The infiltration of nonwetting liquid into nanoporous media and the thermal effect

V. D. Borman¹, A. A. Belogorlov¹, V. A. Byrkin¹, G. V. Lisichkin², V. N. Tronin¹ and V. I. Troyan¹

¹ National Research Nuclear University MEPhI, Kashirskoe sh. 31, Moscow, 115409 Russia
² Lomonosov Moscow State University, GSP-1, Leninskie Gory, Moscow, 119991, Russia
E-mail: vbyrkin@gmail.com

Abstract. In the present work we formulate a model of infiltration nonwetting liquid into the nanoporous medium. This model takes into account the correlation effects in a disordered medium and is based on analytic methods of percolation theory. The infiltration of porous medium is treated as a process of filling pores in an infinite cluster of pores connected with each other. In the framework of the developed model we describe thermal effects that accompany the accumulation of energy by system characterized by different porosity.

1. Introduction
For past few decades the investigation of "nonwetting liquid-nanoporous body" systems behaviour have been drawing increasing attention. For example, Laplace pressure, which for nanometer-sized pores is $10^2 \div 10^3$ atm, must be overcome to make possible the infiltration of nonwetting liquid into the nanoporous medium. Thus, in the transition of bulk liquid into the dispersed state in pores of the nanoporous medium with the specific surface of $\sim 1$ cm$^2$/g, both the absorbed energy and the accumulated energy (which returns back when the liquid flows out) can reach a value of $10 \div 100$ kJ/kg. This value is greater than the value of energy in case of widely used materials like polymer composites or shape-memory alloys by an order of magnitude [1–3]. In view of above the use of such "nanoporous medium — nonwetting liquid" systems opens up broad prospects for development of alternative sources of energy and mechanical energy dissipators [1–13].

So far the following systems were investigated: silochromes, zeolites — liquid metals, hydrophobized silica gels, zeolites — water, aqueous solutions of organic compounds and salts [1–49]. In the infiltration-defiltration cycle the hysteresis is observed, i.e. the threshold infiltration pressure is higher than the threshold defiltration pressure. The value of the accumulated energy is determined by the product of the volume of pores filled with the nonwetting liquid and the difference between values of threshold infiltration and defiltration pressures. During infiltration of nonwetting liquid into the porous medium the thermal effects are observed which depend both on the degree of filling (occupancy) of the porous medium and the porosity $\varphi$ [5, 44, 47, 48]. The integral thermal effect was observed on the infiltration of the modified porous mediums PEP100(C18), PEP300(C18), KSK-G(C16) with water [47, 48]. It was established that for these porous media with the porosity $\varphi = 0.35$ and $\varphi = 0.45$ the value $\Delta Q < 0$ decreases with the increase of occupancy degree and is minimal when the occupancy is complete. Therefore, it
follows from the comparison of the results obtained in [5, 47, 48] that the thermal effect depends on the porosity of medium.

On the other hand it was found in [44] that when the hydrophobized silica gel porous medium Sigma-Aldrich with the porosity $\varphi = 0.68$, was filled with water up to $1/3$ of its volume the temperature of the system in the heat-insulated chamber did not increase within the measurement error ($\leq 0.05$ K). But it follows from the estimates made by the authors that the increase in temperature must be equal to $\Delta T = 0.8$ K.

Within the existing theories during the filling of disordered porous medium the absorbed energy can be spent on the formation of liquid-porous medium surface in pores, the formation of meniscus surface in the pore throats, the heat release that accompanies the formation of these surfaces and on the dissipation caused by the motion of liquid in nanopores [5,9,10,20–23,47,48]. Let us note that viscous dissipation could probably be neglected [50]. In case of closed hysteresis loop the change in the internal energy is equal to zero. Because of that the work must be equal to the heat release $\oint dA = \oint dQ$. Under the assumption that wetting angles during infiltration and defiltration are different the work $\oint dA$ is not equal to zero. However, in accordance with [51] the value of thermal effect ($\Delta Q = - \int T d\sigma dS$) is equal to zero for $\Delta S = 0$ in case of a closed cycle.

From the above it follows that the nature of the observed thermal effects is unclear.

