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Simple fluid in an attractive, disordered polydisperse matrix

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The extension of the replica Ornstein-Zernike (ROZ) equations is applied to the study of the structural properties of a Lennard-Jones fluid confined in an attractive polydisperse disordered matrix. The ROZ equations in combination with the orthogonal polynomial expansions for the correlation functions are used. The radial distribution functions are calculated for the adsorbed fluid at different temperatures. The effect of matrix polydispersity on the excess internal energy is considered in our study as well.

Key words: *fluid, integral equations, polydisperse matrix, molecular dynamics, confinement, silica gel*

PACS: *05.20.Jj, 68.43.De, 82.70.Gg*

1. Introduction

Within the framework of the integral equation theory a porous medium involving the fluid is usually treated as a quenched system of disordered particles and is called a matrix. The method of replica Ornstein-Zernike (ROZ) equations of *Given and Stell* [1] in combination with the corresponding approaches is a powerful theoretical tool in investigating the structural and thermodynamic properties of such *partly quenched* systems. A simple, but quite realistic model, which is reasonable from the practical point of view, was proposed by *Kaminsky and Monson* [2] to describe the system of the methane adsorbed into silica gel pores. Within the framework of the model of *Kaminsky and Monson* (KM), the matrix (M) particles are characterized by large sizes comparatively to the adsorbed fluid (F) molecule sizes ($\sigma_{\mathrm{M}}/\sigma_{\mathrm{F}} \approx 7$). The strong fluid-matrix attractive potential ($\approx 6\varepsilon_{\mathrm{F}}$) causes an adsorption of fluid molecules on the matrix particle surface that is treated as the surface of the silica gel pores. The KM model is widely used in various theoretical studies of structural [2–5], thermodynamic [6–8] and even dynamical [9] properties of the fluid confined

[1] In fond remembrance of Zynoviy Gurskii, excelent scientist and good friend.

in the silica gel. But this model is restricted to the monodisperse matrix particles as constituent parts of a model gel material. Naturally, the structure of porous medium has a more complicated geometry. One of the most essential features that should be taken into account is polydispersity of matrix particle sizes.

In the present paper the ROZ equations [1] in combination with the orthogonal polynomial expansions of size-dependent functions [10] are used in order to study structural properties of fluids in disordered polydisperse porous media. Firstly, the polydisperse replica Ornstein-Zernike (PROZ) equations were applied by *Ilnytski et al* [11], where the structural properties of the hard-sphere fluid in the hard-sphere polydisperse matrix were considered. The model of porous medium that was used in [11] is similar to the KM model but without attractive potential. The authors of the paper [11] did not observe significant effects caused by the matrix polydispersity. However, their investigations were restricted only to the hard-sphere interactions, while the structural properties of the system with the attractive fluid-fluid and fluid-matrix potentials could be more sensitive to the polydispersity of the matrix particle sizes. Thus, we propose the present study in order to continue the main idea of previous investigations and to see how the polydispersity affects the structural properties of Lennard-Jones fluid in the attractive matrix. To see the effect of the matrix attraction, the case of hard-core matrices is considered. The molecular dynamics (MD) simulations are performed for the system of fluid in KM matrix to compare radial distribution functions (RDFs) and the values of internal excess energy with the results obtained from ROZ equations.

2. Model and theory

Following the polydisperse extension of the KM model being proposed in our study, the confinement is modelled as an interconnected network of pores formed by the space between unmovable spherical particles of different sizes presenting the matrix. The fluid molecules fill up the space between the matrix particles. The sizes of matrix particles are defined by some distribution function $f(\sigma_\mathrm{M})$. The important characteristics of the matrix is the porosity $\chi = 1 - \eta$, where η is a packing fraction of matrix particles:

$$\eta = \frac{\pi}{6}\rho_\mathrm{M} \int \sigma_\mathrm{M}^3 f(\sigma_\mathrm{M}) \mathrm{d}\sigma_\mathrm{M}. \tag{1}$$

