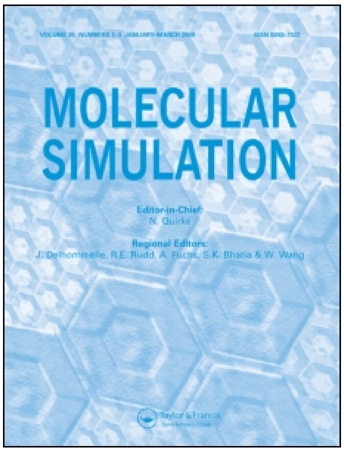

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POTENTIAL FIELDS AND BARRIERS TO DIFFUSION IN NARROW CYLINDRICAL CAPILLARIES

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In this paper, the wall potential along the center line of narrow solid capillaries has been derived. The potential barriers at the open end of such capillaries have been studied in detail. The influence of these potential barriers on the diffusion coefficients and their dependence on temperature and capillary radius have been evaluated. The implications of these energy barriers in the clarification of low pressure hysteresis phenomena have been pointed out.

Keywords: Capillary wall potential; Potential barrier; Diffusion coefficient; Hysteresis

INTRODUCTION

The potential field induced by a solid boundary not only plays an important role in many fluid phenomena and processes, but itself is often the cause for the existence of some phenomena. The distribution of the potential function in very narrow solid capillaries has been of special interest in the chemical physics of confined fluids, because it has a direct relation to such processes and phenomena as adsorption, capillary condensation, high and low pressure hysteresis, and diffusion in narrow capillary systems. Thus, in the strict sense, the equations which describe these phenomena should also take into consideration the presence of this potential field.

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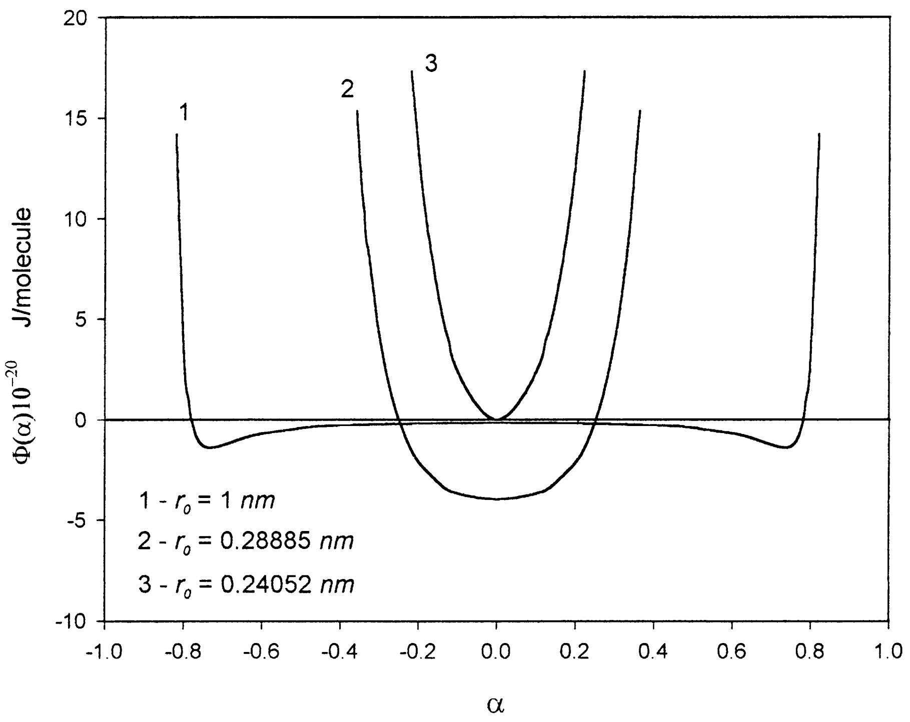

FIGURE 1 Typical shapes of the potential functions for a range of capillary radii showing the attractive and repulsive regions for the argon–graphite capillary system.

In a previous study [1], using the Lennard–Jones (12–6) potential, an explicit form of the potential energy of interaction between a solid thick wall and a test atom placed at an arbitrary point in a long open-ended cylindrical capillary has been obtained. Further, this expression has been used to provide the fluid–wall potential between the capillary wall and a total confined fluid. These results were subsequently used to develop a generalized Kelvin equation. One of the essential results, which is evident from this equation, is the existence of a unique point in the capillary-fluid system, where spherical and cylindrical interfaces coexist without a transition zone. In other words, the spherical and cylindrical interfaces have the same radius and the same equilibrium pressure at this point. A consequence of this is that evaporation or condensation of the fluid will not change the geometry of the interfaces and consequently the equilibrium pressure.