For description of infiltration of nonwetting liquids into nanoporous media the percolation theory [7, 8, 52, 53] and lattice models [54–57] are used. In early works [51] the infiltration transition within the framework of the percolation theory was described using the condition of the Laplace with phenomenological wetting angle. To describe the defiltration process the asymmetric pore size distribution as well as the pore throat size distribution were considered. In [7, 8] based on percolation theory the infiltration was treated within the statistical fluctuation theory. The probability of filling of a pore was calculated with account of the energy expenditure for the formation of nonwetting liquid-nanoporous medium interface and menisci in the throats between the neighbor pores. The condition of liquid reaching the pore to be filled was provided by the creation of clusters of pores, connected with the surface of the porous medium of a finite size. To describe the infiltration of nanoporous medium with nonwetting liquids in [51, 54, 55, 58] the lattice model treated within a mean-field approach and numerical methods were used. In these works the condition for liquid to reach the pores inside the porous medium was not analyzed. The dependence of infiltration and defiltration pressures on the volume of liquid in pores was determined by phenomenological parameters of model lattice Hamiltonian. Energetics of infiltration-defiltration processes were not considered within lattice models and models based on percolation theory.

In the present work to explain the observed thermal effects we constructed a model of infiltration of nonwetting liquid into nanoporous medium that takes into account the correlation effects in the disordered medium. This model is based on analytic methods of percolation theory [50, 52, 58, 59]. Within this model, the process of infiltration of nonwetting liquid into the porous media was described for media with different porosity. Meanwhile, the infiltration is regarded as the filling of pores of an infinite cluster. Within the model of randomly spaced spheres (RSS) [53] the number of nearest neighbor pores and the square of throats between neighbor pores which analytically depend on porosity were calculated. These results allow to take into account the correlation effect of spatial location and connectivity of pores in medium. Another correlation effect of positional relationship of filled and empty pores on a shell of a cluster of filled pores determines the probability of fluctuation of filling. The expression for this probability is obtained in a closed form.
2. "Nanoporous media — nonwetting liquid" system

Now let us consider the infiltration of nonwetting liquid into a single pore in a partly filled porous medium immersed in a nonwetting liquid and being under external pressure. Depending of the pore radius the pore can be in one of two possible states: it can be able or not able to be filled with a liquid at a given pressure $p$. The probability of a pore to be in these states can be written as [8]

$$w(p, R, \theta) = \left[1 + \exp\left(\frac{\delta A(p, R, \theta)}{T}\right)\right]^{-1},$$

where $\delta A(p, R, \theta)$ is the work providing the infiltration of liquid into a pore with the radius $R$ at the pressure $p$ and the temperature $T$.

If depending on pressure and occupancy of the medium $\delta A(p, R, \theta) < 0$ then the probability $w \sim 1$ and the pore can be filled with liquid. If $\delta A(p, R, \theta) > 0$ then $w = 0$. Consequently, the pore can not be filled with liquid.

Let us calculate the work expended on the fluctuating filling of one pore. To calculate it we assume that each pore in the porous medium has $z$ nearest neighbour pores and pores contact with each other through the throats, each of them of the area $S_z$. If an empty pore is in contact with a filled pore, a meniscus occurs in the throat. A pore in a porous medium can be filled only if the liquid can reach this pore. The condition that liquid can reach the pore can be provided by means of formation of an infinite cluster of filled pores. In this case only pores that are located on the shell of such a cluster will be filled. It could be shown that the contribution to the filled volume of a finite size cluster which liquid can reach through the filled pores contacting with the surface of the medium is small. At $\theta \sim \theta_c$ the distribution function $f(N)$ with respect to the number of pores in clusters $N$ in finite size clusters near the percolation threshold is determined by scaling dependence $f(N) \sim \frac{1}{N^\tau}$, $\tau = 2.2$ [52]. It follows from this fact that most clusters contain one or several pores which generally are not connected with the porous medium surface. Liquid can not reach these pores, consequently, they can not be filled at $\theta \sim \theta_c$. Taking it into account we could write the work $\delta A(p)$ providing the filling of one spherical pore at the surface of an infinite cluster of filled pores as