In our study we consider the two cases of interaction between matrix particles and fluid molecules: the first one is the hard-sphere (HS) interaction (the case of HS matrix)

$$\varphi_\mathrm{FM}(r) = \left\{ \begin{array}{ll} \infty, & r < (\sigma_\mathrm{M} + \sigma_\mathrm{F})/2, \\ 0, & r \geqslant (\sigma_\mathrm{M} + \sigma_\mathrm{F})/2, \end{array} \right. \tag{2}$$

and the second one is the interaction by the Kaminsky-Monson (KM) potential [2] (the case of KM matrix)

$$\begin{aligned}\varphi_{\mathrm{FM}}(r) &= \frac{2}{3}\pi\rho_s\sigma_{\mathrm{M}}^3\varepsilon_{gs}\left[\sigma_{gs}^{12}\left(r^6+\frac{21}{20}\sigma_{\mathrm{M}}^2r^4+\frac{3}{16}\sigma_{\mathrm{M}}^4r^2+\frac{\sigma_{\mathrm{M}}^6}{192}\right)\left(r^2-\frac{\sigma_{\mathrm{M}}^2}{4}\right)^{-9}\right.\\ &\qquad\left.-\,\sigma_{gs}^6\left(r^2-\frac{\sigma_{\mathrm{M}}^2}{4}\right)^{-3}\right],\end{aligned} \tag{3}$$

where σ_{M} and σ_{F} are the diameters of a matrix particle and a fluid molecule, respectively. In both cases for the fluid-fluid interaction we use the Lennard-Jones (LJ) potential (4) which is truncated and shifted with $r_c = 2.5\sigma_{\mathrm{F}}$. The KM potential is truncated and shifted as well, but at $R_c = 20.48\sigma_{\mathrm{F}}$.

$$\varphi_{\mathrm{FF}}(r) = 4\varepsilon_{\mathrm{LJ}}\left\{\left(\frac{\sigma_{\mathrm{F}}}{r}\right)^{12}-\left(\frac{\sigma_{\mathrm{F}}}{r}\right)^{6}\right\}. \tag{4}$$

The distribution function of the diameters of matrix particles σ_{M} is chosen to be stepwise:

$$f(\sigma_{\mathrm{M}}) = \begin{cases} 1/(\sigma_U-\sigma_{\mathrm{L}}),\ \sigma_{\mathrm{L}}<\sigma_{\mathrm{M}}<\sigma_U, \\ 0,\ \text{otherwise;}\end{cases} \qquad \sigma_{\mathrm{L}} = 6.055\sigma_{\mathrm{F}} \quad \text{and} \quad \sigma_U = 8.055\sigma_{\mathrm{F}}\,. \tag{5}$$

In order to describe the system of the fluid adsorbed in the polydisperse matrix we use the PROZ equations [11,12] which, in combination with the Percus-Yevick (PY) approximation, represent the reduced form of those in the Madden-Glandt like approach (MGOZ) [13]:

$$\begin{aligned}\tilde{h}_{\mathrm{MM},nm}(k) &= \tilde{c}_{\mathrm{MM},nm}(k)+\rho_{\mathrm{M}}\sum_l \tilde{h}_{\mathrm{MM},nl}(k)\tilde{c}_{\mathrm{MM},lm}(k),\\ \tilde{h}_{\mathrm{FM},n}(k) &= \tilde{c}_{\mathrm{FM},n}(k)+\rho_{\mathrm{M}}\sum_l \tilde{c}_{\mathrm{FM},l}(k)\tilde{h}_{\mathrm{MM},nl}(k)+\rho_{\mathrm{F}}\tilde{c}_{\mathrm{FF}}(k)\tilde{h}_{\mathrm{FM},n}(k),\\ \tilde{h}_{\mathrm{FF}}(k) &= \tilde{c}_{\mathrm{FF}}+\rho_{\mathrm{M}}\sum_l \tilde{h}_{\mathrm{FM},l}(k)\tilde{c}_{\mathrm{FM},l}(k)++\rho_{\mathrm{F}}\tilde{c}_{\mathrm{FF}}(k)\tilde{h}_{\mathrm{FF}}(k),\end{aligned} \tag{6}$$

where a tilde denotes the Fouriez transforms of the pair $h_{\alpha\beta}(r)$ and the direct $c_{\alpha\beta}(r)$ correlation functions (α and β standing for M or F). The PY closure relations to solve (6) can be written

$$c_{\alpha\beta}(r,\sigma_{\alpha,i},\sigma_{\beta,j}) = [\gamma_{\alpha\beta}(r,\sigma_{\alpha,i},\sigma_{\beta,j})+1]F_{\alpha\beta}(r,\sigma_{\alpha,i},\sigma_{\beta,j}), \tag{7}$$

