formation in polymers in the process of expansion of supercritical carbon dioxide was developed in the Ornstein-Zernike approximation based on the Patel-Teja cubic crossover equation of state. Calculations and comparison with experimental data on the example of pore formation in polystyrene showed satisfactory agreement of the theory with experiment and, as a result, its applicability to the solution of scientific and technical problems.



The diffusion coefficient of supercritical carbon dioxide in a polymer takes on a different value than the coefficient of self-diffusion of pure carbon dioxide under the same thermodynamic conditions due to a change in the Lennard-Jones potential profile in a polymeric medium. The obtained values of the parameters of the Lennard-Jones equation, namely, the parameters of the intermolecular interaction potential and the maximum value of the attraction energy, make it possible to adequately estimate the value of the diffusion coefficient under given thermodynamic conditions.

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