$$\delta A_{in}(p, \theta, R) = -p V + \sigma S_m + \delta \sigma (S - S_m) = -p\frac{4\pi R^3}{3} + \delta \sigma (1 - \eta)4\pi R^2 + \eta 4\pi R^2 \sigma W(\theta),$$

where $V$ is a pore volume, $\sigma$ is a liquid surface energy, $\delta \sigma$ is a difference between the surface energies of solid-liquid and solid-gas interfaces, $S = 4\pi R^2$ is a surface area of a pore, $R$ is a pore radius, $S_m = zs_m$ is a total area of menisci per one pore, $s_m$ is area of one meniscus, $z$ is a number of the nearest neighbor pores, $\delta S_m = 4\pi R^2 W(\theta)$ is the change in the surface area of menisci during the filling of a pore with the radius $R$, $\eta = S_m/S$ is a connectivity coefficient equal to the ratio of surface area of menisci to the pore surface area, $W(\theta)$ is a difference between the number of menisci on the shell of the infinite cluster after and before the filling of the pore per one neighbor pore.

In order to describe the porous medium we use the model of randomly spaced spheres (RSS). Within this model pores represent randomly arranged spherical holes [53]. The RSS model does not take into account the correlations in location of pores of different radii in accordance with the assumption made above that the pore size distribution function is narrow $\delta R \ll R$.

In accordance with [53] the area of throats which connect neighbour pores $s_m$ and the average number of nearest neighbour pores $\bar{z}$ depend on porosity $\varphi$ and can be written as
These allow us to take into account the correlation effect of spatial location and connectivity of pores in the medium. This effect occurs as a result of probabilistic realization of interconnected pore system in the infinite cluster in the medium with the porosity $\varphi$. In the porous medium with the porosity $\varphi > \varphi_c$ the infinite cluster of filled pores is formed inside the infinite cluster of empty pores when the degree of occupancy approaches the value $\theta = \theta_c$. It follows from the condition for liquid to reach the cluster of pores that the value of $\theta$ increases only if pores are located on the shell of the cluster of filled pores.

Another correlation effect of positional relationship of filled and empty pores on a shell of a cluster of filled pores determines the probability of filling fluctuation. This effect is connected with changes of the surface of menisci during the filling of a pore with radius $R$.

To calculate $W(\theta)$ let us consider an empty pore located on the shell of the infinite cluster of filled pores. We assume that this pore is in contact with the infinite cluster of filled pores through $n$ throats. In each of $n$ throats the menisci are formed, whereas in other $z - n$ throats menisci are absent. After the filling of the pore under consideration these $n$ menisci disappear and thus the number of menisci becomes equal to $z - n$. In this case $W(\theta)$ could be written as

$$W(\theta) = \sum_{n=1}^{z} (P(\theta))^n (1 - \theta)^{z-n+1} \frac{z - 2n}{z} \frac{z!}{n!(z - n)!}.$$  \hspace{1cm} (4)

Here the first factor determines the probability that empty pore contacts $n$ times with the infinite cluster of filled pores. The second factor corresponds to the probability that empty pore neighbour to the infinite cluster of filled pores if it is surrounded by $z$ empty pores and thus it has $z - n$ throats. The third factor determines the difference between the relative number of menisci after $(z - n)$ and before $(n)$ filling of the pore. Combinatorial factor accounts the number of variants of location of $n$ menisci per the pores neighbouring to the pore under consideration. We have to mention that the expression for $W(\theta)$ obtained above is reduced to the one derived in [58], which coincides with the results of numerical calculations if the third factor is substituted by unity.

The sum in (4) can be performed analytically:

$$W(\theta) = (\theta^2 - 2\theta - P(\theta) + 1 + \theta P(\theta))(P(\theta) - \theta + 1)^{z-1} - (1 - \theta)^{z+1}. \hspace{1cm} (5)$$

It follows from (1) and (5) that the work providing infiltration of nonwetting liquid into a single pore in a partly filled porous medium depends on porosity $\varphi$ and occupancy degree $\theta$ of medium with liquid.