where the indirect correlation function $\gamma_{\alpha\beta}(r)$ is defined as $\gamma_{\alpha\beta}(r)$=$h_{\alpha\beta}(r)-c_{\alpha\beta}(r)$ and $F_{\alpha\beta}(r,\sigma_{\alpha,i},\sigma_{\beta,j})$ is the Mayer function

$$F_{\alpha\beta}(r,\sigma_{\alpha,i},\sigma_{\beta,j}) = \exp[-u_{\alpha\beta}(r,\sigma_{\alpha,i},\sigma_{\beta,j})/k_BT]-1. \tag{8}$$

Any function $\psi(r,\sigma_{\mathrm{M},i},\sigma_{\mathrm{M},j})$ and $\psi(r,\sigma_{\mathrm{M},i})$ can be represented by their expansions

$$\psi(r,\sigma_{\mathrm{M},i},\sigma_{\mathrm{M},j}) = \sum_{k,l}\psi_{kl}(r)P_k(\sigma_{\mathrm{M},i})P_l(\sigma_{\mathrm{M},j}), \tag{9}$$

$$\psi(r,\sigma_{\mathrm{M},i}) = \sum_k \psi_k(r) P_k(\sigma_{\mathrm{M},i}), \tag{10}$$

while the expansion coefficients are given by

$$\psi_{\mathrm{M}M,kl}(r) = \int \mathrm{d}\sigma_{\mathrm{M},i}\mathrm{d}\sigma_{\mathrm{M},j} f(\sigma_{\mathrm{M},i}) f(\sigma_{\mathrm{M},j}) \psi(r,\sigma_{\mathrm{M},i},\sigma_{\mathrm{M},j}) P_k(\sigma_{\mathrm{M},i}) P_l(\sigma_{\mathrm{M},j}), \tag{11}$$

$$\psi_{\mathrm{FM},k}(r) = \int \mathrm{d}\sigma_{\mathrm{M},i} f(\sigma_{\mathrm{M},i}) \psi(r,\sigma_{\mathrm{M},i}) P_k(\sigma_{\mathrm{M},i}). \tag{12}$$

We expand all σ_{M}-dependent functions by using a set of normalized orthogonal polynomials $P_i(\sigma_{\mathrm{M}})$ $(i = 0,1,2,\ldots,n)$ associated with the distribution function $f(\sigma_{\mathrm{M}})$ and defined as follows:

$$\int \mathrm{d}\sigma_{\mathrm{M}} f\,(\sigma_{\mathrm{M}}) P_i(\sigma_{\mathrm{M}}) P_j(\sigma_{\mathrm{M}}) = \delta_{ij}. \tag{13}$$

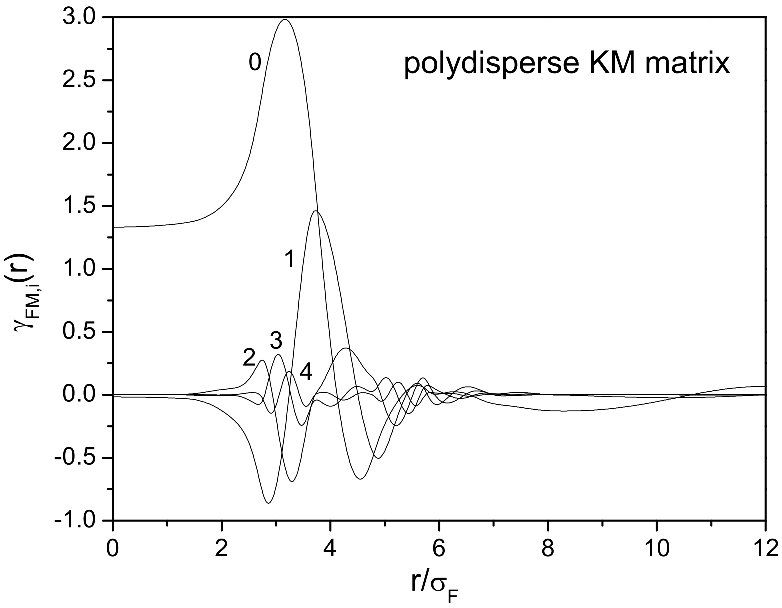

Figure 1. Expansion coefficients of the function γ_{FM} for fluid in KM polydisperse matrix at $T^* = 1.2$.

