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APPLICATION OF THE BOSANQUET APPROXIMATION FOR MODELING MOISTURE TRANSPORT IN POROUS HUMIDITY SENSORS

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Article Info

Abstract

Water vapor transport properties in porous dielectric structures are significantly influencing the performances of porous humidity sensors. Knowledge of diffusion paths that control the movement of moisture will be crucial in developing faster sensor response, sensitivity, and long-term stability. In porous materials, moisture transport is via a combination of bulk molecular transport and Knudsen transport depending on the ratio of pore size to the mean free path of water molecules. Multi-scale porous structures that require both diffusion and transport are often best described using traditional diffusion models. The Bosanquet approximation is a convenient method for including molecular and Knudsen diffusion together in a single effective diffusion coefficient. In this paper, a complete theoretical review of the Bosanquet approximation and moisture transport modelling in porous humidity sensors using the Bosanquet approximation is presented. The fundamentals of molecular diffusion and Knudsen diffusion are described and the Bosanquet equation is derived and discussed with respect to the applicability of the equation in the transition diffusion regimes. Theoretical calculations show the effect of the pore size on the diffusion behavior and the performance of the sensor. The review sets the basis for the current Bosanquet approximation, which is a useful analysis tool for moisture transfer through state-of-the-art porous dielectric materials, and for future coupled diffusion–adsorption modeling methods.

Keywords:

Bosanquet Approximation, Humidity Sensors, Knudsen Diffusion, Molecular Diffusion, Moisture Transport, Porous Materials, Dielectric Sensors.

1. INTRODUCTION

Humidity measurement is important in industrial process control, in environmental monitoring, in semiconductor manufacturing, in the production of pharmaceuticals, in aerospace systems, and in high purity gas processing. For many applications, particularly those where very low moisture contents are required, the ability to accurately measure the water vapor concentration is crucial to assure product quality and operational reliability.

The porous dielectric humidity sensor has gained a great deal of interest due to its high sensitivity, low power consumption and compatibility with modern electronic systems. In general, these sensors use porous oxide materials, like aluminum oxide, silicon dioxide, titanium dioxide, or a combination of dielectrics. The porous morphology creates a high internal surface area for the adsorption of water vapor and also has a significant impact on sensor performance.

Experimental studies conducted repeatedly have shown that the transient response of humidity sensors is highly dependent on pore size distribution, pore connectivity and general surface morphology. However, there are still some physical mechanisms involved in moisture transport process in porous structures that are complex due to the simultaneous possibility of several diffusion mechanisms.

There are in general two limiting mechanisms for the transport of water vapor in porous media: bulk molecular diffusion and Knudsen diffusion (Figure 1). The prevailing mechanism will depend on the ratio of the molecular mean free path and the pore diameter. For many practical porous materials, especially those with pores of tens of nanometers to several micrometers in size, neither of these mechanisms is sufficient to describe moisture transport.

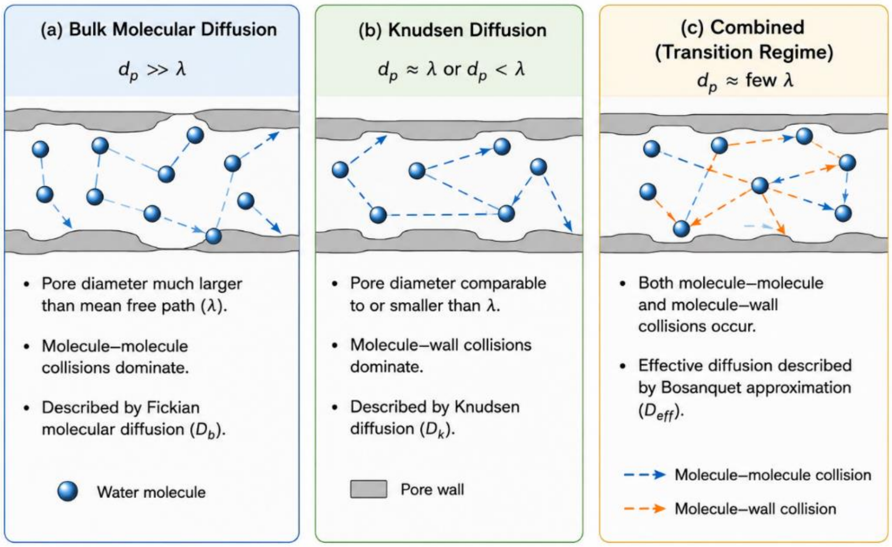

Figure 1: Schematic Illustration of Moisture Transport Mechanisms in Porous Dielectric Materials

The Bosanquet approximation [1-6] has emerged as a viable theoretical model for capturing transport in transition diffusion regimes, which is what is needed to address this challenge. This review covers the physical underpinning, mathematical model and usefulness of the Bosanquet approximation for humidity sensor applications. Bosanquet approximation is widely used in porous material of humidity sensors [7-8].

