APPLICABILITY OF RESULTS OF THE MONTE CARLO METHOD FOR FREE-MOLECULE FLOW PROBLEMS

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Introduction

The region of free-molecule flow is characterized by the fact that collisions between gas molecules are negligible as compared to those with the wall of the vessel containing the gas. Accordingly the gas molecules move independently on each other and many problems arise in connection to the standards and measuring treatments used for the physical-technical characterization of gas systems at higher pressures. For sake of illustration, let us consider the determination of the pressure and the conductance of ducts in detail.

In the presence of getter or cryo-surfaces, molecule flows of high speed rise. In such a case the pressure considerably increases in the direction of the flow and decreases normally to it. In the case of an anisotropy where all the molecules move in the same direction, in the normal direction the pressure will be zero. There is another problem with pressure determination. Namely, the ionization gauges primordial for this pressure region, determine molecule concentration, of course, the concentration of gases entering the gauge. An open-end gauge placed in the unindirectional flow of molecules will indicate a given pressure when the gauge orifice is normal to the flow direction, but rotating it by 90° will show the half of that pressure and upon further 90° of rotation the gauge will show zero pressure. In otherwise identical circumstances, the pressure values will be different if the gauge is open at both ends. Obviously, at higher pressures the collisions among the molecules become dominant and this allows to give and determine a characteristic pressure value at every point of the gas space. In the free-molecule flow region one cannot give characteristic pressure values at all the points just because of the independent motion of the molecules, but only the local concentration can be found by a nude gauge.

Another relevant problem is that of the molecule transmission through tubes. Here the transmission probability, i.e. the ratio of the number of molecules entering to those leaving the tube, depends on the tube geometry since the molecules may back because of the collisions against the wall. The greater this transmission probability, the greater is the conductance, i.e. the reciprocal

resistance of the tube. Connecting tubes of identical cross-section (Fig. 1) it was attempted to get the resistance of the composed tube by adding the resistances on the analogy of series-connection of electrical resistances. and from this it followed for the transmission probability:

$$\frac{1}{\alpha_1} + \frac{1}{\alpha_2} = \frac{1}{\alpha} . \tag{1}$$

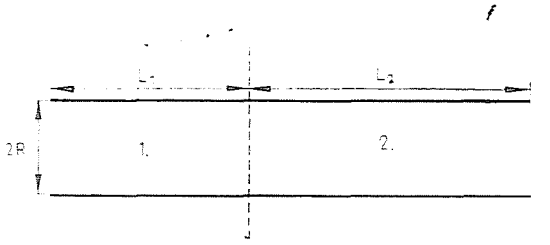

Fig. 1

This formula gives results with errors over 40 per cent which clearly shows the wrongness the analogy. Namely in the free-molecule flow region there is no interaction among the molecules to develop a flow in mass. OATLEY [1] could establish a better formula starting from the real motion of independent molecules colliding with the wall:

$$\frac{1}{\alpha_1} + \frac{1}{\alpha_2} - 1 = \frac{1}{\alpha} . \tag{2}$$

Consideration of Eq. (2) proves the fact too that the concepts valid in the region of higher pressures are not valid any more in the region of the free-molecule flow and so it is necessary to introduce new. characteristic concepts and measuring treatments for its exact physical description.

Calculation of transmission probabilities

One quantity used generally in the calculation of free-molecule flow is the transmission probability. For the sake of exact definition let us consider two large vessels with pressures p_0 and 0, respectively. The two vessels are connected by a tube (Fig. 2). In the vessel of pressure p_0 there is a number N of molecules in unity volume, in accordance with conditions of the free-molecule flow and so the molecule number ν at the entering orifice of the tube of area S in unit time is:

$$\nu = \frac{1}{4} N \bar{v} S , \tag{3}$$

where $\bar{v}$ is the mean velocity of the molecules. The molecule number entering the second vessel is $\nu' = \alpha\nu$ (provided the tube cross-sections are the same at both vessels).

There is no exact analytical solution for the determination of the transmission probability α known for the simplest geometries either. After the pioneering work by SMOLUCHOWSKI and KNUDSEN [2], CLAUSING [3] could

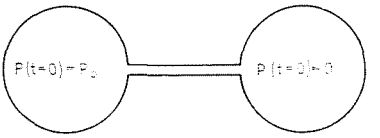

Fig. 2

establish an integral equation by fitting probabilities written for different regions and he solved it by expansion to obtain numerical values — exact within 1 per cent — for α as a function of L/R (L and R being length and radius of the tube). In the same way he could determine α values for narrow rectangular cross-sections. This treatment is applicable, however, for these simple geometries only, while for more complicated ones other possibilities must be found.