According to the chosen distribution function (5) the polynomials are used as the normalized, associated Legendre polynomials. Taking into account that an inclusion of strong attraction between matrix and fluid can adversely affect the convergence of the expansion coefficients, in our calculations we take $n = 10$ of the expansion coefficients number to expect a reasonable accuracy. In figure 1 the first five expansion coefficients of the fluid-matrix indirect correlation function $\gamma_{\mathrm{FM},i}$ are presented for the fluid in KM polydisperse matrix at fluid density $\rho_{\mathrm{F}}^* = \rho\sigma_{\mathrm{F}}^3 = 0.2336$ and the packing fraction of matrix $\eta = 0.386$. As is seen these coefficients converge rapidly and for $i \geqslant 5$ they are negligibly small as opposed to the pair correlation function, where convergence of its coefficients is rather poor, especially in the case of the attractive matrix. The extensive questions concerning an accuracy and the problem of choosing the number of expansion coefficients for the considered system, need additional examination and will be published elsewhere. Now, we stay on the assumtion that the choice $n = 10$ is rather satisfactory for us.

We solve the PROZ equations (6) with the PY closure (7) to obtain the expansion coefficients for pair correlation functions $h_{\mathrm{FM},i}(r) = g_{\mathrm{FM},i}(r) - 1$ and $h_{\mathrm{FF}}(r) = g_{\mathrm{FF}}(r) - 1$. Thus, the excess internal energy for a fluid confined in a polydisperse matrix can be easily calculated in the following form [12]:

$$\frac{U^{\mathrm{ex}}}{N} = 4\pi\rho_{\mathrm{M}} \sum_i \int \mathrm{d}r r^2 g_{\mathrm{FM},i}(r)\varphi_{\mathrm{FM},i}(r) + 2\pi\rho_{\mathrm{F}} \int \mathrm{d}r r^2 g_{\mathrm{FF}}(r)\varphi_{\mathrm{FF}}(r). \qquad (14)$$

3. Results and discussion

We performed our calculations for a LJ fluid confined in a matrix at the constant fluid density $\rho_{\mathrm{F}}^* = \rho_{\mathrm{F}}\sigma_{\mathrm{F}}^3 = 0.2336$ and the matrix packing fraction $\eta_{\mathrm{M}} = 0.386$. In order to see an effect of the matrix polydispersity we calculated the expansion coefficients of fluid-fluid and fluid-matrix pair correlation functions for monodisperse ($f(\sigma_{\mathrm{M}}) = \delta(\sigma_{\mathrm{M}} - [\sigma_U + \sigma_{\mathrm{L}}]/2)$) and polydisperse matrix with particle sizes defined by distribution (5). The packing fraction, η_{M}, was fixed by the fitting of the density of the matrix particles corresponding to the distribution function (5) and the equation (1). In table 1 we present the values of excess internal energy of the adsorbed fluid obtained from (14) at two temperatures $T^* = kT/\varepsilon_{\mathrm{F}} = 1.2$ and 2.0 for the cases of mono- and polydisperse KM matrices. The excess internal energy of the fluid confined in the HS matrix is considered as well. The MD simulations are performed to verify our results for the case of monodisperse matrix. It is seen from the PROZ results that the excess internal energy is larger in the case of polydisperse matrix than in the monodisperse one. Simple calculations that can be made for different

Table 1. Excess internal energy per fluid molecule $u^{\mathrm{ex}} = U^{\mathrm{ex}}/N\varepsilon_{\mathrm{F}}$.

