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ON THE INVESTIGATION OF HEAT TRANSFER IN THE PRESENCE OF CHEMICAL CONVERSIONS

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Abstract—The simplest boundary problem of unstationary heat-conduction equation, with the source depending on temperature as exp $(-E^*/T)$ is investigated in this paper.

The uniform convergence of successive approximations is proved for the corresponding integral equation; the solutions have been calculated in the first approximation at various limit cases. It has been also shown here that in the absence of "explosion" the temperature at each point will not exceed at any moment of time the corresponding stationary temperature.

Résumé—Ce travail traite du problème aux limites le plus simple de l'équation de la chaleur en régime non permanent en présence d'une source dépendant de la température comme exp $(-E^*/T)$.

La convergence uniforme des approximations successives est démonstrée pour l'equation intégrale correspondante; les solutions ont été caluculées pour la première approximation dans divers cas limites. On a montré aussi qu'en l'absence d'"explosion" la température en chaque point ne dépasse à aucun moment la température correspondant au régime stationnaire.

Zusammenfassung—Die Arbeit behandelt ein Problem der nichtstationären Wärmeleitung mit einfacher Randbedingung, bei welchem die Wärmequelle von der Temperatur nach der Funktion exp $(-E^*/T)$ abhängt.

Die gleichmässige Konvergenz für die aufeinanderfolgenden Approximationen wird für die entsprechende Integralgleichung nachgeprüft. Lösungen werden als erste Näherungen für verschiedene Grenzfälle angegeben. Es zeigt sich auch, dass, abgesehen von "Explosionen", die Temperatur an jedem Punkt zu keinem Zeitpunkt die entsprechende stationäre Temperatur überschreitet.

Аннотация—В работе исследуется простейшая краевая задача нестационарного уравнения теплопроводности с источником зависящим от температуры как exp $(-E^*/T)$.

Доказывается равномерная сходимость последовательных приближений для соответствующего интегрального уравнения; вычислены в первом приближении решения в различных предельных случаях. Показано также, что при отсутствии «взрыва» температура в каждой точке не будет превышать в любой момент времени соответствующую стационарную температуру.

IN A number of thermal conductivity problems, e.g. in the case of heat-transfer problem in the capillary–porous media in the presence of chemical conversions† [1], or in the case of heat explosion problem [2, 3], we may meet the heat conduction equation with the heat source depending on the temperature as

$$\exp\left(-\frac{E^*}{T}\right)$$

where $E^* = E/R$ is the activation energy expressed in degrees and T is the absolute temperature.

† As was recommended by Academician Luikov.

Let us consider the boundary problem for the equation

$$\frac{\partial T}{\partial t} = a\nabla^2 T + \frac{K_0}{c_p \rho} \exp\left(-\frac{E^*}{T}\right) \qquad (1)$$

in the range limited by two parallel infinite planes $x = \pm l$

$$T(l, t) = T_c; \frac{\partial T(0, t)}{\partial x} = 0; T(x, 0) = T_0 \qquad (2)$$

Now we introduce dimensionless variables and can take advantage of the similarity criteria known in the heat-transfer theory [1]:

$$\xi = \frac{x}{l};\ Fo \equiv \tau = \frac{at}{l^2};\ Po \equiv \epsilon = \frac{K_0 l^2}{ac_p\rho E^*}$$

$$\theta(\xi, \tau) = \frac{T(x, t)}{E^*};\ \theta_c = \frac{T_c}{E^*};\ \theta_0 = \frac{T_0}{E^*} \quad (3)$$

where Fo is the ordinary Fourier criterion of homocronism and Po is the modified Pomerantsev criterion.

