Nonsteady measurement methods are used to study the thermodiffusional characteristics of substances, and so it is important to know the dynamics of the concentration difference at the ends of the separation system at short times [2]. Using the results of [1], we can show that

$$\Delta c \simeq 4c_0(1-c_0)\left[\sqrt{\frac{\theta}{\pi}}-\chi\theta\right]$$

as $\tau \to 0$, from which it follows that the influence of sampling is negligibly small in the initial stage of the separation process.

NOTATION

c, concentration; t, time; z, coordinate; H, K, σ, transfer coefficients; L, column length; μ, mass of the substance per unit length; c_0, initial concentration; c_e, c_i, concentrations at the positive and negative ends of the column; b = HL/2K.

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ABSORPTION OF RADIATION IN A LAYER OF HIGHLY POROUS MATERIAL

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Radiative transfer through a porous layer, modeled by a uniform system of opaque particles fixed in space, is investigated.

Problems of the interaction of radiation with porous solids are important for many fields of modern thermophysics. Depending on the geometry and physical properties of the frame, as well as on the relation between the wavelength of the radiation and the parameters of the porous structure, it is possible to use various models of porous bodies and various approaches to describing the process of propagation and absorption of the radiation. For example, the case of the passage of radiation through a porous body modeled by a system of parallel cylindrical capillaries was considered in [1]. Highly porous bodies with a frame of globular structure are used very often in practice, however. A model of randomly arranged spheres is more adequate in such cases.

As is noted in [2], three models of radiative transfer in loose layers are usually used. The first model is based on the approximation of a heterogeneous mixture of randomly packed solid particles and pores by a certain regular geometrical arrangement of the solid phase and the voids. In the second model, proposed by Rosseland, it is assumed that when the mean free path of a photon in a loose layer is much less than the geometrical size of the absorbing medium, the path of an individual quantum of radiant energy can be taken as random, and the process is diffusional. In the third type of model, the loose layer is treated as a pseudohomogeneous medium, in which radiative heat exchange is described through differential or integrodifferential equations and the corresponding boundary conditions.

The transmission of radiation in layers with both open and dense packing of particles is analyzed in [3, 4]. Here to determine the transmission coefficient in the case of open packing a two-flux approximation is used, while a layer with dense particle packing is

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TABLE 1. Fraction of Radiation Absorbed in the Layer, Determined by the Monte Carlo Method (κ_d, κ_i) and from the Analytic Solution (κ), as a Function of the Thickness of the Layer for $j_0 \gg 1$ and $\Pi = 0.9$.

L/r	$\varepsilon=0,2$				$\varepsilon=0,8$			
	$\varkappa_d$	$\varkappa_i$	$\varkappa$	$\varkappa_\Sigma$	$\varkappa_d$	$\varkappa_i$	$\varkappa$	$\varkappa_\Sigma$
10	0,34	0,34	0,35	0,47	0,62	0,63	0,67	0,91
20	0,46	0,49	0,48	0,55	0,77	0,78	0,80	0,92
30	0,50	0,54	0,52	0,57	0,82	0,83	0,83	0,92
50	0,55	0,57	0,55	0,57	0,84	0,85	0,84	0,92
100	0,54	0,59	0,55	0,57	0,84	0,86	0,84	0,92

TABLE 2. Fraction of Radiation Absorbed in the Layer as a Function of Its Thickness for $j_0 = 1$, $\Pi = 0.9$, and $\beta = -0.5$.

L/r		10	20	30	50	100
$\varepsilon=0,2$	$\varkappa$	0,178	0,216	0,208	0,171	0,110
	$\varkappa_\Sigma$	0,299	0,299	0,270	0,213	0,138
$\varepsilon=0,8$	$\varkappa$	0,215	0,218	0,193	0,146	0,086
	$\varkappa_\Sigma$	0,542	0,418	0,342	0,260	0,181

likened to a stack of plane-parallel plates. The transmissivity and reflectivity of a layer of transparent spherical particles are determined in [5] on the basis of a numerical solution of the integrodifferential equation of radiative transfer, under the assumption that the radiation intensity field depends essentially on both the polar and the azimuthal angular coordinates. The influence of the profile of particle concentration on the flux distribution of the transmitted and reflected radiation over the thickness of the layer is estimated, in particular. The authors of [6], devoted to an investigation of combined heat transfer by heat conduction and radiation in a highly porous solid, in comparing theoretical and experimental results on radiative transfer, concluded that the asymmetry factor has an insignificant role in the scattering indicatrix. In a calculation of radiative heat exchange in a layer of randomly packed spheres in [2], a two-flux model is used in which the effective coefficients of absorption and backscattering are determined using the Monte Carlo method.