T*		HS mono	KM mono		HS poly	KM poly	bulk	
		ROZ	ROZ	MD	PROZ	PROZ	OZ	MD
1.2	u^{ex}	-2.56	-6.49	-7.35	-2.56	-7.30	-1.58	-1.62
	$u^{\mathrm{ex}}_{\mathrm{FF}}$	-2.56	-2.24	-2.28	-2.56	-2.24		
	$u^{\mathrm{ex}}_{\mathrm{FM}}$	0	-4.25	-5.07	0	-5.06		
2.0	u^{ex}	-2.30	-6.35	-6.27	-2.30	-6.81	-1.38	-1.39
	$u^{\mathrm{ex}}_{\mathrm{FF}}$	-2.30	-2.15	-2.02	-2.30	-2.15		
	$u^{\mathrm{ex}}_{\mathrm{FM}}$	0	-4.20	-4.25	0	-4.66		

matrices at a constant porosity show that the larger is the size dispersity, the smaller is an effective area of the surface of matrix particles. At the same time, most part of excess energy between fluid and matrix is caused by attractive interaction on the contact with the matrix particle surface. The smaller is the surface area, the smaller amount of fluid molecules may be located in the first coordination shell near the surface. Thus, a decrease of potential energy can be expected, and this is the opposite effect to what we have. Although, according to the (3) the minimum of the KM potential for the matrix particle with the large diameter is deeper than the small one. Besides, the matrix particles with large sizes can adsorb a greater amount of the fluid molecules due to a larger surface area. Therefore, the increase of excess internal energy is observed in the polydisperse case. And, in this way, our last reasoning agrees well with the results presented in table 1.

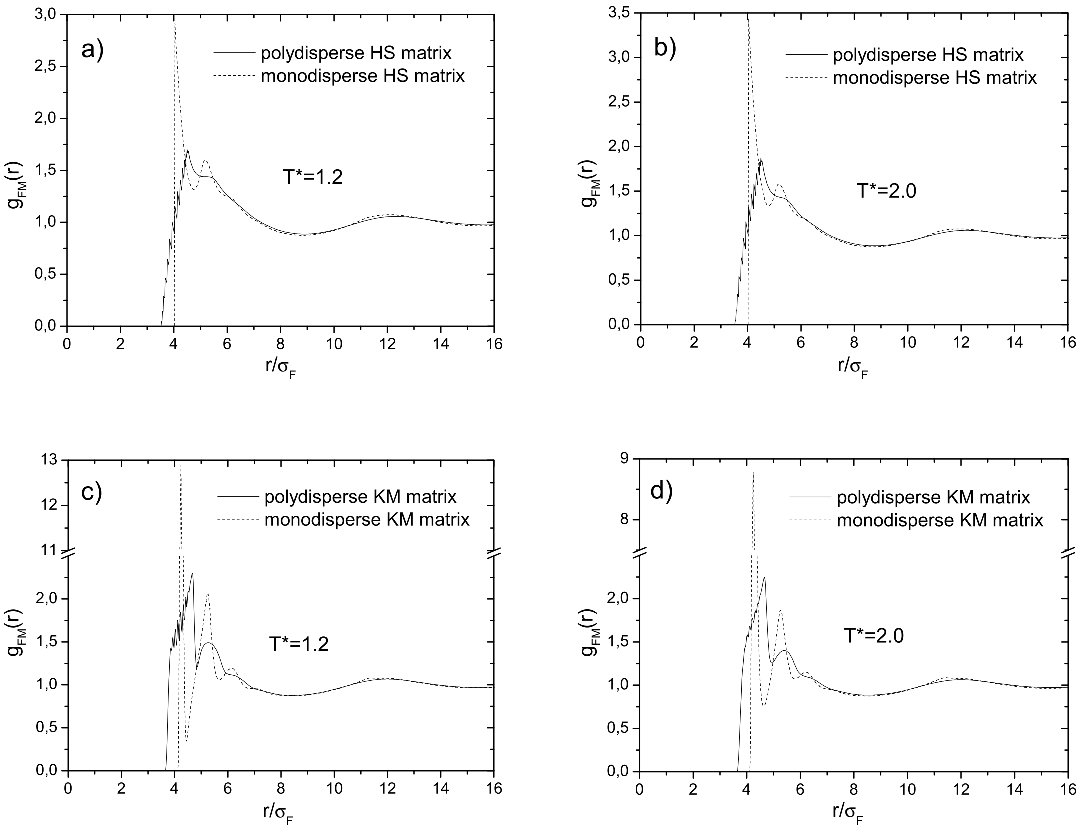

Figure 2. Fluid-matrix radial distribution functions obtained from the PROZ equations.