2. MOISTURE TRANSPORT IN POROUS MATERIALS: FUNDAMENTALS

Concentration gradients, pore geometry, pore pressure and molecular interactions dictate water vapor transport within porous structures. Moisture movement takes place when molecules move from areas of high concentration to areas of low concentration.

There are a number of factors that affect the rate of moisture transport:

- Pore diameter
- Pore connectivity
- Surface roughness
- Temperature
- Pressure
- Material composition
- Adsorption interactions

The response time is much a function of the diffusion rate of water molecules through the porous dielectric structure and the speed of adsorption equilibrium formation at active sensing sites in porous humidity sensors [9-19].

The diffusion process is especially complicated if the pores have more than one length scale. In this case, the transport mechanism is due to the molecule-molecule collisions as well as molecule-wall collisions.

3. BULK MOLECULAR DIFFUSION

If the pore diameter is much greater than the mean free path of the molecules, then bulk molecular diffusion takes place. In such circumstances, molecules mostly collide with each other, but not with the walls of the pores.

According to Fick's First Law:

$$J = -D(dC/dx)$$

J is diffusion flux; D is the diffusion coefficient; dC/dx is the concentration gradient.

The bulk diffusion coefficient of water vapour in air is nearly equal to:

$$D_b = 2.42 \times 10^{-5} m^2/s$$

Bulk diffusion is the predominant process for pores larger than about 1 micrometer. In this regime, moisture transport is similar to that in open air, and more or less independent of the pore wall effects.

Intermolecular collisions play a major role in the transport process, which explains the fact that the diffusion coefficient is not very sensitive to pore geometry.

4. KNUDSEN DIFFUSION

As the pore size gets smaller (nanoscale), the transportation changes dramatically. If the diameter of the pore becomes of the order of the molecular mean free path, more collisions will take place between the molecules and the walls than between the molecules themselves. This type of transport is called Knudsen diffusion, a illustration is given in figure 2.

The Knudsen diffusion coefficient is represented by the following:

$$D_k = (2r/3)\sqrt{(8RT/\pi M)}$$

where:

D_k = Knudsen diffusion coefficient

r = pore radius

R = Universal gas constant

T = absolute temperature

m = mass of the diffusing species

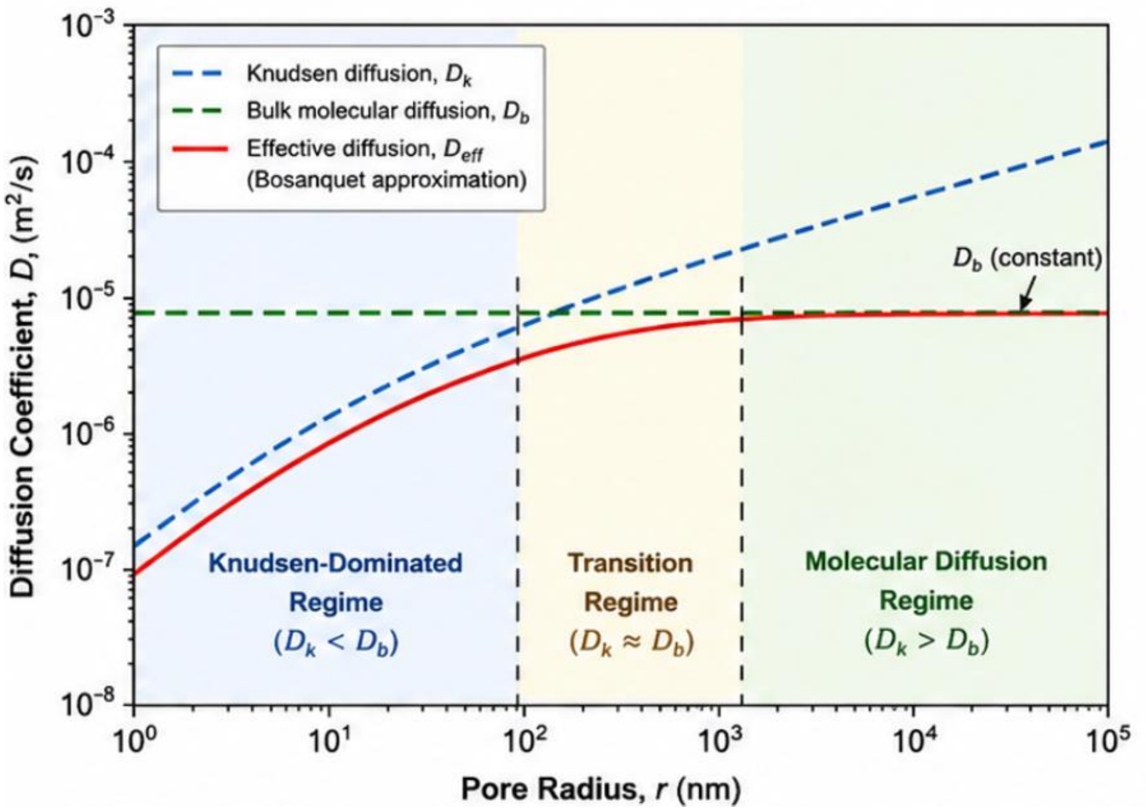

Figure 2: Variation of Diffusion Coefficients as a function of pore radius illustrating Knudsen-dominated, transition, and molecular diffusion regimes.

The Knudsen diffusion is proportional to the pore radius, unlike the molecular diffusion. Smaller pores create higher resistance to transport due to higher number of interactions with pore walls.

Hence the Knudsen diffusion coefficient can be said to decrease with decreasing pore size.

5. TRANSITION DIFFUSION REGIME

In most porous dielectric humidity sensors [9-19], the pores are not all the same size, but have a range of sizes.

Thus, many practical materials are subject to a "mixed" regime between the extremes of bulk diffusion and Knudsen diffusion for which neither can be considered the predominant mechanism of transport.

In this regime:

Collisions between molecules are still significant.

The number of collisions between the molecule and the walls increases.

The transport properties are dependent on both of the diffusion mechanisms.

The transition regime described above is of particular interest for the porous oxide materials that are employed in humidity sensing applications, since the pores are typically in the range of 40nm to a few micrometers.

A model of transport behavior that captures both of these diffusion mechanisms is thus necessary for accurate modelling.

6. BOSANQUET APPROXIMATION

The Bosanquet approximation serves as an actual approach to implementing the addition of bulk molecular diffusion and Knudsen diffusion.

The effective diffusion coefficient is given by:

$$1/Deff = 1/Db + 1/Dk$$

This equation is similar to the parallel electrical resistance circuit and is based on the assumption that the diffusion rate is determined by the slowest diffusion mechanism.

Another way of writing the effective diffusion coefficient is:

$$Deff = (Db \times Dk)/(Db + Dk)$$

The Bosanquet approximation has a number of benefits:

- Simple mathematical implementation.

Physical explanation of the diffusion resistance.

- Applicability to multi-scale porous materials.

- Computational efficiency.

- At least some level of compatibility with numerical simulation methods.

The diffusion coefficient is therefore always less than or equal to either of the individual coefficients, and as such, is a reflection of the slower diffusion mechanism.

Theoretical analysis of pore size effects.

The Bosanquet approximation predicts a strong dependence of transport behavior on pore dimensions.

For large pores:

$$Dk >> Db$$

and therefore:

$$Deff \approx Db$$

The diffusion of molecules is by bulk.

For small nanopores:

$$Dk << Db$$

and therefore:

$$Deff \approx Dk$$

Knudsen diffusion dominates.

If the pore size is in the middle range:

$$Dk \approx Db$$

Both of these mechanisms play a major role.

From this behavior, it is clear that transition diffusion models are of great importance for porous dielectric materials with nanoscopic features.

According to theoretical calculations, reducing the pore radius leads to more resistance to the transport and less effective diffusion coefficient. But smaller pores at the same time contain larger surface area and it is more adsorption capable.

Therefore, it is necessary to optimize the sensors [9-17] in a way that ensures both the diffusion efficiency and adsorption ability.

The next step involves developing humidity sensors. Humidity sensor design is the next step.

The Bosanquet approximation gives useful clues to the design of high-performance humidity sensors.