3. The description of infiltration process in the "nanoporous medium-nonwetting liquid" system

Consider disordered porous medium with the degree of occupancy $\theta_0$. To fill this medium up to the degree of occupancy $\theta_1$ one has to apply the pressure $p_1$. If $f(R)$ is the pore size distribution function normalized in accordance with equation $\int R^3 f(R)dR = 1$, then $\theta_1 = \int w(p_1, R, \theta_0) R^3 f(R)dR$. Increasing pressure in this step-by-step manner and taking into account that the probability $w$ changes abruptly from 0 to 1 in a narrow pressure interval one can get the following expression for the occupancy of the porous medium at the n-th step.
\[ \theta_n = \int_{F(\theta_{n-1})/p}^{\infty} R^3 f(R) dR \]

\[ F(\theta_{n-1}) = 3\delta\sigma\{ (1 - \eta) + \frac{\sigma}{\delta\sigma}\eta W(\theta_{n-1}) \} . \]

Equation (6) is equivalent to the following differential equation

\[ \frac{d\theta}{dp} = \left( \frac{F(\theta)}{p} \right)^3 \frac{F(\theta)}{p^2} f\left( \frac{F(\theta)}{p} \right) \]

The solution of equation (7) allows us to determine the dependence of occupancy on pressure \( \theta(p) \).

Comparison of experimental data [47, 48] and calculation based on the equation (7) for three different porous media: KSK-G(C16), PEP100(C18) and PEP300(C18) is presented in Fig. 1, 2 and 3. Parameters of nanoporous media are presented in Table 1.

Figure 1. The dependence of occupancy on pressure for system KSK-G — water

Thus taking into account the correlation effects we can qualitatively describe the experimental data on infiltration of nonwetting liquid into the nanoporous medium beyond the percolation threshold. Figures 1-3 show that curves of infiltration depend on the porosity and as it increases, there is less and less deviation of theoretical curves from the experimental data at small degrees of occupancy (\( \theta < 0.2 \)). The deviation of theoretical curves from the experimental data is a consequence of not taking into account in this model the filling of clusters of finite size. It should be mentioned that previously, in [8], curves were described not only qualitatively but
Figure 2. The dependence of occupancy on pressure for system PEP100 — water

Figure 3. The dependence of occupancy on pressure for system PEP300 — water

also quantitatively using the distribution function of clusters of finite size. This function takes into account the formation of clusters both less and greater than the correlation length. The dependence of the deviation from porosity can be explained by the fact that with increasing of
Table 1. Parameters of nanoporous media

|               | Mean pore radius, $R$ nm | Standard deviation, $\Delta R$ nm | The ratio of surface energies, $\sigma/\delta\sigma$ | Porosity, $\varphi$ |
|---------------|-------------------------|----------------------------------|-----------------------------------------------|---------------------|
| KSK-G         | 6.5                     | 1.7                              | 1.6                                           | 0.23                |
| PEP100        | 5                       | 2.2                              | 2.4                                           | 0.35                |
| PEP300        | 14.4                    | 0.7                              | 3.1                                           | 0.45                |

Porosity contribution to the infiltration from the infinite cluster becomes dominant in comparison with the contribution from clusters of finite size.

Moreover, the function of pore size distribution probably contributes to the difference between the theoretical curves and the experimental data. It is because we used Gaussian distribution as the function of pore size distribution. Actually, the function of pore size distribution in range of large pores is protracted, because large pores are filled first.

4. The thermal effects

During the infiltration of nonwetting liquid into the porous medium the thermal effect $\Delta Q$ includes the thermal effect $\Delta Q_p$ that takes place due to formation of liquid-solid interface, the thermal effect $\Delta Q_w$ caused by the formation-disappearance of menisci and the thermal effect $\Delta Q_u$ related to the compressibility of a nonwetting liquid-nanoporous medium system, $\Delta Q = \Delta Q_p + \Delta Q_w + \Delta Q_u$.

The values $\Delta Q_p$ and $\Delta Q_w$ can be calculated using thermodynamic relation [60], that determines the thermal effect related to the formation of the surface $\Delta Q_s$:

$$\Delta Q_s = -T \frac{d\sigma}{dT} \Delta S,$$

where $\Delta S$ is the change in the surface of a system.

