

Some Fundamental Problems of Heat-Mass-Transfer through the Thin Materials

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Abstract This paper develops the novel approach to problems arising at the study of permeability for the textile fabrics, natural leathers, thin layers of polymers and other thin porous structures (PS). There is serious gap between the experimental investigation of such PS and the relevant different models proposed to imitate the heat-mass-transfer (HMT) of moist air through the small thickness of PS. The formers are based on the *water-vapor-transmission* (WVT) rate dynamical parameter, which is not, as a matter of fact, the characteristic of PS itself. The same is true for the uncontrolled in the majority of experiments quantity termed as the *gradient of partial moisture pressure*. The well-established methodology proposed in this paper provides the reliable estimate of the *generalized diffusion coefficient*. It characterizes just the properties of PS itself.

Keywords Water-vapor-transmission rate's, Porous structure, Generalized diffusion coefficient

1. Introduction

The specific property of a thin porous structure (PS) is two strong inequalities: $l \gg \delta$, $b \gg \delta$ between its linear sizes l, b determining the normal test area $A_{\perp} = l \times b$ (0.3×0.3 m², for example) and its thickness δ ($10^{-4} - 10^{-3}$ m, in the most cases). The water vapor transmission (WVT) rate of any PS and the textile fabrics, in particular, is of considerable interest for many branches of the practice and science. Such materials provide, for example, the steady moisture transfer from the skin of the weaver through the textile layers into the environment during heavy work or in hot climate conditions.

There is a variety of methods to measure WVT (Δm is mass change):

$$WVT = \frac{\Delta m}{A_{\perp} t} \left[\frac{kg}{m^2 s} \right] \quad (1)$$

which give, however, the quite different results for the same fabric, or, more generally, the same thin PS. The obvious reason of such situation is an absence of the general conception of treatment and interpretation of the experimental data obtained by the different test methodologies, which vary with respect to construction mechanisms, test conditions and measurement parameters.

The aim of this paper is to demonstrate that the general

approach to the WVT-problem becomes still possible if one rejects its physically incorrect but widespread interpretation as the *property of PS itself*. In contrast, it is considered here as the standard density of flow: j_m (i.e. the dynamical parameter) determined for the *quasicontinuous* PS-media by the non-equilibrium thermodynamics:

$$WVT \equiv j_m = \rho u_{\perp} \left[kg/m^2 s \right], \quad (2)$$

where $\rho = \Delta m / (A_{\perp} \delta) \left[kg/m^3 \right]$ is the local density of a moist vapor while $u_{\perp} = \delta / t \left[m/s \right]$ is the effective local kinematic velocity. The main problem of this interpretation is the reliable estimate of both quantities ρ and u_{\perp} separately taking into account the netto-mass m_M and the respective density $\rho_M = m_M / (\delta \cdot A_{\perp})$ of a PS- material (M) itself. During the water vapor transport process its brutto-mass $\bar{\rho}_M = \bar{m}_M / (\delta A_{\perp})$ is increased due to the sorption ability ($\bar{m}_M > m$) of any PS. Of course, these corrections are very different for the hydrophobic or weakly hydrophilic fabrics, on the one hand, and hydrophilic fabrics, on the other hand.

Another fundamental problem of the proposed below approach based on the generalized for PS Fick's law of diffusion:

$$j_m = -D^* \text{grad } P \approx -D^* (P_2 - P_1) / \delta \quad (3)$$

is the reliable estimate of the generalized diffusion coefficient $D^* [s]$ which has the dimensionality of time.

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Indeed the comparison (1) and (3) leads to the interesting possibility to calculate u_{\perp} from (2)

$$u_{\perp} = \frac{\delta}{t} = \frac{D^* \Delta P \cdot A_{\perp}}{\Delta m} \quad (4)$$

is the difference of partial pressures ΔP across PS can be specified (or measured) by experiment. Unfortunately, this is not the case for a majority of WVT-measurements. Our goal below is to demonstrate that some progress can be achieved in the framework of proposed approach too if one measures the same fabric sample by the different test methods.