If we designate the Green function of the heat conduction equation for the range $0 \leqslant \xi \leqslant 1, \tau \geqslant 0$ through $Y(\xi, \xi'; \tau - \tau')$ then for $\theta(\xi, \tau)$ the integral equation takes place:

$$\theta(\xi, \tau) = \psi(\xi, \tau) + \epsilon \int_0^\tau \int_0^1 Y(\xi, \xi'; \tau - \tau') \times \exp\left[-\frac{1}{\theta(\xi', \tau')}\right] d\tau' d\xi' \quad (4)$$

where

$$\psi(\xi, \tau) = \theta_c - \frac{2}{\pi}(\theta_c - \theta_0) \sum_{n=0}^{\infty} \frac{(-1)^n}{n + \frac{1}{2}} \times \exp\left[-\pi^2(n + \tfrac{1}{2})^2\tau\right] \cos(n + \tfrac{1}{2})\pi\xi \quad (5)$$

and the Green function

$$Y(\xi, \xi'; \tau - \tau') = \tfrac{1}{2}\left\{\vartheta_2\left[\frac{\xi + \xi'}{2}, i\pi(\tau - \tau')\right] + \vartheta_2\left[\frac{\xi - \xi'}{2}, i\pi(\tau - \tau')\right]\right\} \quad (6)$$

The ϑ-function on the right side of the equation (6) is determined by the equality [4]:

$$\vartheta_2(u, iv) = 2 \sum_{n=0}^{\infty} \exp\left[-\pi(n + \tfrac{1}{2})^2 v)\right] \cos(2n + 1)\pi u$$

Note that the Green function is symmetric with reference to the variables ξ and ξ' and has nowhere negative values in the range under consideration.

It is possible to solve equation (4) by the method of successive approximation of the form

$$\theta^{(n+1)}(\xi, \tau) = \psi(\xi, \tau) + \epsilon \int_0^\tau \int_0^1 Y(\xi, \xi'; \tau - \tau') \times \exp\left(-\frac{1}{\theta^{(n)}(\xi', \tau')}\right) d\tau' d\xi'$$

$$\theta^{(0)}(\xi, \tau) = \psi(\xi, \tau); \quad (n = 0, 1, \ldots) \quad (7)$$

If the parameter ϵ is small enough then it is possible to show that the succession of functions converges uniformly to the solution of the equation (4).

For the proof it is necessary to compose the difference

$$\theta^{(n+1)}(\xi, \tau) - \theta^{(n)}(\xi, \tau) = \epsilon \int_0^\tau \int_0^1 Y(\xi, \xi'; \tau - \tau') \left\{\frac{\exp[-1/\theta^{(n)}(\xi', \tau')] - \exp[-1/\theta^{(n-1)}(\xi', \tau')]}{\theta^{(n)}(\xi', \tau') - \theta^{(n-1)}(\xi', \tau')}\right\} \times [\theta^{(n)}(\xi', \tau') - \theta^{(n-1)}(\xi', \tau')] d\tau' d\xi' \quad (8)$$

It should be noted that,

$$\theta^{(n+1)} - \theta^{(n)} \geqslant 0, \text{ since } \theta^{(0)}(\xi, \tau) = \psi(\xi, \tau) \geqslant 0$$

and

$$Y(\xi, \xi'; \tau - \tau') \geqslant 0$$

If we designate the maximum of the difference $\theta^{(n+1)} - \theta^{(n)}$ through $M_{n+1} \geqslant 0$ then from the equation (8) it follows that

$$M_{n+1} \leqslant AM_n$$

where

$$A = \max\left\{\epsilon \int_0^\tau \int_0^1 Y \left[\frac{\exp(-1/\theta^{(n)}) - \exp(-1/\theta^{(n-1)})}{\theta^{(n)} - \theta^{(n-1)}}\right] d\tau' d\xi'\right\}$$

It is easy to make sure that $A < 1$, if $\epsilon < e^2/2$. In this case there exists a limit function of sequence (7) which is the solution of the equation (4).

Let us assume the above-mentioned method to get the approximate solutions in some ordinary limit cases. To begin with we shall take the solutions at large values of τ. As a zero approximation it is convenient to admit the stationary temperature distribution which is described by the equation

$$\frac{d^2\theta_{st}(\xi)}{d\xi^2} = -\epsilon \exp\left(-\frac{1}{\theta_{st}(\xi)}\right) \quad (9)$$

with boundary condition as

$$\theta_{st}(1) = \theta_c;\ \frac{d\theta_{st}(0)}{d\xi} = 0 \quad (10)$$

The solution of this equation is of the type:

$$\int_{\theta_c}^{\theta_{st}(\xi)} \frac{du}{\sqrt{[\theta_m \exp(-1/\theta_m) - u \exp(-1/u) + Ei(-1/\theta_m) - Ei(-1/u)]}} = \sqrt{(2\epsilon)}(1-\xi) \tag{11}$$

where the parameter θ_m is the maximum value of $\theta_{st}(\xi)$, which can be achieved because of symmetry at $\xi = 0$, and

$$Ei(x) = -\int_{-x}^{\infty} \frac{e^{-t}}{t} dt$$

is the integral exponential function.