To calculate the thermal effect $\Delta Q_s$ let us assume that each pore in the porous medium has $z$ nearest neighbours and pores contact with each other by throats, each of them has an area $S_z$. If an empty pore has contact with a filled one, a meniscus is formed in the throat. Taking into account this fact we can write the thermal effect related to the filling of one pore in the porous medium $\delta Q$ as

$$\delta Q = -T \frac{d\sigma}{dT} (S - zS_z) - T \frac{d\sigma}{dT} zS_z W(\theta),$$

Considering that infiltration of a porous medium is a result of formation of the infinity cluster of filled pores and taking into account that the probability $P(\theta)$ is normalized, we obtain that the quantity of heat per one pore released during the filling of the porous medium up to the occupancy $\theta$ can be written as
\[ \Delta Q_p(\theta) = -T \frac{d\delta\sigma}{dT} \int_0^\theta < (S - zS_z) > \theta P(\theta) d\theta, \]

\[ < S - zS_z > = \int_0^\infty dR (S - zS_z) f(R), \text{ (10)} \]

\[ \Delta Q_w(\theta) = -T \frac{d\sigma}{dT} \int_0^\theta < zS_z > W(\theta) > d\theta \]

where \( f(R) \) is the pore size distribution function normalized to unity. Within the RSS model the area of a throat and the average number of nearest neighbours \( \bar{z} \) related to the porosity of the medium \( \phi \) can be written in the form (3). Provided that \( (\delta R) \ll \bar{R} \) one can get

\[ \Delta Q_p(\theta) = -T \frac{d\delta\sigma}{dT} (1 - \eta) 4\pi \bar{R}^2 \int_0^\theta \theta P(\theta) d\theta, \text{ (11)} \]

\[ \Delta Q_w = -T \eta \frac{d\sigma}{dT} 4\pi \bar{R}^2 \int_0^\theta W(\theta) d\theta \]

It follows from (11) that the change in thermal energy of the system during the filling of porous medium is determined by the derivatives of specific surface energies \( \frac{d\sigma}{dT} \) and \( \frac{d\delta\sigma}{dT} \), by geometrical properties of the porous medium and by the evolution of the infinite cluster of filled pores which depends on the properties of the disordered porous medium.

To calculate the thermal effect \( \Delta Q_v \) that takes place during the defiltration of the liquid out of the porous medium, one should note that the defiltration of the liquid leads to the formation of empty pores in the filled porous medium. They are surrounded by at least one filled pore connected through the other filled pores with the surface of the porous medium. As in case of infiltration the formation of an empty pore corresponds to the change in the energy of a liquid-solid and liquid-gas interfaces related to the formation-disappearance of menisci [8].

Taking it into account when the degree of occupancy decreases from 1 down to \( \theta \), the thermal effect during the defiltration of liquid from the porous medium can be written like (11) as

\[ \Delta Q_p^v(\theta) = -T \frac{d\delta\sigma}{dT} (1 - \eta) 4\pi \bar{R}^2 \int_0^\theta \theta d\theta, \text{ (12)} \]

\[ \Delta Q_w^v = T \eta \frac{d\sigma}{dT} 4\pi \bar{R}^2 \int_0^\theta W(\theta) d\theta, \]

\[ \Delta Q_v = \Delta Q_p^v + \Delta Q_w^v, \]

Relations (11) and (12) differ by the sign of the last term and the functions \( W(\theta) \) and \( W_1(\theta) \). These functions determine the difference per one nearest neighbor between the number of menisci after and before the infiltration (defiltration) in pores.

Relations (11) and (12) are valid if the process is isothermal. This implies that they can be used for the description of experiments when the characteristic time of heat supply (removal) \( \tau_Q \) is much less than the characteristic time \( \tau_V \) of the change in a volume of the nanoporous
medium-nonwetting liquid system $\tau_Q \ll \tau_V$. At $\tau_Q \geq \tau_V$, the temperature and, correspondingly, the quantities $d\sigma/dT$, $d\delta\sigma/d\theta$ become time dependent and thus occupancy $\theta$ dependent. In this case they should be placed under the integral sign in equations (11), (12). The inequality $\tau_Q \ll \tau_V$ imposes constraints on the rate of compression of a system when the equilibrium properties of this system are investigated.