2. Physical Concepts of Approach

The gradient of partial pressure $grad P$ for a moist vapor in the postulated linear transport equation (3) is, as a rule, uncontrolled by the experimentalist parameter. Its formal definition for the steady process is based on the following reasonable assumption. One supposes the linear decrease of partial pressure on the path from the source moisture 1 (usually it is the saturated water existing in an admitted equilibrium with its saturated vapor at $P_s(T)$) through the tested fabric's layer 1-2 with the thickness δ up to the presumably zero pressure $P_2 \approx 0$ of an experimental vessel 2. Of course, the atmospheric pressure $P_{atm} \approx 101 kPa$ can be added to the both limiting values of the finite difference $\Delta P \approx -P_s(T)$ to make the realistic estimate of its magnitude in terms of the measurable pressure.

Nevertheless the fundamental question remains: Is the saturated vapor pressure of water divided by an arbitrary total width of layers the actual *thermodynamic force* to provide the respective flow of a moisture j through the fabric in accordance with (1)?

$$grad P \approx \frac{P_2 - P_1}{\delta} = -\frac{P_s(T)}{L_1 + \delta + L_2} \quad (5)$$

where L_1 is the measurable width of an air layer between the source of moisture and the internal surface 1 of a tested fabric while L_2 for an outside air layer is a *bad-defined parameter* for any experiment or model.

To elucidate the problem of an *effective local kinematic velocity* u_{\perp} (of its definition, first of all) in total, let us remind the main specific features of the standard permeability test. The most relevant one is, of course, the sweating guarded hot plate test specified in ISO 11092 [2]. Its detailed description and results can be found elsewhere [1] and only the main working equation should be discussed now:

$$R_{et} = \frac{A_{\perp} (P_s - P_a)}{H - \Delta H_e} \left[\frac{m^2 Pa}{W} = \frac{s}{m} \right] \quad (6)$$

where R_{et} is the total evaporative resistance provided by the porous metal plate (imitated the body skin at 35 °C) fabric and boundary air layer L_1 in (5); A_{\perp} - test area, m^2 ; $P_s(T)$ - the water vapor pressure of the above plate surface, Pa; P_a - the water vapor pressure of the air, i.e. of the undetermined layer of L_2 in (5); H - the heating power, W; ΔH_e - the correction evaporative term for heating power, i.e. latent heat of vaporization, W. The intrinsic evaporative resistance of the fabric R_{ef} can be found as the difference:

$$R_{ef} = R_{et} - R_{eb} \quad (7)$$

where R_{eb} is the evaporative resistance of the porous plate and boundary air layer L_1 . Just the reciprocal R_{ef} -value provides in this arrangement, which drives heat and moisture transfer upward only along the specimen thickness direction, the appropriate value of u_{\perp} :

$$u_{\perp} = 1/R_{ef} [m/s] \quad (8)$$

Huang and Qian [3] have proposed the rather informative methodology to test, *simultaneously*, R_{ef} - and WVT-values. It is based on the change of relative humidity, i.e. measurable *water vapor concentration gradient* considered as *thermodynamic force* for the moist vapor transfer. This HQ-approach is closer to the main concept of Fick's law for selfdiffusion formulated originally for the dilute gases:

$$j_m = -D grad \rho \approx -D(\rho_2 - \rho_1)/\delta \quad (9)$$

where the approximate equality demonstrates its possible extension on the thin PS and $D [m^2/s]$ is the molecular-based diffusion coefficient:

$$D = \bar{\lambda} \bar{u} / 3. \quad (10)$$

It is expressed here in terms of the average free path of particles (between two neighboring collisions) and \bar{u} - the average velocity of molecular motion in any transport process realized in the pure dilute gas [4]:

$$\bar{\lambda} = \frac{1}{\sqrt{2} \pi \sigma^2 n} = \frac{k_B T}{\sqrt{2} \pi \sigma^2 P} \quad (a) \quad \bar{u} = \sqrt{\frac{8 k_B T}{\pi m_0}} \quad (b) \quad (11)$$

where $n = \rho/m_0 = N/V$ - concentration of particles with the molecular mass $m_0 = M/N_A [kg]$ and σ - effective diameter of particles.