By considering the behavior of this potential function at the open end of the capillary along a centerline, energy barriers to adsorption and desorption have been found. These computations with the analytical expression for the wall potential function and a simple diffusion model have allowed the evaluation of the diffusion coefficient as function of temperature and radius of the capillary. Activated adsorption on active carbons has been frequently observed experimentally [2] when the size of pores are close to the size of adsorptive molecules.

THEORY AND DISCUSSION

In the solutions for the distribution of the interaction potential in cylindrical capillaries [1], we have used in these calculations, the system graphite as the capillary wall and argon as the test atom. The results are shown in Fig. 1. These show the typical shape of the potential function with an annular minimum in the vicinity of the capillary wall (curve 1), which is common for sufficiently large radii. With decreasing radius, the function changes to curve 2, which has the deepest minimum at the capillary center, which, for the this system, is $r_0 = 0.28885$ nm. It is interesting to note that, in this case, the contribution of repulsive energy between argon test atom and five nearest carbon atoms of the wall do not outweigh the contribution of the attractive energy between argon and all the remainder of the carbon atoms. Therefore, the resulting potential energy is attractive with the deepest minimum. However, in the case of a capillary radius of 0.2405 nm (curve 3) the contribution of the repulsive energy dominates the attractive component providing a net overall repulsive energy.

Considering the behavior of the potential function at the open end of the capillary, energy barriers to adsorption may be expected from our previous theory

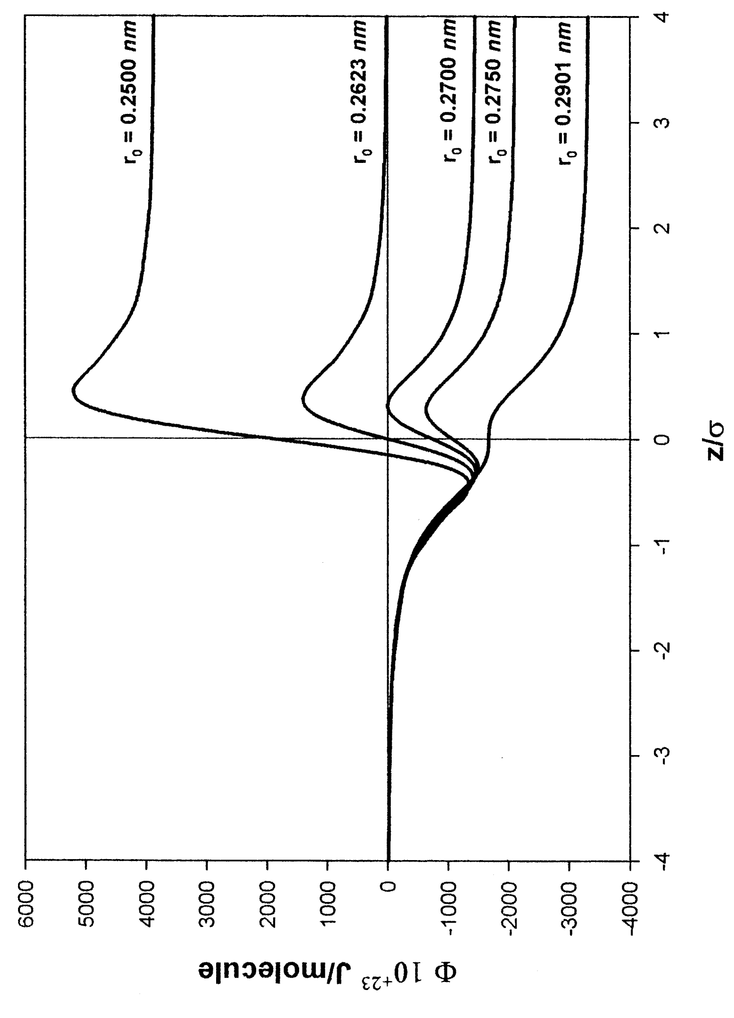

FIGURE 2 The behavior of the potential function near the open end of the capillary along its centerline.

[1]. Here we now examine these energy barriers along the capillary centerline as a test atom approaches an open ended capillary.

