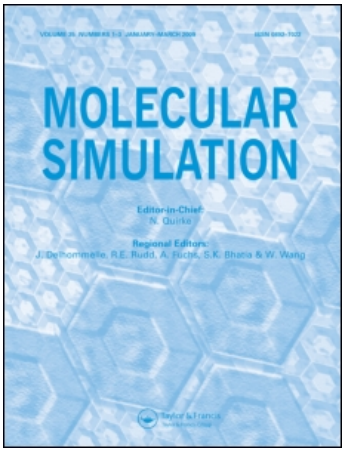

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Geometrical and Physical Modeling of Dilute Adsorbable Gas Flow in Porous Media: An Insider's Account of the Nicholson-Petropoulos Contribution

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GEOMETRICAL AND PHYSICAL MODELING OF DILUTE ADSORBABLE GAS FLOW IN POROUS MEDIA: AN INSIDER'S ACCOUNT OF THE NICHOLSON–PETROPOULOS CONTRIBUTION

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INTRODUCTION

Our joint research grew out of our postdoctoral work with RMB on related topics, namely gas flow in single capillaries (DN) and in porous media (JP); which led us to the realization that the conventional interpretation (in terms of pore models) of gas transport, especially adsorbable gas transport, in porous adsorbents, porous separating barriers and porous catalysts, was rather rudimentary.

Following Gibbs, it is generally considered that, during gas sorption by a porous medium, the pores fill up with non-adsorbed gas to a concentration equal to that of external gas; any excess over this concentration is regarded as gas adsorbed on the pore surfaces. On exactly the same basis, the gas permeability is conventionally written as

$$P = P_g + P_s = \varepsilon D_g + A k_s D_s \tag{1}$$

where ε is the porosity and A the specific surface area per unit volume of the porous medium; k_s, is the adsorption coefficient (assumed constant in our studies); while P_g, D_g and P_s, D_s represent non-adsorbed (gas-phase) and adsorbed (surface) gas permeabilities or diffusivities, respectively.

Gas-phase transport is modeled by assuming that the physics of flow is not materially dependent on the geometry of the pore space. Thus, D_g may be related to the value calculated for an idealized single pore of the same hydraulic radius $r_h = \varepsilon/A$ as the porous medium under consideration, through a geometrical or pore structure factor κ_g. A long straight cylindrical capillary of radius $r_e = 2r_h = 2\varepsilon/A$ is usually chosen for this purpose. Then, for Knudsen flow with diffuse reflection at the wall (which was the main object of our study), we have

$$D_g = (8/3)\kappa_g r_e v_1 = (8/3)\kappa_0 \kappa_{g1} \kappa_{g2} \kappa_{g3} r_e v_1; \quad v_1 = (RT/2\pi M)^{1/2} \qquad (2)$$

where v_1 is the unidimensional mean gas molecular speed and M the gas molecular weight. The deviations of κ_{g1}, κ_{g2} and κ_{g3} from unity represent pore structural effects on three different scales relating to: (a) properties of elementary pores (microscopic scale, κ_{g1}) other than width, notably length and cross-sectional shape; (b) collective pore properties (mesoscopic scale, κ_{g2}), which include the statistical variation of individual pore properties (width, length, shape) and interconnections between elementary pores (tortuosity of long capillaries, network structure); and (c) properties of the porous medium (macroscopic scale, κ_{g3}), primarily in the form of non-uniform porosity and pore structure, resulting from the manufacturing process. Finally, κ_0 is an anisotropy factor (=1/3 for an isotropic medium).

Surface transport is modeled as diffusion of the admolecules along the surface of the pores by an activated jump mechanism. We have

$$D_s = k_s^* D_s^* / k_s; \quad D_s^* = \kappa_s \lambda_s v_1 \qquad (3)$$

where k_s^*, D_s^* refer to activated admolecules; λ_s is the typical diffusion jump length and κ_s is a structure factor. Both λ_s and κ_s are conventionally assumed to depend on the nature of the surface. Experimentally, D_s is obtained by deducing P_g from the measured permeability of He (the nearest experimental approximation to a non-adsorbed gas), which yields the value of κ_g in Eq. (2).