It is worthwhile to note that the authors of HQ-method [3] themselves did not consider its generalized molecular interpretation for PS based on (9-11). However, the remarkable correlation between their measurements obtained

by two different (HQ and ISO 11092) methods confirms completely the possibility of such analysis. It is found by us in terms of the reciprocal resistances (8), i.e. the effective diffusion velocities and is shown in Table 1.

Table 1. Correlation of Intrinsic Diffusion Reciprocal (8) Resistances for Six Fabrics Measured in [1]

| Sample code | u_{\perp} (HQ) (m/s) | u_{\perp} (ISO) (m/s) | $\bar{u}_{\perp}/u_{\perp}$ |
|--|------------------------|-------------------------|-----------------------------|
| 1 | $3.135 \cdot 10^{-2}$ | $3.846 \cdot 10^{-1}$ | 0.082 |
| 2 | $1.314 \cdot 10^{-2}$ | $2.564 \cdot 10^{-1}$ | 0.051 |
| 3 | $3.191 \cdot 10^{-3}$ | $7.463 \cdot 10^{-2}$ | 0.043 |
| 4 | $2.630 \cdot 10^{-3}$ | $6.623 \cdot 10^{-2}$ | 0.040 |
| 5 | $3.199 \cdot 10^{-4}$ | $3.630 \cdot 10^{-3}$ | 0.088 |
| 6 | $2.537 \cdot 10^{-4}$ | $2.748 \cdot 10^{-3}$ | 0.092 |
| mean of (u_{\perp} (HQ)/ u (ISO)) = 0.066 for 6 fabrics | | | |

While the absolute magnitudes are different in two orders for the both columns, their ratio is the oscillating value near its mean level 0.066. The Pearson correlation test was performed also to demonstrate the quite high level of correlation (0.999) between two discussed methods.

It is interesting to remind here the works of Chyjkova et al [5] dated by 1980 and published only in Russian journal KOP. These authors studied the so-called *capillar model of porosity* in terms of Fick's law (3). The following molecular-based equations [4] have been used for the small ($\bar{\lambda} > \bar{d}$) and large ($\bar{\lambda} \leq \bar{d}$) mean diameters of capillars, i.e. model of pores:

$$j_m = -\frac{4}{3} \sqrt{\frac{M}{2\pi RT}} \bar{d} g \frac{P_2 - P_1}{\delta} \quad (12)$$

$$j_m = -D \frac{M}{RT} g \frac{P_2 - P_1}{\delta} \quad (13)$$

where D is the diffusion coefficient (10) for a mixture, M [kg/mol] – the molar mass of air ($M_a = 29 \cdot 10^{-3} \text{ kg/mol}$)

and water ($M_W = 18 \cdot 10^{-3} \text{ kg/mol}$),

$R = 8.31 \text{ J/mol K}$ – the universal gas constant and g – porosity determined by the common area of the surface pores A_P , i.e. $g = A_P/A_{\perp} = N_P \pi \bar{d}^2 / (4A_{\perp})$.

Unfortunately, the respective molecular approximations of generalized diffusion coefficient D^* [s]:

$$D_{\bar{\lambda} > \bar{d}}^* = \frac{1}{3} \sqrt{\frac{\pi M}{2RT}} \frac{N_P \bar{d}^3}{A_{\perp}} \quad (14)$$

$$D_{\bar{\lambda} \leq \bar{d}}^* = \frac{DM}{4RT} \frac{N_P \pi \bar{d}^2}{A_{\perp}} \quad (15)$$

are rather uncertain ones because the enormous number

N_P and the very small \bar{d} either should be a priori given or should be measured by the quite formidable experiment [5]. Besides, Chyjkova et al [5] have not measured the *grad P*-value in (12,13) but have predicted it on the base of some unreliable, to our mind, estimates for D^* in (14,15) and calculated j_m -values.