Any effect of polydispersity cannot be seen when there is no attraction between fluid and matrix (HS matrix). We suspect that it must be a drawback of PY MGOZ like approach which we use in our study. It is known that within the framework of the PY ROZ approximation, the blocking part of the fluid-fluid direct correlation function that was originally introduced in [1] vanishes making an additional equation for the connected parts unnecessary. The resulting simplified version of the ROZ equations (6) are the polydisperse version of MGOZ equations and they do not take into account the interaction between fluid molecules belonging to different replicas. Therefore, the results obtained from the ROZ equations, in combination with PY and the ones obtained from MD simulations (table 1) for the fluid in monodisperse matrix, essentially differ, especially at low temperatures (see $T^* = 1.2$).

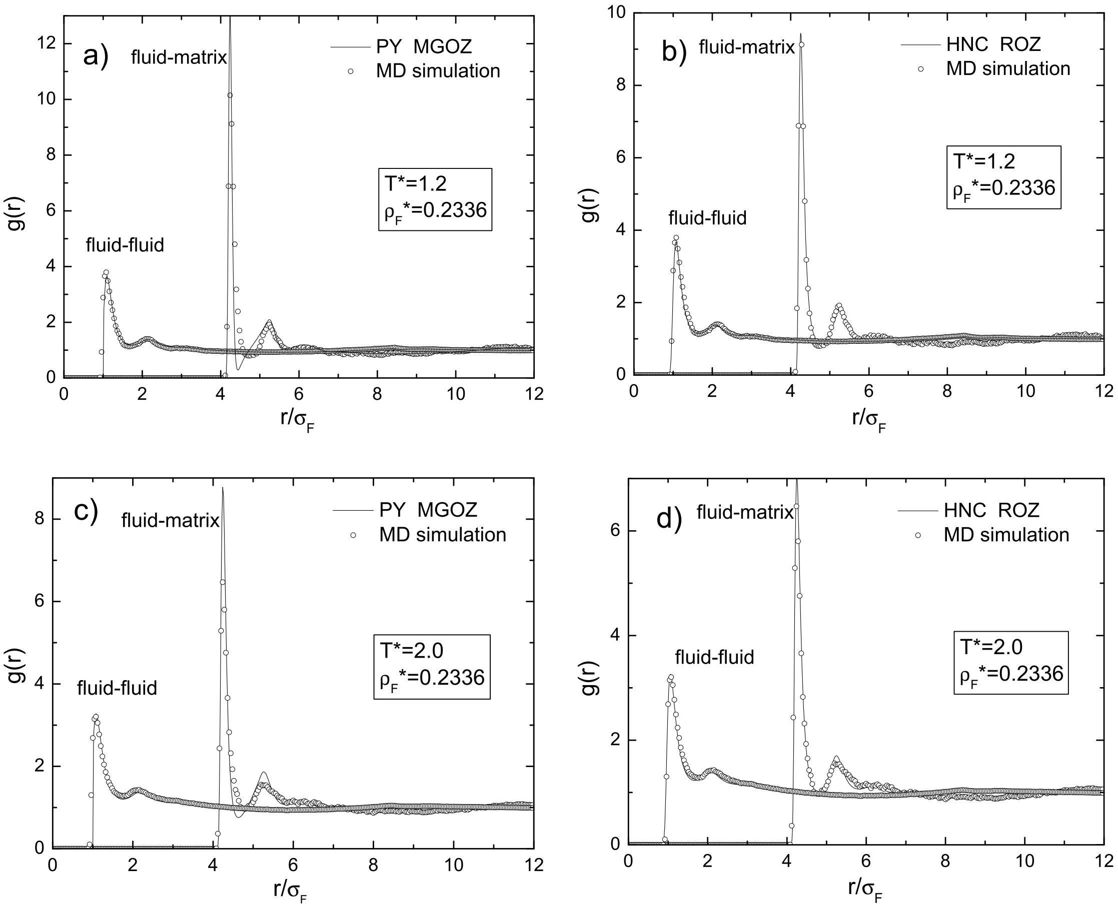

Figure 3. Radial distribution functions for the system of fluid confined in monodisperse matrix. Lines correspond to the results obtained from the ROZ equations and points correspond to the MD simulation results.