Equations (11), (12) allow to describe thermal effects that take place during the filling of porous medium by the nonwetting liquid. It follows from (11) that total thermal effect is determined by parameters $\Delta Q_p$, $\Delta Q_w$. These parameters depend on derivatives $d\sigma/dT$, $d\delta\sigma/dT$ and on integrals of $P(\theta)$ and $[W(\theta) + W_1(\theta)]$. The sign and the value of the thermal effect that occurs due to formation of liquid solid interface $\Delta Q_p$ depend on the sign and on the value of parameter $d\delta\sigma/dT$. The sign and on the value of parameter $d\sigma/dT$ could be determined with the help of known dependencies of the threshold pressures of the beginning of the infiltration $p_m$ and defiltration $p_{out}$ on temperature.

Experimental data related to the thermal effect measured in three different systems water-silica gel KSK-G(C16) [48], PEP100(C18) and PEP300(C18) [47] are presented in Fig. 4, 5. The porosity after the modification was estimated with the help of the dependencies of pressure on volume presented in [47,48]. It was shown that porosity of these systems has the following values: $\varphi = 0.23$ for KSK-G(C16), $\varphi = 0.35$ for PEP100(C18) and $\varphi = 0.45$ for PEP300(C18). Both differential and integral thermal effects were investigated in [48]. In [47] only integral effect was investigated and the experimental data obtained were corrected with account of compressibility of water. The author of the work [48] does not write anything about such correction of his experimental data. However, the description of measurement procedure presented in [61] allows one to suppose that correction of thermal effects related to compressibility of water was done.

It follows from Fig. 4, 5 that the value of differential thermal effect (for KSK-G(C16), $\varphi = 0.23$) is negative at $\theta > 0.04$, decreases with occupancy $\theta$, at $\theta \sim 0.8$ it approaches minimum and vanishes at $\theta = 1$. At $\theta < 0.04$ experimental points are systematically located in a region where $\Delta Q$ is positive. However, they are close to zero within the measurement error. Integral heat release for the system KSK-G(C16)-water at $\theta > 0.07$ is negative and monotonously decreases approaching minimum at $\theta = 1$. Similarly at $\theta < 0.07$ experimental points corresponding to integral effect are systematically located in a region where $\Delta Q$ is positive and close to zero within the measurements error. For systems PEP100(C18), $\varphi = 0.35$ and PEP300(C18), $\varphi = 0.45$ the integral thermal effect is negative and monotonously decreases with increase of occupancy.

Theoretical dependencies, presented in Fig. 4, 5 were calculated with the help of equations (11), (4). It was supposed that the pressure in the beginning of infiltration is temperature independent similar to the situation with porous medium with modification C8. Relying on this condition we determined the value of derivative $d\delta\sigma/dT$. It appeared to be equal to $d\delta\sigma/dT = 0.1 \cdot 10^{-4}$ J/m$^2$ K for KSK-G(C16), $d\delta\sigma/dT = 3.5 \cdot 10^{-4}$ J/m$^2$ K for KSK-G(C16), and $d\delta\sigma/dT = 5.0 \cdot 10^{-4}$ J/m$^2$ K for PEP100(C18). One can see that calculated dependencies satisfactory coincide experimental dependencies for PEP100(C18) and PEP300(C18) (Fig. 5). It could be also seen the qualitative agreement of the calculated and experimental dependencies for a KSK-G(C16) (Fig. 4a, 4b). The account of thermal effect related to compressibility of water and partly filled porous medium leads to satisfactory coincidence of experimental and calculated dependencies for KSK-G(C16) (Fig. 4c, 4d). It is worth noting that within the developed model one should expect the occurrence of positive thermal effect (both integral and differential) at small values of occupancy ($\theta < 0.07$ )(inserts in Fig. 4a, 4b). Experimental data obtained in [48] are located in this region within the measurements error. Because of that to determine the sign of thermal effect at small values of occupancy additional experiments are needed.
Figure 4. The occupancy dependence of integral thermal effect (b), (d) and differential thermal effect (a), (c). Points correspond to experimental data [48], solid lines correspond to calculation, (a), (b) — without the account of compressibility of water and porous medium during the infiltration, (c), (d) — with account of compressibility of water and porous medium during the infiltration. $Q_0 = 9 \text{ J} [48]$ is maximal absolute value of integral thermal effect, $q_1 = 40 \text{ J/g} [48]$ is maximal absolute value of differential thermal effect.

