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Letter

Comments on a partial differential equation model of the temperature of a growing spherulite

Dear Sir

In a recent article, Huang *et al.*[1] presented a mathematical model of the evolution of the temperature distribution in the vicinity of an isolated spherulite undergoing linear radial growth. There is an error, and there are some ambiguities, in their presentation. The purpose of this short note is to correct the error and to identify the ambiguities.

I mean only to comment on the mathematics of this model. I mean neither to endorse nor to criticize the scientific underpinnnings of the model.

POSING OF THE MATHEMATICAL PROBLEM

Equations (6), (7), (8) and (9) of the paper constitute the authors' mathematical formulation of the model. These equations (I shall use the notation that was used in the paper, and I shall number the equations here as they are numbered in the paper) are:

$$\frac{\partial T}{\partial t} = a\left[\frac{\mathrm{d}^2 T}{\mathrm{d}r^2} + \frac{2}{[R(t)+r]}\frac{\partial T}{\partial r}\right] + \frac{\mathrm{d}R}{\mathrm{d}t}\frac{\partial T}{\partial r} \qquad (6)$$

$$\frac{\mathrm{d}R}{\mathrm{d}t} = V = \text{constant} \qquad (7)$$

$$T(\infty, t) = T_c \qquad (8)$$

$$\frac{\partial T}{\partial r}\Big|_{r=0} = -\frac{L\beta}{C_p} \qquad (9)$$

Since equations (6) and (7) are time-dependent, they ought to be supplemented with initial conditions. Thus, to specify the mathematical problem fully—to have a well posed problem—two more equations, of the form:

$$T(r,0) = T_0(r)$$

$$R(0) = R_0$$

are needed. From the context of the paper, and from the computed results, I infer that $T_0(r) \equiv T_c$ and $R_0 = 0$ are the appropriate initial values.

PROPOSED SOLUTION

In the paper, it is stated that the function:

$$T = T_c + \frac{L\beta}{C_p}R^2\left[\frac{\mathrm{e}^{-\beta r}}{R+r} + \beta\mathrm{e}^{\beta R}\mathrm{Ei}(-\beta(R+r))\right] \qquad (10)$$

where

$$\mathrm{Ei}(p) = \int_p^\infty \frac{\mathrm{e}^{-x}}{x}\mathrm{d}x$$

is a solution of equation (6). Presumably, the authors intended this to be a solution that also satisfied the boundary conditions that they specified. There are two problems. First, the authors did not intend the function given in equation (10) to be a solution of equation (6). Rather, they intended it to be a solution of the equation[2]:

$$0 = a\left[\frac{\mathrm{d}^2 T}{\mathrm{d}r^2} + \frac{2}{[R(t)+r]}\frac{\partial T}{\partial r}\right] + \frac{\mathrm{d}R}{\mathrm{d}t}\frac{\partial T}{\partial r} \qquad (6')$$

They refer to a solution of this equation—presumably a solution that satisfies the boundary and initial conditions—as a quasi-stationary approximation to the solution of the original problem[2]. Secondly, the function given in equation (10) is not a solution of equation (6), nor is it a solution of equation (6′) for the quasi-stationary approximation, nor does it satisfy either of the boundary conditions given in equations (8) and (9). That this is so is easily established by performing the required differentiations and making the appropriate substitutions.

THE CORRECT QUASI-STATIONARY APPROXIMATION

The actual solution of equations (6′), (7), (8), (9) and the inital conditions is:

$$T = T_c + \frac{L\beta}{C_p}R^2\left[\frac{\mathrm{e}^{-\beta r}}{R+r} - \beta\mathrm{e}^{\beta R}\mathrm{Ei}(\beta(R+r))\right] \qquad (10')$$

with $R(t) = V$. Here, we have used the definition of the function Ei (p) given in the paper. The notation used in connection with the exponential integral function and related functions varies, and this variation frequently causes confusion. In their standard reference, 'An Atlas of Functions'[3], Spanier and Oldham define the exponential integral differently, as:

$$\mathrm{Ei}(p) = \int_{-\infty}^p \frac{\mathrm{e}^x}{x}\mathrm{d}x$$

If the authors had used *this* definition, their solution, presented in equation (10), would be correct. The function that is presented in the paper as the exponential integral function is the second Schlomilch function[3] usually denoted $E_1(p)$, which is related to the exponential integral, in the notation of Spanier and Oldham, by:

$$E_1(p) = \int_p^\infty \frac{\mathrm{e}^- x}{x}\mathrm{d}x = -\int_{-\infty}^{-p}\frac{\mathrm{e}^x}{x}\mathrm{d}x = -\mathrm{Ei}(-p)$$

I repeated the computations presented in the paper, using the parameters given in the paper, and setting $r = 0$. The computations with the formula in equation (10), using the paper's definition of the exponential integral, reproduced the graphs in Figure 8 of the paper,