There are several rather reliable testing equipments (see, for example UTX-3360) for the so-called air permeability (AP) which is simply the velocity of a dry air u flowing through the thickness of PS:

$$u = \frac{\Delta V}{A_{\perp} t} = \frac{\Delta m \delta}{\rho V_M t} = \frac{\Delta V}{V_M} u_{\perp} \quad (16)$$

where V is the measurable volume change and t – time during which ΔV occurred, $V_M = A_{\perp} \delta$ – the measurable volume of a porous material (M). At first sight, one obtains from (16) the alternative to (4) variant for determination of a kinematic velocity if the condition $\rho = \Delta m / \Delta V = \text{const}$ is fulfilled:

$$u_{\perp} = \frac{V_M u}{\Delta V} = \frac{V_M \rho u}{\Delta m} = \frac{V_M j}{\Delta m} \quad (17)$$

However, just this condition for the volume density $\rho [\text{kg/m}^3]$ of an air stream becomes questionable when the certain mass of a moist vapor remains in PS due to the sorption phenomenon. One should take into account the discontinuity of a relative humidity and the respective density “jump” between the ingoing 1 and outgoing 2 flows of a moving through fabric vapor.

Another serious problem of the relevant experimental WVT-methodologies is itself their interpretation. One considers the WVT-quantity as the fabric's characteristic parameter. Evidently, that this concept is an elusive one because the density of flow j_m (1) is a typical dynamic parameter of the linear non-equilibrium thermodynamics. In the formalism of a continuous media, it is simply a reply of system to the action of a thermodynamic force, which is the appropriate gradient. In other words, only the effective coefficient D^* can be the fabric's parameter.

The non-equilibrium thermodynamics states that the actual *diffusion coefficient* $D [\text{m}^2/\text{s}]$ from (9) plays also the role of *kinematic velocity* and/or *temperature-conductivity* in the Newton's and Fourier's laws, respectively ($\eta [\text{kg/m} \cdot \text{s}] = Pa \cdot \text{s}$; $\vartheta [\text{J}/(\text{m} \cdot \text{s} \cdot \text{K})] = W/(\text{mK})$) at least, for a diluted gas:

$$\eta = D \rho \quad (a) \quad \vartheta / C_v = D \rho \quad (b) \quad (18)$$

where $C_v [\text{J}/(\text{kg} \cdot \text{K})]$ is the specific isochoric heat capacity.

We assumed now that the discussed here well-established

formalism for the small densities of bulk gases can be extended and applied to the dense fluid (most vapor) states and, even, to the gas-liquid-transition states if the following conditions are fulfilled:

- 1) the density profile $\rho(x)$ along the chosen direction of a mass-transfer process *should be given* to determine the stationary (or, about the equilibrium for a phase-transition state) *grad* ρ in (9);
- 2) the density of a mass-flow j_m along the same direction *should be measured by experiment* to evaluate then the diffusion coefficient D ;
- 3) the dynamical viscosity η in (18a) as well as the heat transfer coefficient \mathcal{G} in (18b) have to be calculated from the *measurable value of the heat capacity* C_v and the above estimates of D - and $\rho(x)$ -values;
- 4) the effective modified quantity ρ from (18) determined for the special *thin* δ -layer along the x -direction becomes in the proposed here methodology the *main parameter if the divergence of its profile* $\rho(x)$ is locally possible just in this layer;
- 5) accordingly to the statement 4) the thin layer of any fabric with the surface $A_{\perp} = l \cdot b$ located normally to the x -direction of a mass-heat transfer is a reason to change sharply the local value of density ρ taking into account the porous (fractal) structure of its distribution.