The purpose of the present work is to analyze the passage of radiation through a layer of a highly porous solid, modeled by a uniform system of randomly distributed, opaque spherical particles of equal radius, determine the fraction of radiation absorbed, and find an expression for the internal heat source in the porous solid. The assumption of isotropy of the scattering used in the model is verified through calculations by the Monte Carlo method.

If the radiation wavelength is much less than the diameter of the spheres and the distance between them, then wave effects are negligibly small and the process can be treated as the passage of a "photon gas" through a layer of opaque particles. Let the radiation of a diffuse source with a flux density j_0 fall on a plane layer of thickness L and porosity Π, i.e., a flux Πj_0 penetrates into the layer. For the solution of the problem, we use a method of description analogous to that used in an investigation of free-molecule gas flow in a porous solid in the presence of a heterogeneous chemical reaction [7], which enables us to allow for the geometry of the system, the properties of the particle surface, and the multiplicity of the scattering.

With allowance for the thermal self-emission of the surfaces of the spheres, we write the following integral equation for the radiant energy emerging from a unit volume of the porous solid per unit time:

$$\Phi(X) = \varepsilon S\sigma T^4(X) + (1-\varepsilon) N(X), \tag{1}$$

where S is the surface area of the spheres per unit volume $\left(S=\frac{1-\Pi}{\frac{4}{3}\pi r^3}4\pi r^2=\frac{3(1-\Pi)}{r}\right)$;

N(X) is the radiation incident per unit volume of the solid, consisting of the sum of the fluxes coming from the external source, the lower boundary of the layer, and the rest of the volume. In the approximation of isotropic scattering, N(X) has the form

$$N(X)=2\Pi j_0E_2\left(\frac{X}{\lambda}\right)\frac{1}{\lambda}+2j_1E_2\left(\frac{L-X}{\lambda}\right)\frac{1}{\lambda}+\\+\frac{1}{2}\int_0^L\Phi(\xi)E_1\left(\frac{|X-\xi|}{\lambda}\right)\frac{1}{\lambda}\,d\xi. \tag{2}$$

Here E_n is an exponential integral function defined by the expressions [8]

$$E_n(y)=\int_0^1\mu^{n-2}\exp\{-y/\mu\}\,d\mu,$$

$$E_{n+1}(y)=-\int E_n(y)\,dy. \tag{3}$$

The flux density of the radiation from the lower boundary of the layer is found from the relation

$$j_1=\Pi\varepsilon\sigma T_1^4+(1-\varepsilon)N_1, \tag{4}$$

where N_1 is the density of the flux incident on this surface, equal to

$$N_1=2\Pi j_0E_3\left(\frac{L}{\lambda}\right)+\frac{1}{2}\int_0^L\Phi(\xi)E_2\left(\frac{L-\xi}{\lambda}\right)d\xi. \tag{5}$$

The presence of the factor Π in the first term of (4) is due to the fact that it describes the radiation of the part of the surface of the bottom free of spheres, while the radiation of the particles is already taken into account by the function $\Phi(X)$ at $X = L$.

We assume that the photon mean free path, in accordance with [9], is defined by the expression

$$\lambda=\frac{4\Pi}{3(1-\Pi)}r. \tag{6}$$

We use an approximation often applied for the solution of problems of radiative transfer [8], which is based on replacing the integral $E_n(y)$ by the exponential b exp {-cy}. For this we first approximate the function E_1 inside the integral in (2),

$$E_1(y)=2\exp\{-2y\}, \tag{7}$$

while we use (7) and the recurrent relation (3) to determine the functions E_2 and E_3.