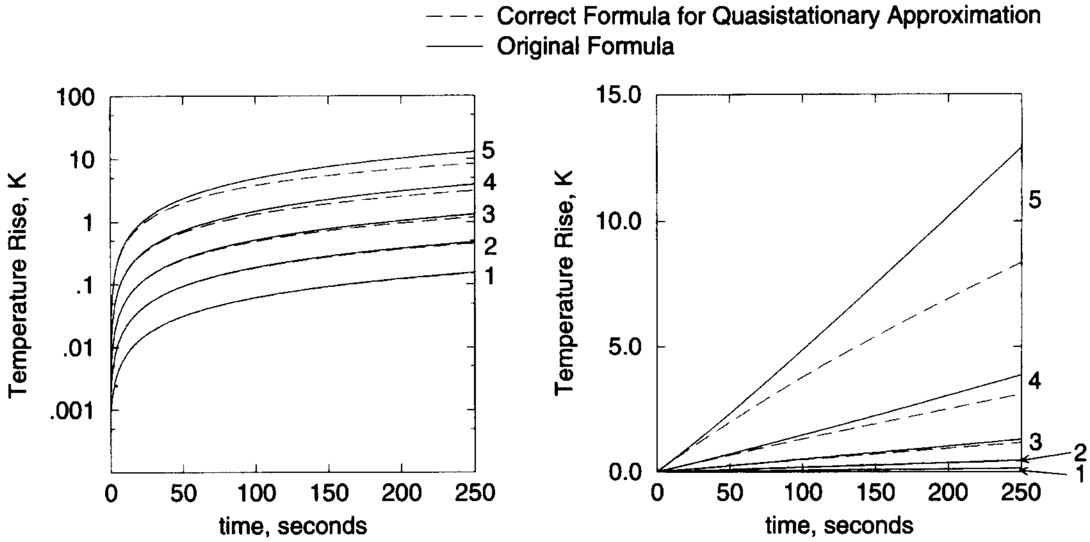

Figure 1 Calculated increase in surface temperature as a function of time for PEO

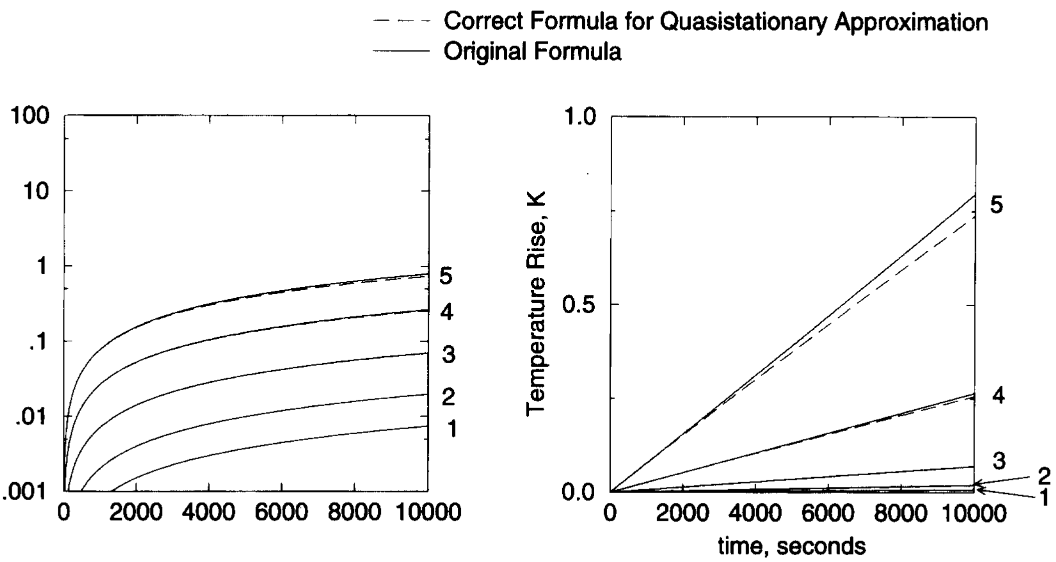

Figure 2 Calculated increase in surface temperature as a function of time for iPP

for PEO. They are plotted as solid curves in *Figure 1*. The computations with the formula in equation (10′), the actual quasi-stationary solution, using the paper's definition of the exponential integral, produced similar graphs for slow radial growth rates, but for the largest growth rate the difference reached a maximum of 35%. These are plotted as dotted curves in *Figure 1*. The graphs are shown in both linear–log and linear–linear scales.

I also tried to repeat the computations for iPP that are presented in Figure 9 of the paper. The results are shown in *Figure 2*. Again, the graph produced by the correct formula, given in equation (10′), using the paper's definition of the exponential integral, are dotted curves. The graphs produced by the formula given in equation (10), using the paper's definition of the exponential integral, are solid curves. In this case, the two formulae produce more similar results, differing by at most 7% in the case of the most rapid growth rate. However, neither of these formulae yields the results that are present in Figure 9 of the paper, from which they differ by an order of magnitude. It appears that the authors used yet another formula to obtain the graphs in that figure.

