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# Nonlinear heat conduction in solid $H_2$

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On the basis of recent empirical data, the temperature distribution in solid crystalline hydrogen is shown to be governed by the essentially nonlinear diffusion equation $\partial\theta/\partial t = D\theta^2\nabla^2\theta$ in which there appears the dimensionless variable $\theta \equiv [1 + (T/T_c)^4]^{-1}$ with the constants $D$ and $T_c$ dependent on the ortho-$H_2$ percentile. It is observed that this governing equation can be transformed to an equivalent linear diffusion equation for situations with one-dimensional spatial symmetry. By utilizing this remarkable linear-theoretic correspondence, exact solutions to initial-value boundary-value problems of current experimental interest are derived and reported here.

In solid crystalline molecular hydrogen, the temperature distribution $T = T(\vec{x}, t)$ is governed by the Fourier equation[1,2]

$$\rho c_p \partial T/\partial t = \nabla \cdot (k\nabla T)\,, \tag{1}$$

where the density $\rho \cong 0.088\,\text{g/cm}^3$ at low pressures ($\ll$1Mbar), the specific heat[3,4] $c_p \cong (0.531\,\text{mJ/g K}^4)T^3$ at constant pressure, and the thermal conductivity[5,6] is given to within the experimental accuracy of about 5% by the empirical expression

$$k \cong (19.4\,\text{mW/cm K})\chi^{-1}(T/T_c)^3[1+(T/T_c)^4]^{-2}\,, \tag{2}$$

in which $\chi$ denotes the ortho-$H_2$ fraction ($1-\chi$ the para-$H_2$ fraction) and $T_c \equiv 6.26 + 6.53\chi$. Valid as a good approximation for $T \lesssim 14$ K and $0.05 \lesssim \chi \lesssim 0.75$, our empirical expression (2) features a mathematically tractable dependence on $T$ in place[7] of the unwieldy Arrhenius-type umklapp term in the semitheoretical formula for the thermal conductivity [see Ref. 5, Eq. (4)]. Substitution of these empirical expressions for $c_p$ and $k$ into (1) yields the essentially nonlinear heat conduction equation

$$\partial\theta/\partial t = D\theta^2\nabla^2\theta\,, \tag{3}$$

in which the dimensionless thermal variable $\theta = \theta(\vec{x}, t) \equiv [1+(T/T_c)^4]^{-1}$ is patently positive but less than unity, and the diffusion constant appears as

$$D \equiv \frac{415\ \text{cm}^2/\text{sec}}{\chi T_c^3} = \frac{1.69\ \text{cm}^2/\text{sec}}{\chi(1+1.043\chi)^3}\,. \tag{4}$$

Steady-state solutions to (3) feature harmonic functions for $\theta$ (e.g., $\theta = \text{const} + \text{const}\,x$ for steady heat transport with one-dimensional symmetry), but the associated temperature distribution $T = T_c(1-\theta)^{1/4}\theta^{-1/4}$ varies with the spatial coordinates in a much more complicated fashion. Because there is no inclusion of the $\chi$-dependent Schottky-type term[3] in the specific heat for $T \lesssim 2$ K, nor local heat release due to the conversion of ortho-$H_2$ to para-$H_2$,[8-10] solutions to (3) can be expected to correspond more closely to experimentally observed temperature distributions in cases for which $T \gtrsim 2$ K prevails throughout most of the solid volume.

The general time-dependent solution is obtainable for one-dimensional spatial symmetry, with $\partial\theta/\partial y = \partial\theta/\partial z = 0$ and $\nabla^2\theta = \partial^2\theta/\partial x^2$, by noting that the specialized version of (3) guarantees existence of an *extensible distance coordinate* $\hat{x} = \hat{x}(x, t)$ such that

$$\partial\hat{x}/\partial x = \theta^{-1}\ (>1)\,,\quad \partial\hat{x}/\partial t = -D\partial\theta/\partial x\,, \tag{5}$$

since the one-dimensional form of (3) is the integrability condition for $\hat{x}$ (obtained by cross differentiation) that follows from Eqs. (5). From the latter we have $\theta(\partial/\partial x)_t = (\partial/\partial\hat{x})_t$ for differentiation with $t$ held fixed, and $(\partial/\partial t)_x = (\partial/\partial t)_{\hat{x}} - D(\partial\theta/\partial x)(\partial/\partial\hat{x})_t$ by the chain rule. Hence, if viewed as a function of the extensible distance coordinate, the thermal variable $\theta \equiv \theta^*(\hat{x}, t)$ satisfies the familiar linear diffusion equation

$$\partial\theta^*/\partial t = D\partial^2\theta^*/\partial\hat{x}^2\,. \tag{6}$$

To eliminate $\hat{x}$ from a solution to (6), one uses the connection formula implied by (5),

$$x = \int [\theta^* d\hat{x} + D(\partial\theta^*/\partial\hat{x})\,dt]\,, \tag{7}$$

with the line-integral taken along any convenient path in the $\hat{x}, t$ plane. Note that $\theta^* \cong 1$ and hence $x \cong \hat{x} + \text{const}$ throughout spatial regions with $T \ll T_c$, while $\theta^*$ is significantly less than unity and $x$ varies more slowly with changes in $\hat{x}$ throughout regions with $T \gtrsim T_c$. This means that more pronounced thermal gradients will evolve and persist in physical $x$ space than those admitted in $\hat{x}$ space by (6) in regions with $T \gtrsim T_c$.