The further procedure for solving Eq. (1) is analogous to that used in [1] to investigate the absorption of radiant energy in an individual cylindrical channel. We substitute (2), (4), and (5) into (1), converting to the dimensionless quantities $x=\frac{X}{\lambda}$, $\overline{T}=\frac{T}{T_*}$, $\overline{\Phi}=\frac{\Phi L}{\Pi\sigma T_*^4}$, and $\overline{j}=\frac{j}{\sigma T_*^4}$ for this and approximating the functions E_n by the aboveindicated means. At the same time, we assume that the temperature in the layer can be represented in the form

$$\overline{T} = \overline{T}_0 \exp\{\beta x\}. \tag{8}$$

As a result, we obtain the integral equation

$$\overline{\Phi}(x) = (1-\varepsilon)\int_0^l \overline{\Phi}(\xi)\exp\{-2|x-\xi|\}\,d\xi + 2(1-\varepsilon)\,l\overline{j}_0\exp\{-2x\} + 4\varepsilon l\overline{T}_0^4\exp\{4\beta x\} + 2(1-\varepsilon)\exp\{-2(l-x)\}\times$$
$$\times\left[\frac{1}{2}(1-\varepsilon)\int_0^l \overline{\Phi}(\xi)\exp\{-2(l-\xi)\}\,d\xi + (1-\varepsilon)\,l\overline{j}_0\exp\{-2l\} + \varepsilon l\overline{T}_0^4\exp\{4\beta l\}\right], \tag{9}$$

where $l = L/\lambda$.

It is seen that the solution of Eq. (9) is determined by three dimensionless parameters, ε, β, and l, i.e., the porosity Π and the radius r do not enter into the solution directly, but affect the value of l owing to the dependence of λ on Π and r.

Differentiating (9) twice and combining the result with the original equation, we arrive at the differential equation

$$\frac{d^2\overline{\Phi}}{dx^2} - 4\varepsilon\overline{\Phi} = 16\varepsilon l\overline{T}_0^4(4\beta^2-1)\exp\{4\beta x\},$$

the solution of which has the form

$$\overline{\Phi}(x) = a_1\exp\{2\sqrt{\varepsilon}x\} + a_2\exp\{-2\sqrt{\varepsilon}x\} + \frac{4\varepsilon l\overline{T}_0^4(4\beta^2-1)}{4\beta^2-\varepsilon}\exp\{4\beta x\}. \tag{10}$$

Thus, the approximation of the functions E_n by exponentials and the use of a temperature distribution in the form (8) enabled us to obtain an approximate analytic solution of Eq. (1).

Substituting (10) into (9) and equating the coefficients of exp {-2x} and exp {2x}, we obtain a system of linear algebraic equations for determining a_1 and a_2 (in the case of $\varepsilon \neq 1$):

$$\frac{a_1}{1+\sqrt{\varepsilon}} + \frac{a_2}{1-\sqrt{\varepsilon}} = -\frac{4\varepsilon l\overline{T}_0^4(2\beta-1)}{4\beta^2-\varepsilon} + 4l\overline{j}_0,$$

$$[(1-\sqrt{\varepsilon})(\exp\{-2l\} - \exp\{2\sqrt{\varepsilon}l\}) + \frac{1}{1-\sqrt{\varepsilon}}\exp\{2\sqrt{\varepsilon}l\}]\,a_1 +$$
$$+\left[(1+\sqrt{\varepsilon})(\exp\{-2l\} - \exp\{-2\sqrt{\varepsilon}l\}) + \frac{1}{1+\sqrt{\varepsilon}}\exp\{-2\sqrt{\varepsilon}l\}\right]a_2 =$$
$$= 4\varepsilon l\overline{T}_0^4\exp\{4\beta l\} + 4(1-\varepsilon)\,l\exp\{-2l\}\,\overline{j}_0 + \frac{4\varepsilon l\overline{T}_0^4}{4\beta^2-\varepsilon}\times$$
$$\times[(1-\varepsilon)(2\beta-1)(\exp\{4\beta l\} - \exp\{-2l\}) + (2\beta+1)\exp\{4\beta l\}].$$