GAS-PHASE FLOW

Previous quantitative studies concerned κ_{g1} in single pores and proved relevant to porous media primarily with respect to flow behavior in the transition from the Knudsen to the Poiseuille regime with increasing pressure. D_g typically passes through a minimum in this range. It was shown that this minimum tends to be suppressed by short pore length (as in a repeatedly kinked capillary) and to

become deeper in flattened pores (DN's contribution to these studies is noteworthy). These results helped explain the observation that the said minimum is typically suppressed in real porous media and tends to survive only in media with slit-like pores (like porous graphite).

Thus, the porous medium may be modeled as a bundle of repeatedly kinked capillaries (but note that three such mutually perpendicular bundles are required to accommodate the anisotropy factor κ_0) of radius $r_e = 2\varepsilon/A$. Within the Knudsen flow regime, finite length and any flattening of the circular shape have opposite effects on κ_{g1} ($\kappa_{g1} < 1$ and $\kappa_{g1} > 1$, respectively). In practice, however, attention focuses primarily on the tortuosity of flow paths in the kinked capillaries, which leads to $\kappa_{g2} < 1$; but this is usually done only as a qualitative means of accounting for experimental $\kappa_g < 1$ values. Experimental $\kappa_g > 1$ values are similarly rationalized in terms of continuous pathways via wider pores.

For deeper and more systematic analysis, a more realistic and quantitatively useful model was clearly needed for κ_{g2} (but not one so cumbersome as to be of little or no practical utility).

A bundle of capillaries of differing radius constitutes the basis of a well established practical method of determining the pore size distribution, by analysis of vapor sorption isotherms. However, this model was considered still too limited for treating gas permeability, especially relative permeability, behavior in a reasonably realistic manner (see below).

Accordingly, another long (and at that time rather daring) step towards greater realism was taken and a capillary network model was adopted. In all other respects, the model was kept as simple as possible. Its primary characteristics are a random distribution of radius, according to a given frequency function $f(r)$, among the elementary capillaries joining neighboring nodes of the network and a connectivity parameter, n_T, denoting the number of capillaries meeting at a typical node.

This model has a number of significant advantages over the simpler ones referred to above. In particular:

(a) It encompasses a considerably wider range of phenomena, notably gas permeability, relative gas permeability and vapor absorption–desorption isotherms.

(b) The practice of vapor sorption isotherm analysis for determination of pore size distribution remains essentially unaffected, but is put on a sounder scientific basis; particularly with respect to the interpretation of the hysteresis loop, which was previously a source of ambiguity and now becomes a source of information about n_T; (DN has done significant independent work in this respect).

(c) In relation to relative permeability properties (namely the progressive decline of permeability when the pore system is increasingly blocked by a foreign sorbate), the network model (in contrast to capillary bundle models) correctly predicts the occurrence of a "percolation threshold" well before complete blockage of the pore system. This phenomenon constitutes another useful source of information for the value of n_T in practice (in fact, the percolation threshold was found experimentally in our laboratory to coincide with the steep part of the desorption vapor isotherm).

(d) With respect to permeability, both $\kappa_{g2} > 1$ and $\kappa_{g2} < 1$ are predictable at high and low values of n_T, respectively (as can be proven mathematically for the limiting cases $n_T \rightarrow \infty$ and $n_T \rightarrow 2$, which correspond to parallel and serial arrays of pores, respectively). The tortuosity factor of capillary bundle models is no longer relevant.

(e) Thus, the much higher versatility of the network model described above is gained essentially without increasing the number of salient parameters (Occam's razor). On the contrary, the fact that the tortuosity "fudge" factor is here replaced by network connectivity (which, as noted above, is experimentally tractable, at least in principle) may be regarded as another clear advantage.

On the other hand, the network model had admittedly the disadvantage of not being analytically tractable (although this is not so for the aforementioned limiting cases of parallel and serial pore arrays, which were studied analytically). This fact limited its usefulness, especially for practical application purposes. However, this drawback was eventually eliminated or at least greatly alleviated.