This remarkable linear-theoretic correspondence for one-dimensional heat conduction in solid $H_2$ facilitates the exact solution of initial-value boundary-value problems of current experimental importance,[11] as illustrated by the following two examples.

*(a) Semi-infinite solid subject to surface cooling or warming:* $\theta \equiv \theta_0$ (= const) at $x=0$ for all $t>0$, $\theta \equiv \theta_i$ (= const) at $t=0$ for all $x>0$. The desired solution to (6) is

$$\theta = \theta_i + (\theta_0 - \theta_i)(1 - \mathrm{erf}\eta_0)^{-1}(1-\mathrm{erf}\eta) \quad \text{for } \eta_0 \le \eta < \infty , \tag{8}$$

in which

$$\mathrm{erf}\eta \equiv 2\pi^{-1/2}\int_0^{\eta} \exp(-\alpha^2)\, d\alpha ,$$

with $\eta \equiv \hat{x}/2(Dt)^{1/2}$ given implicitly by evaluating (7):

$$\begin{aligned} x/2(Dt)^{1/2} = {} & [\theta_i + (\theta_0 - \theta_i)(1-\mathrm{erf}\eta_0)^{-1}]\eta \\ & + (\theta_i - \theta_0)(1-\mathrm{erf}\eta_0)^{-1} \\ & \times [\eta\, \mathrm{erf}\eta + \pi^{-1/2}\exp(-\eta^2)] . \end{aligned} \tag{9}$$

By setting $x=0$ and $\eta=\eta_0$ in Eq. (9) and making algebraic simplifications, one obtains a formula for the constant parameter $\eta_0$ in (8) and (9):

$$1-\theta_0^{-1}\theta_i = \pi^{1/2}\eta_0(1-\mathrm{erf}\eta_0)\exp\eta_0^2$$

$$= \begin{cases} 1-\frac{1}{2}\eta_0^{-2} + O(\eta_0^{-4}) & \text{for } \eta_0 \gtrsim 1 \\ \pi^{1/2}\eta_0 - 2\eta_0^2 + O(\eta_0^3) & \text{for } |\eta_0| \ll 1 \\ 2\pi^{1/2}\eta_0[\exp\eta_0^2 + O(|\eta_0|^{-1})] & \text{for } \eta_0 \lesssim -1 . \end{cases} \tag{10}$$

A unique positive value of $\eta_0$ satisfies (10) for surface cooling with $\theta_0 > \theta_i$, while a unique negative value of $\eta_0$ is obtained as the solution to (10) for surface warming with $\theta_0 < \theta_i$. In the neighborhood of the surface in either case, the solution (8)–(10) produces

$$\theta = \theta_0 - \eta_0 x/(Dt)^{1/2} + O(x^2/Dt) . \tag{11}$$

*(b) Thermally isolated finite slab:* $0 \le x \le L$ with $\partial\theta/\partial x = 0$ at both $x=0$ and $x=L$ for all $t \ge 0$ and $\theta \equiv \theta_i(x)$ at $t=0$ (prescribed general initial value). The desired solutions to (6) and (7) are expressible as

$$\theta = \bar{\theta} + \pi^{-1/2}\int_{-\infty}^{\infty} A'(\hat{x} + 2(Dt)^{1/2}\beta)\exp(-\beta^2)\, d\beta , \tag{12}$$

$$x = \bar{\theta}\hat{x} + \pi^{-1/2}\int_{-\infty}^{\infty} A(\hat{x} + 2(Dt)^{1/2}\beta)\exp(-\beta^2)\, d\beta , \tag{13}$$

in which the constant $\bar{\theta} \equiv L[\int_0^L \theta_i(x)^{-1}dx]^{-1}$, the domain of $\hat{x}$ is $0 \le \hat{x} \le \bar{\theta}^{-1}L$, and the function $A(\,)$ is odd, of period $2\bar{\theta}^{-1}L$,

$$A(\gamma) \equiv -A(-\gamma) \equiv A(\gamma + 2\bar{\theta}^{-1}L) \quad \text{for all real } \gamma , \tag{14}$$

and given over a half period by the equation derived from (12) and (13) at $t=0$,

$$\int_0^{A(\gamma)+\bar{\theta}\gamma} \theta_i(x)^{-1}dx = \gamma . \tag{15}$$

From our original equation (3), it follows that

$$\int_0^L \theta(x,t)^{-1}dx = \bar{\theta}^{-1}L \quad \text{for all } t \ge 0 ,$$

and differential-inequality analysis[12] can be applied to (3) to show that $\lim_{t\to\infty}\theta = \bar{\theta}$ for $\partial\theta/\partial x = 0$ at $x=0$ and $L$, the boundary conditions preserved here for all $t \ge 0$ by the symmetry conditions in Eq. (14). Further analysis shows that the characteristic time for asymptotic approach to the uniform distribution $\bar{\theta}$ is generally given by $\tau = L^2/\pi^2 D\bar{\theta}^2$, as in the representative special forms for (12) and (13),

$$\theta = \bar{\theta} + \delta\exp(-t/\tau)\cos(\pi\bar{\theta}\hat{x}/L) , \tag{16}$$

$$x = \bar{\theta}\hat{x} + (\pi\bar{\theta})^{-1}\delta L\exp(-t/\tau)\sin(\pi\bar{\theta}\hat{x}/L) , \tag{17}$$

where the constants $\delta$ and $\bar{\theta}$ ($>|\delta|$) are prescribed by the initial temperature distribution.


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