The resultant quantities characterizing the absorption of radiant energy in the layer are of interest. The power density of the absorbed radiation can be represented in the form

$$\overline{\varphi}(x) = \varepsilon[\overline{N}(x) - 4l\overline{T}_0^4\exp\{4\beta x\}], \tag{11}$$

or since in accordance with (1)

$$\overline{\Phi}(x) = (1-\varepsilon)\overline{N}(x) + 4\varepsilon l\overline{T}_0^4 \exp\{4\beta x\}, \tag{12}$$

for $\varepsilon \neq 1$ we have from (11) and (12)

$$\overline{\varphi}(x) = \frac{\varepsilon}{1-\varepsilon}\overline{\Phi}(x) - \frac{4\varepsilon}{1-\varepsilon} l\overline{T}_0^4 \exp\{4\beta x\} = \frac{\varepsilon}{1-\varepsilon}(a_1 \exp\{2\sqrt{\varepsilon}\, x\} + a_2 \exp\{-2\sqrt{\varepsilon}\, x\}) + \frac{16\varepsilon\beta^2 l\overline{T}_0^4}{\varepsilon - 4\beta^2}\exp\{4\beta x\}. \tag{13}$$

For $\varepsilon = 1$ we obtain the relations for $\overline{\Phi}$ and $\overline{\varphi}$ from (9) and (11), respectively:

$$\begin{gathered}\overline{\Phi}(x) = 4l\overline{T}_0^4 \exp\{4\beta x\},\\ \overline{\varphi}(x) = 2l\left(\overline{j}_0 - \frac{\overline{T}_0^4}{2\beta+1}\right)\exp\{-2x\} + \frac{4\beta l\overline{T}_0^4}{2\beta-1}\exp\{2[x + l(2\beta-1)]\} - \\ - \frac{16\beta^2 l\overline{T}_0^4}{4\beta^2 - 1}\exp\{4\beta x\}.\end{gathered} \tag{14}$$

Equations (13) and (14), written for the dimensional $\varphi(x)$, can be used to determine the internal heat source in a porous solid.

The radiation absorbed in the layer lying between the surface $x = 0$ and a certain section x is found as follows:

$$\overline{I}(x) = \frac{1}{l}\int_0^x \overline{\varphi}(\xi)\, d\xi.$$

The flux density of the radiation absorbed by the lower boundary is determined from the expression

$$\overline{\varphi}_1 = \varepsilon(\overline{N}_1 - \overline{T}_0^4 \exp\{4\beta l\}).$$

It must be kept in mind that the radiation of an external isotropic source not only penetrates into the layer but is also absorbed at its outer surface. Thus, the total fraction of the radiation absorbed is

$$\varkappa_\Sigma = \varkappa + \frac{\Pi\overline{\varphi}_1}{\overline{j}_0} + (1-\Pi)\varepsilon = \frac{I(L) + \varphi_1}{j_0} + (1-\Pi)\varepsilon,$$

where

$$\varkappa = \Pi\overline{I}(l)/\overline{j}_0 = I(L)/j_0.$$

While the replacement of the kernel of the integral equation by an exponential has been approved on a number of other problems of radiative transfer [10], it is desirable to test the assumption that the scattering is isotropic by direct numerical modeling. For this purpose, we solve the problem under consideration by the Monte Carlo method. For this the flux of incident radiation is divided into a certain number of bundles of energy, the path of each of which is traced with allowance for the collision cross section and the laws of scattering and absorption on the model spheres.

For the diffuse flux the polar (θ) and azimuthal (ψ) angles are chosen from the relations [11]

$$\theta = \arcsin\sqrt{R_\theta},\quad \psi = 2\pi R_\psi. \tag{15}$$

Then the run of a bundle is played out until a collision with a model sphere,

$$\lambda_s = -\lambda \ln(1 - R_\lambda).$$

Here R_θ, R_φ, and R_λ are random numbers distributed uniformly over the segment from zero to one, while λ is determined from (6).

Then absorption or reflection is played out on the basis of the given emissivity ε of the surface of a sphere. In the case of absorption, the history of the given test bundle ends and the analysis of the next one begins. For diffuse reflection, the position of the normal to the surface of the sphere at the point of collision is played out from the condition of a uniform distribution of the centers of the model particles over the surface of the front hemisphere of radius r, and then the new direction of the bundle is played out from the relations (15). The case of isotropic scattering, when $\theta = \arccos(1 - 2R_\theta)$ and $\varphi = 2\pi R_\psi$, is also considered for comparison. Then the process of passage of the bundle through the porous layer is played out again until it is absorbed or leaves the layer.