For tubes very long compared to the linear dimensions of the cross-section, already CLAUSING supposed that the flow process might be described as a diffusion with unchanging diffusion constant. (In this case the diffusion constant D characterized the conductance of the tube rather than the transmission probability α). Solving the diffusion equation

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2} \tag{4}$$

for long, straight cylinders, CLAUSING has got D value adequate to α.

GORDON and PONOMARIEV [4] have given the explanation of applicability of the diffusion equation proving the adaptability of the Fokker—Planck equation

$$\frac{\partial \omega}{\partial t} = -\bar{n}\langle x\rangle\frac{\partial \omega}{\partial x} + \frac{1}{2}\bar{n}\langle x^2\rangle\frac{\partial^2 \omega}{\partial x^2} \tag{5}$$

for the probabilities $W(x,t)$, because the independent molecular collisions correspond to such random walks which represent discrete Markow-chain, and in the case of a great number of collisions there is no difference between continuous and discrete Markow-chains. (In Eq. (5) $\bar{n}$ is the number of the random walks in unit time, $\langle x\rangle$ is the mean removing along the x axis during a collision.) Since the directional distribution after collision with the wall follows the cosine law, i.e. the number of the molecules rebounded at the ele-

mentary solid angle is proportional to the cosine of the angle between the given direction and the normal of the surface, the distribution function is symmetrical and so $\langle x \rangle = 0$. Hence, (5) may be written in the form:

$$\frac{\partial W}{\partial t} = D' \frac{\partial^2 W}{\partial x^2} . \tag{4a}$$

where

$$D' = \frac{1}{2} \bar{n} \langle x^2 \rangle . \tag{6}$$

So the calculation of D' can be substituted for $\varkappa$, possible by determining $\langle x^2 \rangle$ and $\bar{n}$ for various geometries. The authors calculated D' in the case of two long coaxial cylinders besides of that of the straight cylinder.

In spite of these results, there are only a few cases, where numerical values can be obtained, provided there is no adsorption on the walls, though the molecules stick on the wall of the tubes at a considerable probability in most cases.

The application of the stochastic simulation, the Monte Carlo method has given the solution of the problem. DAVIS [5] was the first to use this method for transmission probability calculations of tubes of different geometries without adsorption. The main point of this method is to simulate the individual molecules trajectories by random numbers, after feeding the geometry characteristics into a computer. Space and directional co-ordinates of the starting molecule are plotted by random numbers, the computer outputs the place of collision with the wall and draws new directional angles. Be N_v the number of molecules leaving the tube, the computer must find this number and divide it by N, the number of the entering molecules, and so $= N_v/N$. The exactness of the method depends on the number of the simulated trajectories, in general, for an accuracy of a few per cent it is necessary to follow 10^4 molecule trajectories.

A further advantage of the Monte Carlo method is that the adsorption on the wall may be taken into account by a slight modification of the program. To consider the sticking coefficient s only a random number of interval (0,1) has to be drawn for each collision with the wall — if this number is lesser than s then the molecule trajectory is terminated at the given place.

Transmission probabilities with different values of sticking coefficient s have been determined for several geometries by the Monte Carlo method. In addition, it was possible to calculate the radial and axial concentration distribution of the molecules entering or leaving the tube, the directional distribution in different points, the beaming effect of passing through the tube, etc.

Two kinds of problems arise in relation to the Monte Carlo method. The first problem derives from the nature of the method, namely it can give values

only in a restricted number of points and so it requires a reliable interpolation. In the case of straight tubes a convenient additive formula is Eq. (2), in other cases one is constrained to use special formulas or to graphical interpolation. A part of the former problem is the exactness of the method. An increase of the exactness by one order raises the number of the required trajectories by two orders and this fact sets a limit to the exactness since the method needs anyhow much computer time. This is a problem especially in the case of longer tubes where the time to follow the individual trajectories is much protracted. As a consequence, one may find errors greater than 10 per cent. An additive formula of great correctness could be of help, because it would be enough to determine the transmission probability values for a few short tubes at the required exactness and the necessary values could be calculated from these by the additive formula.