5. Conclusion
In the present work we constructed the model of infiltration of nonwetting liquid into nanoporous medium that takes into account the correlation effects in the disordered medium and is based
Figure 5. The occupancy dependence of integral thermal effect (per one gram of porous body) for PEP100(C18) (a) and PEP300(C18) (b). Points correspond to experimental data [47], solid lines correspond to calculation. $Q_1 = 5.5 \text{ J/g } [47]$, $Q_2 = 1.6 \text{ J/g } [47]$ are maximal absolute values of integral thermal effect

on analytic methods of percolation theory. This model allows one to find a linkage between the effective parameters of porous medium such as an average number of neighbour pores and an average size of throats and macroscopic characteristics of porous medium such as porosity and specific surface.

Using the proposed model we can describe both the process of filling of nanoporous medium by nonwetting liquid and thermal effects accompanying the energy absorption by systems with different porosity. This allowed us to remove the contradictions in the available experimental data on thermal effects during infiltration of water into modified porous media KSK-G(C16), PEP300 (C18) and PEP100(C18).

Acknowledgments

This work was supported by the Federal target program "Scientific and scientific-educational personnel of innovative Russia" under grant P536.

References

[1] Qiao Y, Punyamurtula V K, Han A, Kong X and Surani F B 2006 Appl. Phys. Lett. 89 251905
[2] Han A and Qiao Y 2007 Appl. Phys. Lett. 91 173123
[3] Han A and Qiao Y 2008 Chem. Phys. Lett. 454 294
[4] Bogomolov V N 1995 Phys. Rev. B 51 17040
[5] Erochenko V A 2002 Rus.Chem.Journal XLVI 31
[6] Fadeev U and Erochenko V A 1997 J. of Coll. and Interface Sci. 187 275
[7] Borman V D, Grekhov A M and Troyan V I 2000 JETP 91 170
[8] Borman V D, Belogorlov A A, Grekhov A M, Lisichkin G V, Tronin V N and Troyan V I 2005 JETP 100 385
[9] Lefevre B, Saugey A, Barrat J L, Boequet L, Charlaix E, Gobin P F and Vigier G 2004 *Coll. and Surf. A* 241 265–272
[10] Lefevre B, Gobin P F, Martin T, Saugey A, Barrat J L, Boequet L, Charlaix L and Vigier G 2004 *J. Chem. Phys.* 120 4927
[11] Iwatsubo T, Suciu C V, Ikenagao M and Yaguchio K 2007 *Journal of Sound and Vibration* 308 579
[12] Chen X, Surani F B, Kong X, Punyamurtula V K and Qiao Y 2006 *Appl. Phys. Lett.* 89 241918
[13] Eroshenko V A, Piatiletov I, Coiffard L and Stoudenets V 2007 *Proc.I MechE*, Part D 221 301–312
[14] Sebastian I and Halasz I 1974 *Chromatographia* 7 371
[15] Unger K K 1979 *Porous silica, its properties and use as support in column liquid chromatography.* (J.Chromatogr.Libr. V.16) (Elsevier, Amsterdam)
[16] Bokasanyi L, Liardon O and Kovats E 1976 *Adv. Colloid Interface Sci.* 6 95
[17] Lisichkin G V and Fadeev A Y 1996 *Russ.Chem.Journal* XL 65
[18] Fadeev U and Eroshenko V A 1996 *J. Phys. Chem.* 70 1482
[19] Fadeev U and Eroshenko V A 1995 *Colloid. Journal.* 57 480
[20] Suciu C V, Iwatsubo T and Deki S 2003 *J. of Coll. and Interface Sci.* 259 62