Thus, apart from delineating, in considerable detail, the behavior of κ_{g2} for Knudsen flow (as a function of the connectivity and the breadth and shape of the pore radius distribution), the numerical results obtained for networks were also used to validate the applicability of "effective medium theory (EMT)". From this analytical (but in implicit form) approximate approach to random network conductivity, an *explicit* analytical expression for κ_{g2} was developed, in the form of a series of terms involving the connectivity and ascending central moments of $f(r)$. This result (which may easily be extended to other modes of transport also) facilitates theoretical insight into the aforementioned numerical data, on one hand, and greatly enhances the practical applicability of the network model, on the other hand. The latter aspect was further reinforced by the subsequent derivation of an analogous explicit EMT expression for the initial portion of the relative permeability curve, which may be used, in practice, as a cross-check on the interpretation of experimental κ_g values in terms of κ_{g2}.

Other results of note include confirmation of the previously discussed view that the permeability minimum in the transition from Knudsen to Poiseuille flow is primarily a function of pore structure at the microscopic (κ_{g1}) and only secondarily at the mesoscopic (κ_{g2}) level (and hence provide *post facto* justification for non-inclusion of variability of pore shape or length in our model). Another conclusion of practical importance is that "bidisperse" porous solids (typically in the form of a relatively loose pack of porous particles) are characterized by values of κ_{g2} markedly in excess of unity and may thus be distinguished from "monodisperse" solids (in the form of packs of non-porous particles or tight packs of porous particles), which yield κ_{g2} below or (at most) only very modestly above unity.

Finally, the realization (coupled with experimental demonstration in our laboratory) that most powder compaction or pelletization processes are likely to produce porous solids of non-uniform porosity, led us to model studies of the resulting effect on gas permeability and relative permeability. The effects noted were analogous to those of pore size distribution; with axially non-uniform porosity ($\kappa_{g3} < 1$) corresponding to the serial pore array ($\kappa_{g2} < 1$) and radially non-uniform porosity ($\kappa_{g3} > 1$) resembling the parallel pore array ($\kappa_{g2} > 1$).

This study (coupled with more extensive theoretical and experimental studies in our laboratory) suggests that characterization of porous solids in terms of porosity distribution, may be as important, in practice, as characterization in terms of pore size distribution.

SURFACE FLOW

Here, our results revealed fundamental defects in the conventional treatment of Eq. (1), with respect to both the effect of pore structure and the underlying physics.

Geometrical Modeling

Inclusion of the structure factor κ_s in Eq. (3) was originally suggested (by RMB) on the consideration that the "broken-up" nature (roughness) of the real surface causes "interruption" of the, theoretically envisaged as continuous, surface flow of the admolecules. This means that the said admolecules, in reality spend part of their time in the gas phase, where they can move faster. Hence, the measured D_s would be expected to be an overestimate of the value D_s^0, characteristic of the surface in its ideally "smooth" state; hence $\kappa_s > 1$. Such D_s^0, values have not been

given, so absolute values of κ_s are not known. Nevertheless, differences in surface roughness have been invoked to explain the (sometimes marked) discrepancies between measured D_s values, which have been observed even among porous barriers prepared by subjecting the same powder to different degrees of compaction.

However, the belief that D_s, (as measured by the "non-adsorbed gas calibration" method indicated above) reflects the characteristics of the relevant (real) pore surface was *not* called into question.

Our model studies showed clearly that this is not so. D_s values calculated by simulating the non-adsorbed gas calibration method were found to be, in general, dependent on pore structure (pore size distribution and connectivity) and correspondingly on macroscopic non-homogeneity (non-uniformity in porosity). Hence, κ_s, in Eq. (3) should be defined as an overall structure factor consisting of components analogous to those of κ_g, namely