The solution (11) agrees with the boundary conditions not at any values of ϵ [2, 3] if ϵ is greater than some ϵ_{cr}, then the establishment of a stationary state is impossible. It means physically that heat supply exceeds heat output and the heat explosion will take place. The critical temperature θ_m^{cr} corresponding to the parameter ϵ_{cr} is being determined from the equation:

$$\left.\begin{aligned} &\frac{\theta_c}{\sqrt{[\theta_m \exp(-1/\theta_m) - \theta_c \exp(-1/\theta_c) + Ei(-1/\theta_m) - Ei(-1/\theta_c)]}} + \\ &+ \int_{\theta_c}^{\theta_m} du \frac{\theta_m \exp(-1/\theta_m) - u \exp(-1/u) + 2Ei(-1/\theta_m) - 2Ei(-1/u)}{[\theta_m \exp(-1/\theta_m) - u \exp(-1/u) + Ei(-1/\theta_m) - Ei(-1/u)]^{3/2}} \\ &= 0 \end{aligned}\right\} \tag{12}$$

[2] gives a physically interesting case of the latter solution when θ_m differs slightly from θ_c.

So, at $\epsilon < \epsilon_{cr}$ and $\tau \gg 4/\pi^2$ the approximation to the stationary state is being described by the relation

$$\theta(\xi, \tau) = \theta_{st}(\xi) + \frac{4}{\pi} \exp\left(-\frac{\pi^2}{4}\tau\right) \cos\frac{\pi}{2}\xi \left[\theta_0 - \frac{\pi}{2}\int_0^1 \theta_{st}(\xi')\cos\frac{\pi}{2}\xi' d\xi'\right] \tag{13}$$

where $\theta_{st}(\xi)$ is given by the formula (11).

Normally such a case as $\theta \ll 1 (T \ll E^*)$ takes place in chemical kinetics. This allows one to simplify the initial integral equation by the method of "steepest descent"; for large $\tau (> 4/\pi^2)$ we have:

$$\theta(\xi, \tau) = \theta_{st}(\xi) - \frac{4}{\pi} \exp\left(-\frac{\pi^2}{4}\tau\right) \cos\frac{\pi}{2}\xi \left[\theta_c - \theta_0 + 2\sqrt{\left(\frac{2\epsilon}{\pi}\right)}\vartheta_m \exp\left(-\frac{1}{2\theta_m}\right)\right] \tag{14}$$

θ_m has been determined above.

Now we shall consider another extreme case, when τ is small. Here we can take the initial temperature θ_0 as a zero approximation. It is possible to simplify the kernel of the integral equation using the known relation for ϑ-functions [4]:

$$\vartheta_2(u, iv) = \frac{1}{\sqrt{v}} \exp\left(-\frac{\pi u^2}{v}\right) \vartheta_0\left(\frac{u}{iv}, \frac{i}{v}\right)$$

and retaining only the principal terms in the kernel at $\tau \to 0$. All the integrations are being easily carried out and we have:

$$\left.\begin{aligned} \theta(\xi, \tau) = \theta_c &+ \epsilon \exp(-1/\theta_0)\Big\{1 - \xi^2 + \\ &+ \sqrt{\left(\frac{\tau}{\pi}\right)}\Big[(1-\xi)\exp\left(-\frac{(1-\xi)^2}{4\tau}\right) + \\ &+ (1+\xi)\exp\left(-\frac{(1+\xi)^2}{4\tau}\right) - 2\exp\left(-\frac{1}{\tau}\right)\Big]\Big\} + \Big\{\theta_0 - \theta_c + \epsilon\exp\left(-\frac{1}{\theta_0}\right) \\ &\left[\frac{(1-\xi)^2}{2} + \tau\right]\Big\} \operatorname{erf}\left(\frac{1-\xi}{2\sqrt{\tau}}\right) + \\ &+ \Big\{\theta_0 - \theta_c + \epsilon\exp\left(-\frac{1}{\theta_0}\right) \\ &\left[\frac{(1+\xi)^2}{2} + \tau\right]\Big\} \operatorname{erf}\left(\frac{1+\xi}{2\sqrt{\tau}}\right) - \\ &- \Big\{\theta_0 - \theta_c + \epsilon\exp\left(-\frac{1}{\theta_0}\right) \\ &\left[2 + \tau\right]\Big\} \operatorname{erf}\left(\frac{1}{\sqrt{\tau}}\right)\Big\} \end{aligned}\right\} \tag{15}$$