Because of the vanishing effect of the matrix polydispersity on the fluid-fluid structure in all considered cases, we do not present figures with the fluid-fluid pair distribution functions. However, it should be noticed that the negligible effect of polydispersity on fluid-fluid radial distribution functions is an evidence of the fact that within the framework of the considered approximation the fluid-fluid structure is sensible to the matrix packing fraction only. Therefore, the contribution into excess internal energy due to fluid-fluid interaction is practically permanent in the range of the considered dispersity of matrix particle sizes. Also, the difference between internal energy of the fluid confined in the HS matrix and the bulk one (see table 1) can be most probably caused only by the excluded volume effect.

While the fluid-fluid structure is unaffected by matrix geometry, one can see a strong effect of the matrix polydispersity on the fluid-matrix pair distribution functions. In figure 2 the radial distribution functions $g_{\mathrm{FM}}(r)$ for the cases mentioned above are presented. The low smoothed first peak with a weird shape in the case of the polydisperse matrix is quite expectable: due to the wide range of sizes of the matrix particles ($\sigma_{\mathrm{M}}/\sigma_{\mathrm{F}} = 6.055 - 8.055$) the fluid molecules can localize at different distances to the matrix center. One can observe that such localization is additionally enforced by the attractive potential (figures 2c and 2d) and this is clearly seen at low temperature $T^{*} = 1.2$. The large difference between the fluid-matrix pair distribution functions in the case of the polydisperse and monodisperse matrices is an evidence of the strong effect of the matrix polydispersity on the internal energy of the system.

Finally, we would like to focus on the problem of the approach chosen in our study. As it was mentioned above, the internal energy of the adsorbed fluid obtained from the PY-MGOZ like approach does not agree with the one obtained from MD simulations at a low temperature. A reasonable way to find out the cause of the deviation is to calculate fluid-matrix RDFs for the fluid confined, for example, in the monodisperse KM matrix. Earlier, in [4] it was shown that the PY-MGOZ approach gives unphysical results for fluid-matrix RDF at fluid temperature $T^{*} = 1.2$, but for a higher density $\rho_{\mathrm{F}}^{*} = 0.36$. Moreover, an adverse tendency was observed for other parameters as well. The same problem was discussed in the previous paper [3], in which the difference between values of the internal energy obtained from the GCMC simulation and the MGOZ equations was observed for different densities of the fluid adsorbed in the monodisperse KM matrix. Therefore, in order to check the RDFs for our system the radial distribution functions calculated from ROZ equations in the PY and the hypernetted chain (HNC) approximations are presented in figure 3. The lack of coincidence of the PY-MGOZ with MD is clearly observed in the vicinity of the gap between the first and the second peaks of the fluid-matrix RDF at $T^{*} = 1.2$ (see figure 3a). Also, the height of the first peak is noticeably higher than the one obtained from MD simulation for both temperatures, while the RDFs obtained from the HNC-ROZ approach almost completely fit the MD results (figures 3b and 3d). The short review presented here is the evidence of the cruel necessity to introduce the blocking parts of the correlation functions into the PROZ equations using at least the HNC approach.

In our study, the effect of the matrix polydispersity on the excess internal energy has been shown. However, the chemical potential would be more important to consider in order to see an effect of the matrix polydispersity on, for example, the adsorption isotherms. Besides, if we compare the systems with the different distributions of matrix particle sizes, but with the same thermodynamic conditions (say with equal chemical potentials), the amount of fluid molecules in both cases can differ. Thus, when we compare the same amount of the fluid adsorbed even in the hard-sphere matrices, the physical conditions for this fluid are different and the effects that are (or not) observed could be also related to this fact. The application of the HNC approximation in the PROZ equations to the study of the chemical potential and other thermodynamic properties of the fluid confined in a polydisperse matrix is under study and will be published in future.

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Проста рідина в невпорядкованій полідисперсній матриці із притягаючою взаємодією

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Використовуючи розвинення рівнянь реплік Орнштейна-Церніке (РОЦ), досліджувались структурні властивості Леннард-Джонсівського флюїду адсорбованого в полідисперсній матриці із притягальною взаємодією. Для цього було застосовано РОЦ рівняння в поєднанні із розкладами кореляційних функцій по ортогональних поліномах. Пораховано радіальні функції розподілу адсорбованого флюїда при різних температурах. Також, в даному дослідженні, розглядався ефект полідисперсності матриці на внутрішню енергію системи.

Ключові слова: *флюїд, полідисперсність, пористе середовище, силікагель, інтегральні рівняння, матриця, молекулярна динаміка*

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