The other problem, connected with the Monte Carlo method, is of physical character. In the free-molecule flow region, the gas molecules and the solid surfaces, i.e. the atoms of these surfaces are only in interaction. So, for the description of physical process of the interaction, further quantities would be needed, above all the accomodation coefficient characterizing the energy exchange. Using the Monte Carlo method incorporation of this single quantity into the program would increase the needed computer-time out of all proportions, i.e. it decreases rather than to increase in merit the correctness of the obtained information. At present it is practically impossible to do more than to complete the stochastic model by an empirical sticking coefficient characterizing the adsorption properties on an average. Also this fact shows that the Monte Carlo method is first suitable to answer the questions of technical nature emerging in the free-molecule flow region and its use in scientific research may only be indirect for the moment.

Investigation of complex systems with adsorbing walls

From the available investigations it seems evident that in the case of complex systems in the free-molecule flow region it is hopeless to characterize even steady states by the usual analytical methods on the basis of practically available informations. One can expect at most to obtain experimental data giving the gas-concentration at several points, characteristics of the interaction between gas molecules and surfaces within the system, adsorption isotherms, desorption rates as a function of temperature and pressure, etc. In most cases the whole of the system in inaccessible to quantitative physical characterization because the Maxwellian velocity distribution is not valid any more, the density is inhomogeneous and the directional distribution of velocities is anisotropic. If all these irregularities could be characterized by

measurements, a mathematical treatment could be realized. Drastical simplifycations of the real situation are necessary and the Monte Carlo method applied to this simpler model may yield data essential first of all for technical applications (e.g. dimensioning of vacuum systems). This needs the knowledge of geometrical data of the system, of the gas-sources and of the sticking coefficients. The emerging problems are similar to those discussed in connection with the transmission probabilities, these are, however, more complicated making the programming difficult unduly increasing the necessary computer-time and though the final result means only a restricted number of numerical data hard to interpolate.

In 1968 PISANI [6] suggested a treatment, where the starting suppositions were identical to the assumptions used in the case of the Monte Carlo method, but the molecule trajectories were given by expressions of vectors and matrices. Fundamentally he set up two quadratic matrices and two vectors for the experimental data: the matrix A characterizing the surface, the matrix S giving the sticking coefficient, the source-vector D and the vector F combining the surface and the volume. He derived two matrix-expressions: the first gave the rate of sorption of molecules on the surface and the second one a relationship between the density — measured by ionization gauges — and the gas-load, adsorption and geometrical data of the system. The used mathematical formalism permitted a very concise formulation and if one can produce matrix A characterizing the surface, the matrix operations are easy by a computer even in the case of different distributions of gas-sources and sticking coefficients. The production of the matrices and vectors is rather difficult in the case of a complex geometry, and a further problem is to estimate the size of these quantities to determine the correctness of the method.

Discussion

The available mathematical means don't lend themselves to find an analytical description for the characterization of ultrahigh vacuum systems. So one has to rely up on data possible by stochastic simulation. The difficulties connected with the use of data on the interaction between gas atoms and solid surfaces will probably decrease along the progress of knowledge of such interactions of the involved phenomena. Incorporation of empirical parameters or tabulated test data into the program overburdens the anyhow complex Monte Carlo method, and is impossible in the case of analytical methods.

In conformity with the present knowledge, it seems most expedient to use tabulated data obtained by Monte Carlo calculations, together with interpolation formulas permitting the required correctness and easy to handle mathematically. Derivation of the interpolation formulas has to start from physical laws of the free-molecule flow region, since the numerical values of

restricted number, obtained by the Monte Carlo method are no basis for this derivation.

As an illustration for such a connection between interpolation formulas and the Monte Carlo method let us consider the problem of transmission probability for straight tubes. Here relatively correct values are available in cases of different geometries and as interpolation formula there is OATLEY's equation (2). (The concept of the interpolation formula is used in a wider sense, because by this formula one can derive the transmission probability of a longer tube connected from two tubes rather than further values between two known values — so it can be termed additive formula.) In the least favourable case Eq. (2) gives further α values from the known ones with a 6 per cent error for cylindrical tubes if the sticking coefficient is zero. OATLEY derived (2) supposing the tubes of equal cross-section and of different length to be independent of each other and for every tube the transmission probability to the connected tube was defined by forward and backward molecule flow depending on the L/R ratio. He ignored, however, that the entering directional distribution following the cosine law was valid only for the cross-section at the inflow, at the next one the beaming effect of the first tube would act.