$$\kappa_s = \kappa_0 \kappa_{s1} \kappa_{s2} \kappa_{s3}$$

where κ_0 is the same anisotropy factor as in κ_g; κ_{s1} accounts for the state of the pore surface (or, more accurately, for single pore properties, see following subsection); and κ_{s2}, κ_{s3} account for pore and macroscopic non-homogeneous structure, respectively. We find $\kappa_{s2} = 1$ for $n_T \to \infty$ (parallel array of pores), meaning that capillary bundle models cannot account for the effect under consideration, which is maximized at $n_T = 2$ (serial array of pores). Correspondingly, we have $\kappa_{s3} = 1$ for radial macroscopic non-homogeneity and maximum effect for axial non-homogeneity. *Ad hoc* model calculations revealed that these effects offer a much more plausible explanation of the discrepancies among experimental D_s values referred to in the preceding paragraph. The deviations of these structure factors from unity may be positive or negative, depending on the characteristics of the porous or macroscopic structure, as well as on the adsorbability of the gas (and hence on the temperature). For the case of relatively weak surface flux, it has recently proved possible to obtain an explicit analytical EMT expression for κ_{s2} analogous to those referred to above.

Physical Modeling

As the work described above progressed, the inadequacy of the conventional physical treatment of adsorbable gas flow, embodied in Eq. (1), became increasingly apparent. Accordingly, a strategy was developed whereby the elaborate geometrical modeling work used the simplest physics, while

development of a more rigorous physical approach was based on the simplest geometrical pore models.

Equations (1)–(3) yield

$$P/v_1 = (8/3)\kappa_g \varepsilon^2/A + A\kappa_s\lambda_s k_s^* = B_g + B_s k_s^* \tag{4}$$

thus making clear that the physical behavior of P is largely governed by that of k_s^*. In particular, P/v_1 is expected to decline smoothly with decreasing adsorbability, or increasing temperature, ultimately to a limiting value corresponding to the first term on the right hand side of Eq. (4). Reasonable concordance between the observed trend and that predicted by application of simple adsorption theory to k_s^*, is usually found in the range of moderate temperatures and gas adsorbabilities, where data are usually available and the said theory holds reasonably well. However, detailed data extending to high temperatures revealed an unexpected reversal of this trend at sufficiently high T (low k_s^*); so that P/v_1, after passing through a minimum, ultimately approached the aforementioned limiting value from below. This unusual behavior (subsequently confirmed in our laboratory as well as in other laboratories) could not be plausibly attributed to either λ_s or κ_s.

A physically more realistic molecular model appeared to be the only option left. Using appropriate previously developed partition functions, a slit-shaped model pore with "structureless" pore wall surfaces (justified by the consideration that attention was focused exclusively on admolecules which were activated and hence not confined at any "sites") yielding a 9:3 adsorption potential, was chosen, because of its geometrical simplicity.

In this context, however, the rationale of Eq. (1) is clearly not tenable, in view of the fact that *all* gas molecules within the pore are subject to the adsorption force field. One may then distinguish meaningfully only between those molecules energetic enough to overcome the desorption potential energy barrier at the midplane of the slit, i.e. to cross from one wall to the opposite one, as in normal Knudsen flow ("gas-phase" molecules), and those unable to do so, which may, therefore, be regarded as bound to (but able to diffuse along) the wall surface (activated admolecules).

So, to allow for this new definition of gas-phase and activated adsorbed molecules (denoted by dashed symbols), Eq. (4) should be rewritten as follows:

$$P/v_1 = B_g C_g' \lambda_g'/\lambda_g C_g + B_s k_s^{*\prime} \tag{5}$$

where C_g refers to concentration of gas-phase molecules whose mean effective trajectory length is denoted by λ_g; while the behavior of $k_s^{*\prime}$ should not differ materially from that of k_s^*. Calculation shows that (except in very narrow pores)

$C'_g < C_g$; while $C'_g \to C_g$ as $T \to \infty$ ($k_s^* \to 0$). It is presumably this tendency of C'_g/C_g which accounts for the aforementioned reversal of the normal trend of P/v_1 as $k_s^* \to 0$. This hypothesis was confirmed by realistic numerical examples based on the relevant partition function expressions and treating λ'_g and λ_g as constants.