[21] Suciu C V, Iwatsubo T, K Y and M I 2005 *J. of Coll. and Interface Sci.* 283 196
[22] Coiffard L and Eroshenko V A 2006 *J. of Coll. and Interface Sci.* 300 304–309
[23] Denoyel R, Beurroies I and Lefevre B 2004 *J. of Petroleum Science and Engineering* 45 203
[24] Han A, Kong X and Qiao Y 2006 *J. Appl. Phys.* 100 014308
[25] Kong X and Qiao Y 2005 *Philosophical Magazine Letters* 85 331
[26] Qiao Y, Cao G and Chen X 2007 *J. Am. Chem. Soc.* 129 2355
[27] Kong X, Surani F B and Qiao Y 2005 *J. Mater. Res.* 20 1042
[28] Kong X and Qiao Y 2005 *Appl. Phys. Lett.* 86 151919
[29] Surani F and Qiao Y 2006 *J. Appl. Phys.* 100 034311
[30] Surani F, Qiao Y and Kong X 2005 *Appl. Phys. Lett.* 87 251906
[31] Surani F B, Han A and Qiao Y 2006 *Appl. Phys. Lett.* 89 093108
[32] Han A, Lu W, Punyamurtula V K, Kim T and Qiao Y 2009 *J. Appl. Phys.* 105 024309
[33] Kim T, Han A and Qiao Y 2008 *J. Appl. Phys.* 104 043404
[34] Han A, Punyamurtula V K and Qiao Y 2008 *Appl. Phys. Lett.* 92 153117
[35] Eroshenko V A, Regis R and Soulard M and Patarin J 2001 *J. Am. Chem. Soc.* 123 8129–8130
[36] Eroshenko V A, Regis R and Soulard M and Patarin J 2002 *C.R. Physique* 3 111–119
[37] Han A, Lu W, Chen X and Kim T 2008 *Phys. Rev. E.* 78 031408
[38] Lu W, Han A, Kim T, Punyamurtula V K, Chen X and Qiao Y 2009 *Appl. Phys. Lett.* 94 023106
[39] Qiao Y, Liu L and Chen X 2009 *Nanolett.* 9 984–988
[40] Liu L, Chen X, Lu W, Han A and Qiao Y 2009 *Phys. Rev. Lett.* 1-2 184501
[41] Kim T, Lu W, Han A, Punyamurtula V K and Qiao Y 2009 *Appl. Phys. Lett.* 94 013105
[42] Chen X, Cao G, Han A, Punyamurtula V K, Liu L, Culligan P, Kim T and Qiao Y 2009 *Nanolett.* 8 2988–2992
[43] Liu L, Chen X and Qiao Y 2008 *Appl. Phys.Lett.* 92 101927
[44] Qiao Y, Punyamurtula V K, Xian G, Karbhar V M and Han A 2008 *Appl. Phys. Lett.* 92 063109
[45] Han A, Lu W, Punyamurtula V K and Qiao Y 2008 *Appl. Phys. Lett.* 103 084318
[46] Han A, Lu W, Punyamurtula V K, Chen X, Surani F B, Kim T and Qiao Y 2008 *J. Appl. Phys.* 104 124908
[47] Gomez F, Denoyel R and Rouquerol J 2000 *Langmuir* 16 4374–4379
[48] Gusev Y V 1994 *Langmuir* 10 235–240
[49] Surani F, Kong X, Panchal D and Qiao Y 2005 *Appl. Phys. Lett.* 87 163111
[50] Borman V D, Belogorlov A A, Lisichkin G V, Tronin V N and Troyan V I 2009 *JETP* 108 389–410
[51] Sashimi M 1993 *Rev.Mod.Phys.* 65 1393
[52] Isichenko M B 1992 *Rev. of Mod. Phys* 64 961
[53] Heifetz I and Neimark A V 1982 *Multiphase processes in porous media,* [Russian translation] (Chemistry, Moscow)
[54] Woo H J and Monson P A 2003 *Phys.Rev. E* 67 041207
[55] Surani F 2006 Ph.D. thesis Science University of Akron
[56] Porcheron F and Monson P A 2005 *Langmuir* 21 3179
[57] Porcheron F, Thommes M and Ahmad R 2007 *Langmuir* 23 3372–3380
[58] Grinchuk P S and Rabinovich O S 2003 *JETP* 96 301
[59] Abrikosov A A 1979 *ZhETF* 29 72
[60] Landau L D and Lifschitz E M 1980 *Statistical Physics, Part 1,* 3rd ed (Oxford, England: Pergamon Press)
[61] Gusev V Y and Pomkin A A 1994 *J. of Coll. and Interface Sci.* 21 4567

12