Diffusion analysis: Several Design Considerations

In the first place, the dimensions of the pores must be chosen to provide a maximum of accessibility of moisture and at the same time have an adequate adsorption surface area.

Second, hierarchical pore structures with both micro-scale and nano-scale features might enhance transport efficiency.

Third, diffusion limitations allow diffusion time to be predicted, thus allowing sensor response and recovery times to be predicted.

Fourth, diffusion modelling can be helpful in understanding experimental observations on the transient sensor behaviour.

The Bosanquet approximation is therefore a convenient theoretical model for development of materials and optimization of devices.

9. LIMITATIONS OF THE BOSANQUET APPROXIMATION

Although the Bosanquet approximation is useful, it has some drawbacks.

The model assumes:

- Ideal pore geometry.
- Uniform pore dimensions.
- Negligible adsorption effects.
- Constant temperature conditions.
- No capillary condensation.

In reality, the humidity sensor model described above is quite complex, and generally, the pores of a real sensor are not explicitly represented, and the surfaces are not homogeneous, nor is there an explicit representation of adsorption-desorption interactions.

Hence, in advanced models, adsorption kinetics as well as capillary effects and surface diffusion were also included in addition to diffusion transport.

However, the Bosanquet approximation is still highly relevant for the first order analysis of moisture transport behavior.

10. FUTURE RESEARCH DIRECTIONS

Further studies are needed to combine the Bosanquet approximation with adsorption-desorption kinetics and pore-network modeling (Figure 3).

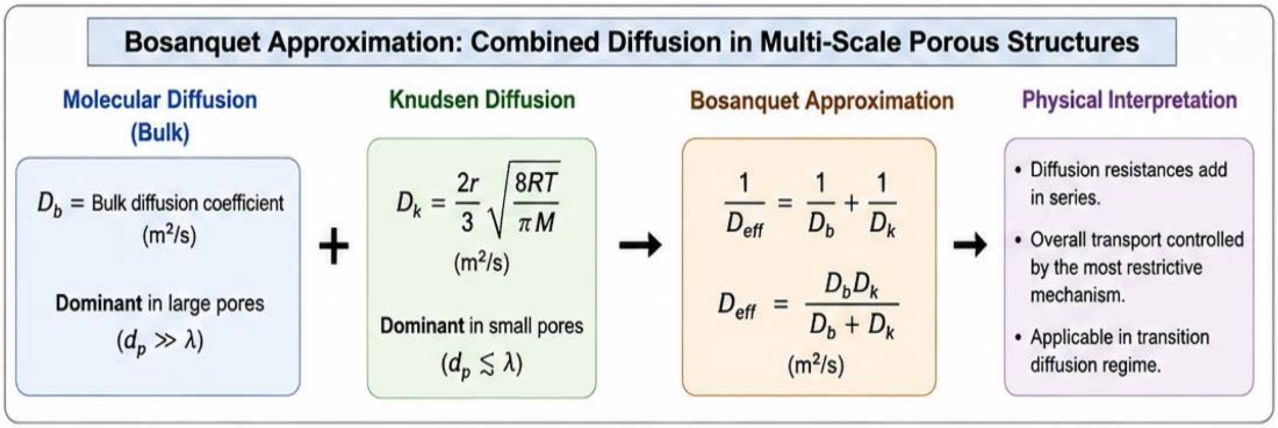

Figure 3: Summary of Bosanquet Approximation for combining molecular diffusion and Knudsen diffusion in multi-scale porous materials.

Examples of possible areas of investigation are coupled diffusion-adsorption simulations. multi-scale pore network analysis, capillary condensation effects, machine-learning-assisted transport prediction, and three dimensional pore reconstruction using SEM images. The developments will allow for more precise prediction of the performance of the transient sensors and help optimize new humidity sensing materials.

11. CONCLUSION

The Bosanquet approximation successfully describes the moisture transport process and can be used to model moisture transport in porous humidity sensors for the transition diffusion regime. The model incorporates the effect of pore geometry by lumping the molecular diffusion and Knudsen diffusion together in one effective diffusion coefficient. The approximation provides insight into transport resistance as a function of pore size and dimension, and is a valuable tool for studying the characteristics of sensor responses. The Bosanquet approximation is not explicitly used, but is still a basic analytical method to be used to study diffusion processes in porous dielectric materials. The theoretical models and frameworks set up in this review can be used as a basis for new coupled diffusion–adsorption models and advanced numerical studies of the performance of the humidity sensor.

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