To commence, the general form of the potential between a test atom placed at an arbitrary point along the centerline and a semi-infinite thick cylindrical capillary wall may be expressed as

$$\Phi = \int_0^{+\infty} \mathrm{d}z \int_{r_0}^{+\infty} r\mathrm{d}r \int_0^{2\pi} \mathrm{d}\varphi \left[\frac{C_{12}}{R_i^{12}} - \frac{C_6}{R_i^6}\right] M \tag{1}$$

In cylindrical co-ordinates, the distance between a test atom and i-th atom of the wall may be written as

$$R_i^2 = r^2\cos^2\varphi + r^2\sin^2\varphi + (z - z_0)^2 = r^2 + (z - z_0)^2$$

where r is the radius-vector; φ is the position angle; z_0 is the position of the test atom in the centerline. The origin of co-ordinates is placed at the center of capillary end. For atom–atom interactions we have used the Lennard–Jones potential (12–6). Upon integration Eq. (1) yields

$$\begin{aligned}\Phi = {} & \frac{7\pi C_{12}M}{128 r_0^9}\left[\frac{16x}{35(x^2+1)^4} + \frac{8x}{15(x^2+1)^3} + \frac{2x}{3(x^2+1)^2} + \frac{x}{x^2+1} + \frac{\pi}{2} + \mathrm{arctg}(x)\right] \\ & - \frac{\pi C_6 M}{4 r_0^3}\left[\frac{x}{x^2+1} + \frac{\pi}{2} + \mathrm{arctg}(x)\right]\end{aligned} \tag{2}$$

where C_{12} and C_6 are the Lennard–Jones repulsive and attractive parameters, respectively; $M = 1.128 \times 10^{29}\ \mathrm{atom/m^3}$ is the number of the carbon atoms per $1\ \mathrm{m}^3$ of a solid graphite; r_0 is the radius of the capillary, defined as the distance between a centerline and a center of the wall carbon atom and $x = z_0/r_0$.

Figure 2 shows this potential calculated from Eq. (2) as it depends on the capillary radius. As may be seen from this figure, for any capillary radius, there are attractive potential wells at the approach to the capillary with minima that are only weakly related to capillary radius. However, inside the capillary, the potential maxima are strongly dependent on capillary radius. It can be seen that the potential curve may be completely positive at $r_0 \le 0.2623$ nm or completely negative at $r_0 \ge 0.2700$ nm as well as partially negative and partially positive at $0.2623 < r_0 < 0.2700$ nm. Further, an increase in the size of the radius r_0 leads to the disappearance of the potential barrier at $r_0 = 0.2901$ nm. While at $r_0 = 0.3150$ nm, the attractive potential field reaches its maximum value along the centerline, after which the potential only decreases to zero as $r_0 \rightarrow \infty$. Notably,

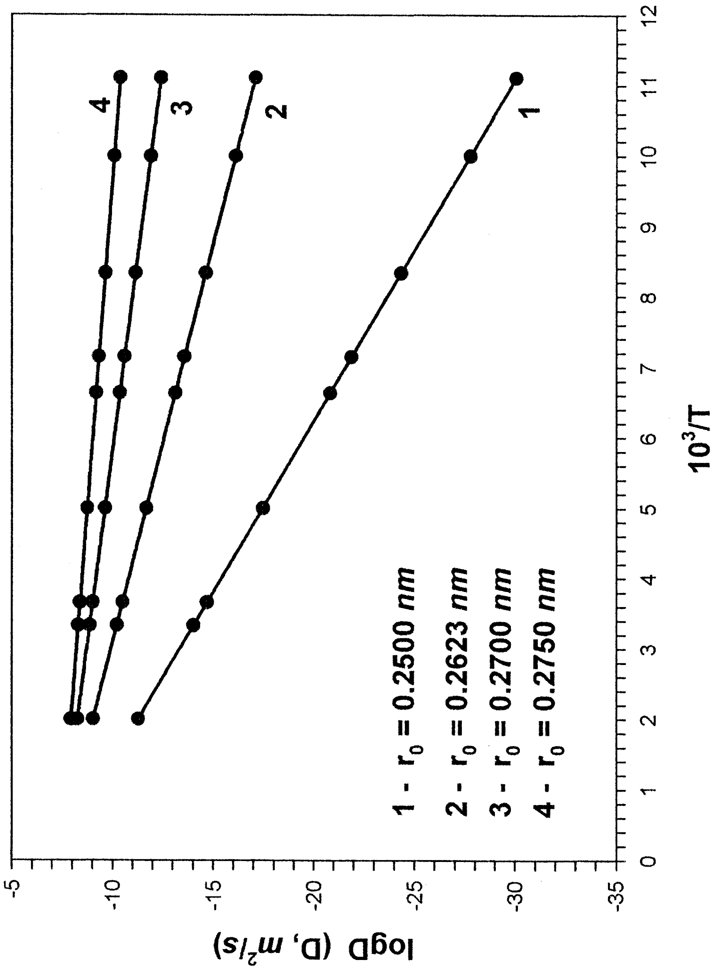

FIGURE 3 Dependence of the diffusion coefficient on temperature.

the three inflection points in potential curves degenerate to one at $r_0 = \sigma$, where σ is the Lennard–Jones parameter for argon–carbon interactions.