The program enables one to record the bundles absorbed and reflected by the layer. The number of test bundles is 10,000, providing an accuracy on the order of 0.01.

Let us turn to a discussion of the conclusions from the solution of the problem. First of all, we note that they depend essentially on the value of $\bar{j}_0$. For $\bar{j}_0 \gg 1$, nonisothermicity hardly affects the distribution $\varphi(x)$, i.e., in this case one can, as in [1], obtain an analytic expression, independent of the temperature distribution, for the internal heat source and use it to solve the problem of heat exchange in a model porous solid. Here the character of the function $\varphi(x)$ is determined by the relative thickness l of the layer and the emissivity ε. For thin layers ($l \approx 1$) the characteristic region of variation of $\bar{\varphi}(x)$ extends to the entire layer, while for thick ones ($l \geqslant 10$), $\bar{\varphi}(x)$ declines rather rapidly with an increase in x; this decline lessens with a decrease in ε.

In Table 1 we present values of the fraction κ of the radiation absorbed in the layer as a function of the ratio L/r for $\beta = 0$ and $\Pi = 0.9$ (for such a porosity, $\lambda = 12r$, i.e., $l = 0.0833L/r$). With an increase in the thickness of the layer, κ first increases and then, starting with a certain value of L/r, it becomes constant. It is seen that for all L/r quantities κ, κ_d, and κ_i agree sufficiently well. Such are the results of a comparison of the values of the power density $\bar{\varphi}(x)$ of the absorbed radiation and the flux density $\bar{\varphi}_1$ of the radiation absorbed at the lower boundary of the layer, found from the analytic solution and by the method of direct numerical modeling.

Thus, the assumption that the scattering of radiation on the model spheres is isotropic is fully justified when finding the distribution of the absorbed energy. A difference in the results for the isothermal and nonisothermal cases is characteristic for low and zero values of the flux density of the external radiation. For $\bar{j}_0 = 1$, for example, thermal equilibrium in the layer is observed in the isothermal case ($\kappa = 0$), while the fraction of absorbed radiation depends on the emissivity and the thickness of the layer in the nonisothermal case (see Table II, where values of κ and κ_Σ obtained from the approximate analytic solution of the problem are presented).

NOTATION

σ, Stefan–Boltzmann constant; r, radius of a particle; λ, photon mean free path; ε, emissivity of the particle surface and the lower boundary; T_*, characteristic temperature; T_0 and T_1, temperatures of the upper and lower boundaries of the layer; κ, fraction of the radiation absorbed in the layer. Indices: d and i, diffuse and isotropic scattering of radiation by the particles.

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PHASE TRANSITIONS IN ELEMENTS AND COMPOUNDS. PART 3

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There is shown to be good agreement for certain systems between the optical and thermodynamic parameters characterizing collective phenomena: laser emission and phase transition.

Thermodynamics arose from practical heat engineering (macroscopic thermophysics) and has since been extended to all known physical, chemical, and biological phenomena and has thus had a substantial effect on many disciplines. The role of thermodynamics in science is evident from the general use of concepts such as temperature, energy, and entropy. As thermodynamics is a phenomenological discipline, it influences thermophysics at the macroscopic level. Although advances in thermodynamics were stimulated originally by heat engineering, the subject has had a large effect not so much on the latter but on disciplines concerned with phenomena at the microscopic level. Statistical mechanics enables one to relate phenomena observed at the microscopic level to general measured macroscopic parameters.

A major task in thermophysics, the theory of elasticity, hydrodynamics, and so on is to establish relationships between the macroscopic parameters (observed ones) and the microscopic ones. Difficulties arise here both because of the complexity of the phenomena (these being determined by several forms of interaction) and also in difficulties in obtaining information on the elementary steps giving rise to the observed macroscopic parameters. Phenomena determined by single forms of interaction have usually been thoroughly researched, and such simple phenomena include laser emission. In research on complicated processes such as for example phase transitions, it is desirable to establish the roles of simpler phenomena.

In that respect, considerable interest attaches to processes responsible for phase transitions, which may be compared with the collective phenomena determining lasing. It has been shown [1, 2] that quantities such as the latent heats of phase transitions and the positions of peaks in absorption spectra are related to phase-transition temperatures under normal conditions via Wien's displacement law.

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