3. Generalized Diffusion Coefficient of Fabrics

To illustrate the usefulness of the proposed in this work approach (Section 2) the following (see also Table 1) set of six fabrics (Table 2) studied experimentally [1] by six different test methods (Table 3) have been chosen below.

Huang and Qian represented graphically the comparison of other five methods 1)-5) with that 6) developed in [3]. There were: 1) the upright cup method used according to ASTM E96, Procedure B [6]; 2) the inverted cup method used according to ASTM E96, Procedure BW [6]; 3) the desiccant inverted cup method used according to ISO standard [7]; 4) the dynamic moisture permeation cell (DMPC) method used according to ASTM F2298 [8]; 5) the sweating guarded hot plate method used according to ISO 11092 [2].

Table 2. Specification of the Fabrics

| | Sample code and description | Surface density kg/m ² | ρ_M , kg/m ³ | δ , mm |
|---|--|-----------------------------------|------------------------------|---------------|
| 1 | PTFE laminated to a nylon tricot | $94.5 \cdot 10^{-3}$ | 410.9 | 0.23 |
| 2 | Cotton/polyester knitted fabric | $237.8 \cdot 10^{-3}$ | 264.2 | 0.90 |
| 3 | Polyester fabric laminated with PU film | $148.3 \cdot 10^{-3}$ | 449.4 | 0.33 |
| 4 | Densely woven polyester fabric | $96.9 \cdot 10^{-3}$ | 969.0 | 0.10 |
| 5 | Polyester polar fleece laminated with TPU film | $275.8 \cdot 10^{-3}$ | 195.6 | 1.41 |
| 6 | Nylon rip stop weave laminated with TPU film | $125.8 \cdot 10^{-3}$ | 405.8 | 0.31 |

The results of latter one 5) has been analyzed in Section 2 (see Table 1). We have used below in Table 4 the same technique to test the reciprocal by ratio of WVT-values 1)-4) derived by the WVT-standard obtained by HQ-method. The only result of such comparison is the rather rough (in accuracy) confirmation of the linear Fick's law. Besides, the such approximate graphic analysis contains an *unphysical feature* because the average slopes from Table 4 as well as in Figure 1 [1] do not provide the correct limiting passing through the point at the coordinate origin ($j_m = 0$ when *grad* $P = 0$).

In opposite to the above-discussed comparison we propose the next steps to estimate the realistic D^* -value:

- 1) It follows from (1) and (3) that an WVT-ratio (see Table 4) represents also the ratio of the respective gradients:

$$j_i/j_j = \text{grad } P_i / \text{grad } P_j \approx \Delta P_i / \Delta P_j \quad (19)$$

if the same δ -specimen of a fabric has been measured by the different methods;

- 2) as a result, one must estimate only one method-dependent gradient of pressure ΔP_j to predict the others (effective) ΔP_i -values for the different methods from the WVT-ratio:

$$\Delta P_i = (j_i/j_j) \Delta P_j \quad (20)$$

Table 3. Comparison of Experimental Setup for Six Test Methods

| Descriptors | ASTM E96 B | ASTM E96 BW | ISO 15496 | ASTM F2298 | ISO 11092 | HQ |
|-----------------------------|-------------------------|----------------|----------------|-------------------------------|----------------------------|-------------------------|
| relative humidity | 50% | 50% | 23% | 5% | 40% | 0 |
| air velocity | 2.8 m/s | 2.8 m/s | not controlled | not controlled | 1 m/s | 0.4 m/s |
| test temperature | 23 °C | 23 °C | 23 °C | 20 °C | 35 °C | 20 °C |
| air layers (al) | al on either side of PS | external al | no al | small al on either side of PS | boundary al subtracted out | small al subtracted out |
| pressure gradient across PS | not controlled | not controlled | not controlled | 0 | not controlled | not controlled |

3) then, the generalized diffusion coefficient of fabric can be estimated accordingly to (3):

$$D_i^* = j_i \delta_i / \Delta P_i \quad (21)$$

4) we have used for the simplicity the standard change of pressure for the basic HQ-method: $\Delta P = 1 \cdot 10^5 \text{ Pa}$

to calculate the D_i^* -values represented in Table 5.