The above simplified modeling approach has the advantage that k_s^* and C'_g/C_g may be expressed analytically; while the distinction between gas-phase and activated admolecules clarifies the cause of failure of the conventional treatment; which, in the region of minimum P/v_1, yields the unphysical result $P_s < 0$. In fact, both this distinction (which, in any case, becomes less clear in cylindrical model pores) and the assumed constancy of λ'_g and λ_s are not necessary; and were not, in fact, used in subsequent calculations, wherein the mean effective trajectory length of all molecules present in the model pore was evaluated. The results obtained fully confirmed the general behavior described above. The general tendency of P to drop below P_g and go through a minimum was found to be most prominent in long pores of moderate width and was not materially affected by the functional form of the adsorption force field (9:3 potential versus a "synthetic" triangular one) or by pore shape (cylindrical or two-dimensional slit) geometry.

In view of the fact that these calculations must be carried out numerically, care was subsequently taken to delineate the conditions under which the basic concepts of conventional surface flow theory are at least formally tenable. Thus, it was found that, to a first approximation, in the stronger adsorption region and in sufficiently narrow pores, Eq. (1) is formally valid, with D_s independent of pore size, although its value does not reflect solely the structural characteristics of the pore wall surface and the relevant activation energy is not identical with the height of the corresponding potential energy barrier.

Care was also taken to confirm (through model studies based on parallel and serial pore arrays) our original supposition that the permeability minimum under consideration here is (as was the case with the gas-phase permeability minimum in the Knudsen to Poiseuille transition region previously discussed) primarily a function of individual pore properties.

Extension of the above work to non-isothermal adsorbable gas transport led to the prediction of corresponding "unusual" behavior, the most striking feature of which was a drop of the absolute value of the heat of transport, in the low k_s (high T) region, below the value (=1/2) characteristic of a non-adsorbed gas, thus enabling us to explain the (previously incomprehensible) behavior of extensive relevant data reported by the Barrer school.

By way of an epilogue, it is noteworthy that another step towards greater realism of the basic pore model has been taken, in the form of a two-dimensional slit with structured walls and adsorption force field resulting from summation of

atomic/molecular 12:6 LJ interaction potentials. The results (i) fully confirmed previous findings (hopefully to the satisfaction of the purists) and (ii) extended our study to pores of molecular sieving dimensions (which are difficult to treat otherwise).

SUMMARY AND CONCLUSIONS

With regard to geometrical modeling, the network model which has been developed is considerably more realistic and comprehensive than those previously applied to the interpretation of gas flow in porous adsorbents, separation barriers or catalysts. It encompasses gas permeability, relative permeability and equilibrium sorption properties. Its use in the present work has led to new significant theoretical insights into the interrelation of these properties through their dependence on salient features of mesoscopic pore structure, notably pore size distribution and pore interconnectivity. Detailed insight was also achieved into previously unsuspected effects of these structural features on the "surface flow" of adsorbable gases.

On the practical side, this model sets the stage for substantially more comprehensive and consistent analysis of sorption and flow data. A crucial feature of the model in this respect is that it has no more parameters than (and no freely adjustable parameter like) its predecessor (namely the capillary bundle with distributed pore radius) in this field. On the other hand, the demonstration that it is amenable to, at least approximate, analytical treatment, effectively lays it on the doorstep of the experimentalists!

With regard to physical modeling, the conventional treatment of adsorbable gas flow was shown to be inadequate for the interpretation of permeability behavior in the weak adsorption region. The fault was found to lie in the physical rationale adopted in this treatment for the analysis of the permeability into gas-phase and surface components. A more sophisticated molecular approach (based on model pores with structureless walls) was developed, in which this kind of analysis can be made in a more rational manner or (in the more general form of this approach) avoided altogether. Model calculations performed on this or basis was in accord with the aforesaid observed permeability behavior. The same approach was applied with similar success to non-isothermal adsorbable gas permeability behavior. In a more recent development, a model pore, with structured walls and adsorption potential derived by summation of atomic/molecular LJ interactions, was used; thus bringing this treatment to the doorstep of the MD simulation practitioners!

Further Reading

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