Finally, let us consider such a case, when the parameter ϵ is small. One may get the solution in the form of ϵ power series, taking $\psi(\xi, \tau)$ as a zero approximation (see (5)). At $\epsilon \to 0$ the difference $\theta_m - \theta_c \to 0$. If the time is large enough then it is possible to neglect the second term of (5) in comparison with the first one. The same can be done at any point of time, if

$|\theta_c - \theta_0| \ll \theta_c$. In the first approximation we can easily get:

$$\theta(\xi, \tau) = \psi(\xi, \tau) + \epsilon \exp\left(-\frac{1}{\theta_0}\right)\left\{\frac{1-\xi^2}{2} - \right.$$

$$\left. - \frac{2}{\pi^3}\sum_{n=0}^{\infty}\frac{(-1)^n}{(n+1/2)^3}\exp\left[-\pi^2(n+1/2)^2\tau\right] \cos(n+1/2)\pi\xi\right\} \tag{16}$$

We tried on all occasions to write down only the first approximations because of the bulky results. It is difficult to get the higher approximations as it involves difficulty in calculation.

And now we would like to show, that the temperature at any given point for the process as a result of which the stationary distribution will be established ($\epsilon < \epsilon_{cr}$), will not exceed the stationary temperature in the same point. For this the difference will be

$$\Delta(\xi, \tau) = \theta(\xi, \tau) - \theta_{st}(\xi)$$

The latter satisfies the integral equation

$$\Delta(\xi, \tau) = \phi(\xi, \tau) + $$

$$+ \epsilon \int_0^\tau \int_0^1 Y(\xi, \xi'; \tau - \tau') \times$$

$$\left\{\exp\left[\frac{-1}{\theta_{st}(\xi') + \Delta(\xi', \tau')}\right] - \right.$$

$$\left. - \exp\left[\frac{-1}{\theta_{st}(\xi')}\right]\right\} d\tau' \, d\xi' \tag{17}$$

where

$$\phi(\xi, \tau) = 2\sum_{n=0}^{\infty}\left\{\int_0^1 [\theta_0 - \theta_{st}(\xi')] \times \right.$$

$$\left. \cos(n+1/2)\pi\xi' \, d\xi'\right\} \exp\left[-\pi^2(n+1/2)^2\tau\right]$$

$$\times \cos(n+1/2)\pi\xi$$

Applying the method of successive approximations to equation (17) we assume that

$$\Delta^{(0)}(\xi, \tau) = \phi(\xi, \tau)$$

If we take into account that $\phi(\xi, \tau) \leqslant 0$ (at $\theta_c > \theta_0$) and give the reasons analogous to those mentioned above in the proof of the existence of the solution, then it will be possible to find that $\Delta^{(n)}$ is not zero at any finite τ and the difference $\Delta^{(n)} - \Delta^{(n-1)} \to 0$ at $n \to \infty$.

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REFERENCES

1. A. V. Luikov and Y. A. Mikhailov, *Teoria Perenosa Energii i Veschestva*. Izdanie Akademii Nauk B.S.S.R., Minsk (1960).
2. D. A. Frank-Kameneckii, *Difuzia i Teploperedacha v Khimicheskoi Kinetike*. Izdanie Akademii Nauk S.S.S.R. (1947).
3. V. N. Condratjev, *Kinetika Khimicheskih Gazovyh Reaktsii*. Izdanie Akademii Nauk S.S.S.R. (1958)
4. F. Mors and G. Feshbah. *Metody teor. fiz.* 1958, **1**, IL.