It may be supposed that the consideration of ths beaming effect by a parameter β gives a better result for α. If one considers the resulting α not to be the function of values α_i only — as it was when (2) was derived — but that

$$\alpha = \varphi(\alpha_i, \beta_i)$$

and determines the form of function φ by considerations similar to the derivation of (2), then β_i can be calculated from tabulated α values. According to rhe new parameter a further equation is necessary given by the symmetry tondition, i.e. by the fact that the inversion of order of the tubes affects the cesults. The establishment of the new parameter is of use only in that case where values β_i corresponding to the L/R ratios differ only slightly from each other fitting them to the different α values.

Our calculations on straight tubes of different geometry show that the errors involved with (2) decrease to such a degree that by the application of this one parameter the error of α values calculated by interpolation never exceeds the error of the starting data. Table I compiles CLAUSING's α values as the values obtained by use of (2) and by use of values β considering the beaming effect — both with the percentage deviation from CLAUSING's data.

α values were calculated by equation

$$\alpha = \frac{(\beta_1+\beta_2)\,\alpha_1\alpha_2-(\alpha_1+\alpha_2)}{1+(\alpha_1+\alpha_2)\,(\beta_1+\beta_2)-\alpha_1\alpha_2\beta_1\beta_2-\dfrac{(\alpha_1+\alpha_2)^2}{\alpha_1\alpha_2}}$$

Table 1

L_1/b	L_2/b	α *Clausing*	α Eq. (2)	Error %	α with β	Error %
0.5	0.2	0.7503	0.7452	0.68	0.7503	0.00
0.5	0.5	0.6848	0.6783	0.95	0.6848	0.00
0.5	1.0	0.6024	0.5873	2.50	0.6023	0.02
0.5	1.5	0.5417	0.5256	2.97	0.5415	0.04
3.0	1.0	0.3999	0.3776	5.58	0.3997	0.05
3.0	5.0	0.2789	0.2513	9.89	0.2787	0.07
3.0	7.0	0.2457	0.2212	9.97	0.2451	0.24

for narrow, rectangular cross-sections with dimensions $a \gg b$ and $a \gg L$ which are correct within 1 percent when tubes of different L/b are connected, as well where β_i for a given L/b is obtained by use of the adequate α_i and of the α_i' belonging to $2L/b$:

$$\beta_i = \frac{3\,\alpha_i' - 2\,\alpha_i}{\alpha_i\,\alpha_i'} .$$

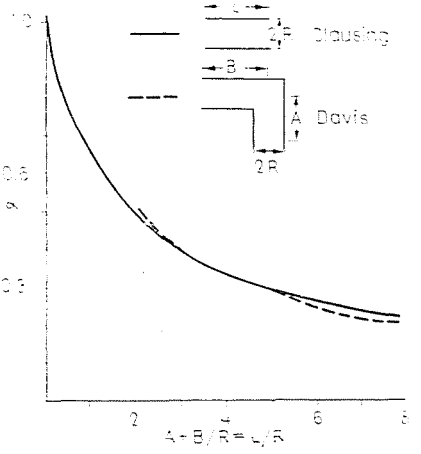

Fig. 3

Detailed derivation of these formulas is published in [7].

Interpolation formulas fitting the parameters to the calculated data yield only a few values — e.g. of L/b — and the further required values are delivered by the interpolation formulas. Consequently, the correctness of computer values can be increased for the same running time, hence a possibility to increase the accuracy of all the required values.

These considerations are valid also for else than straight tubes since the transmission probability little depends on the bend of the tubes in the free-molecule flow region. Figure 3 shows the results of DAVIS [5] obtained by Monte Carlo calculation on 90° cylindrical elbows with lengths A and B. together with CLAUSING's values for straight tubes of length $L = A + B$. Surprisingly, applying (2) for the elbow, the deviations are not higher than in the case of straight tubes.

Among the present possibilities the use of the Monte Carlo method is considered to be unavoidable in one way or another to characterizing the UHV systems working in the free-molecule flow region. The particular problems determine whether the Monte Carlo method will be used for the compact treatment suggested by Pisani or for characterizing the part-systems connected by interpolation formulas or otherwise. It may be supposed that these possibilities are not contradictory but they complete each other and have their optima in different fields.

Summary

For the transmission probabilities of tubes of various geometries the calculation by the Monte Carlo method is more effective than the analytical treatment, and ultra high vacuum systems only can characterized by Monte Carlo calculations. It seems to be proper to use reliable interpolation formulas to apply the results by Monte Carlo calculations. Even derivation and applicability problems of the interpolation formulas will be treated.

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