Yet another important characteristic of the potential curves is the existence of potential barriers not only for inward diffusion, but also for outward diffusion. This circumstance could particularly clarify the origin of the low pressure hysteresis phenomena, which are often observed in conditions, where capillary condensation hysteresis can not operate [3]. Equation (2) may be used to estimate the inward diffusion coefficients for the argon–graphite capillary system. For this purpose, as a first approximation, we can use the following equation [4]

$$D = \delta^2(6\tau_0)^{-1} \exp\left\{\frac{\Delta E}{k_B T}\right\} \tag{3}$$

or noting that

$$\tau^{-1} = \nu_0 = (f/m)^{1/2}(2\pi)^{-1}$$

we obtain

$$D = \delta^2(12\pi)^{-1}(f/m)^{1/2} \exp\left\{-\frac{\Delta E}{k_B T}\right\} \tag{4}$$

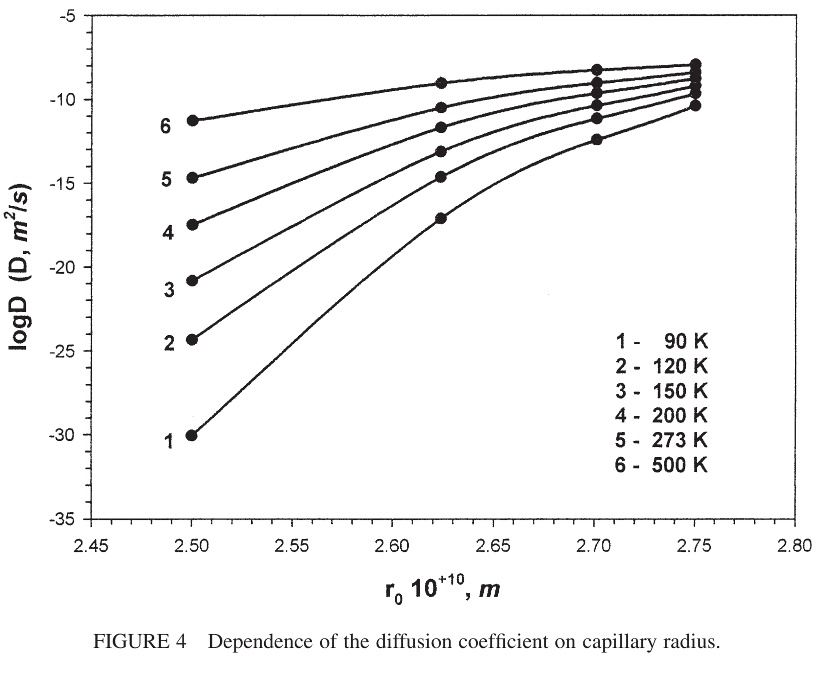

FIGURE 4 Dependence of the diffusion coefficient on capillary radius.

where D is the diffusion coefficient (m^2/s), ΔE is the activation energy of the process of diffusional movement, δ is the distance which the atom moves, τ_0 and ν_0 are the period and the frequency of free vibrations, respectively, m is the mass of the diffused atom, $f = (\mathrm{d}^2\Phi/\mathrm{d}z^2)$ at the point $z_0 = z_{0(\mathrm{min})}$, k_B is the Boltzmann's constant and T is the absolute temperature.

The results of our calculations using Eq. (4) are presented as the dependence of diffusion coefficient on temperature at four fixed capillary radii (Fig. 3), and as the dependence of diffusion coefficient on radius of the capillary at six fixed temperatures (Fig. 4). From close inspection of Figs. 3 and 4, it is evident, that the diffusion coefficient depends more strongly on temperature at small capillary radii and more weakly at larger radii. Alternatively, the diffusion coefficient depends more strongly on the capillary radius at low temperatures and more weakly at higher temperatures. As would be expected, the range of the diffusion coefficients, for the adsorption process is limited both by the size of the capillary radius and the adsorption temperature. Thus, the capillaries with $r_0 = 0.25\,\mathrm{nm}$ and less are impracticable for adsorption at any temperatures, whereas the capillaries with $r_0 = 0.275\,\mathrm{nm}$ and larger, adsorption is in practice possible at any of the temperatures examined above. In general, the numerical values of the diffusion coefficients calculated from our theoretical model, as an order of magnitude, are in good agreement with experimental data for similar systems [5].

CONCLUSION

With the aim of clarifying the behavior of the interaction potential at the open end of the cylindrical capillary, we have obtained the explicit form of the potential function between a test atom and a semi-infinite thick capillary wall along the centerline.

It has been found that, in the vicinity of the capillary end, significant potential barriers exist. The temperature and size dependence of these barriers were subsequently examined. On the basis of our analytical expression for the potential energy of interaction in a long open-ended cylindrical capillary and a simple model of diffusion, the diffusion coefficient has been numerically evaluated as a function of temperature and capillary radius.

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