Table 4. Ratio of the WVT-value from HQ-method 6) to those following from 1)-4) methods

| Sample code | WVT-ratio HQ/E96-B | WVT-ratio HQ/E96-BW | WVT-ratio HQ/F2298 | WVT-ratio HQ/ISO 15496 |
|----------------|--------------------|---------------------|--------------------|------------------------|
| 1 | 7.88 | 1.49 | 1.45 | 0.38 |
| 2 | 4.85 | 1.47 | 1.16 | 0.50 |
| 3 | 4.21 | 1.64 | 1.30 | 0.74 |
| 4 | 3.41 | 2.11 | 1.03 | 0.75 |
| 5 | 1.55 | 0.65 | 0.58 | 0.44 |
| 6 | 2.43 | 0.67 | 0.91 | 0.45 |
| average slopes | 4.06 | 1.34 | 1.07 | 0.54 |

Table 5. Generalized Diffusion Coefficient D^* for Six Fabrics 1-6 from Table 2

| Specimen | 1 | 2 | 3 | 4 | 5 | 6 |
|-------------------------------|------|------|------|------|------|------|
| $D^* \cdot 10^{15} \text{ s}$ | 2.84 | 8.34 | 1.36 | 34.8 | 74.4 | 13.0 |

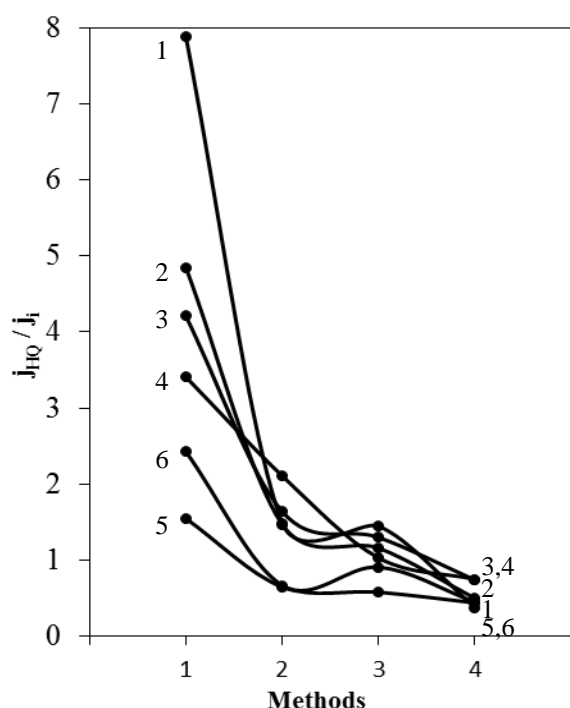


Figure 1. Non-linearity of WVT-ratio for the chain of regular changes in the sequence of test methods1)

Nevertheless, Fig.1 demonstrates that the experimental WVT-ratio changes its values mainly monotonically but nonlinearly from one method to another one. The supposed here generalized reason of such behavior is the respective monotonic but non-regular change of the respective thermodynamic force i.e. of the gradient of partial pressure.

4. Conclusions

This work is an attempt to classify the set of standard methods directed usually to estimate WVT. The purpose is to modify approach, in general, and to study the thin PS-property D^* itself instead of the dynamic WVT-characteristic which is mainly determined by the appropriate thermodynamic force in the variants (1,3) of the generalized linear Fick's law, formulated for PS.

Obviously that the remaining problem is the measurement of pressure drop across the sample. An absence of such experimental parameter cannot be compensated, from our viewpoint, by its theoretical estimates. This arbitrary estimate may cause a large shift in diffusion resistance even if the WVT-value is reliably measured. A combination of AP- and WVT-measurements of the same sample at the same conditions may be essential to solve independently this fundamental problem.

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