Readers should not infer, from the surprisingly good agreement of the two formulae for the cases presented in *Figures 1* and *2*, that the formula in equation (10) is in any way reliable. In general, the function represented by this formula is qualitatively and quantitatively wrong.

VALIDITY OF THE QUASI-STATIONARY APPROXIMATION

One must justify the use of quasi-stationary approximation by showing that the time derivative on the left side of equation (6) is negligible. Sometimes it is, sometimes it is not. The applicability of the quasi-stationary approximation will depend on the parameter values, and on the accuracy that is required.

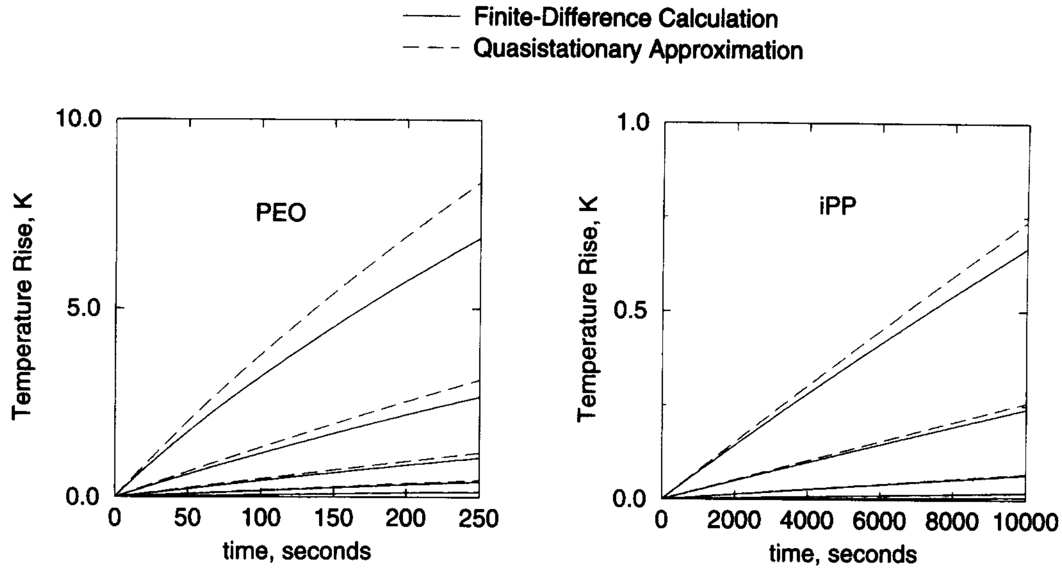

Figure 3 Comparison of the quasi-stationary solution with a finite-difference solution

I shall not give a complete analysis of the quasi-stationary approximation. However, the basic issue is simple and is worth stating. If thermal diffusion is much faster than the growth rate of the spherulite, we might expect the temperature distribution around the spherulite at any time to approximate a steady-state temperature distribution. In time t, heat diffuses a distance on the order of $\sqrt{at}$. In the same time, the spherulite grows radially by an amount V. If the ratio of these two distances:

$$V\sqrt{at}$$

is small—and what counts as small will be determined by the precision required for a particular application—quasi-stationary approximation may apply.

I solved the initial–boundary value problem specified by equations (6), (7), (8), (9), $T(r,0) = T_c$, and $R(0) = 1\,\mu\text{m}$ by a finite-difference method, for the cases considered in Figure 8 and Figure 9 of the paper. (If $R(0) = 0$, equation (6) is singular, which is why I used a non-zero value; for our purposes, the differences in the solutions are negligible.) By successively refining the finite-difference grid, I obtained solutions, which are plotted as solid curves in *Figure 3*, that are more than sufficiently accurate for our purposes. The quasi-stationary approximations are also plotted, as dotted curves, in *Figure 3*. As our rough criterion suggests, the accuracy of the quasi-stationary approximation decreases with increasing time and with increasing growth rate. For PEO, the worst of the cases presented in the paper occurs at $t = 250\,\text{s}$, $V = 6.668\,\text{ms}^{-1}$, where the quasi-stationary approximation is off by 21%. For iPP, the worst of the cases occurs at $t = 10\,000\,\text{s}$, $V = 0.24\,\text{ms}^{-1}$, where the quasi-stationary approximation is off by 10%.

IPP DATA

This observation is not related to the differential equation model. In Figure 6 of the paper, the authors present graphs of iPP spherulite radius as a function of time at four temperatures. In the figure caption, they indicate the growth velocities associated with each of the four cases. However, the growth velocities reported in the caption do not correspond to the slopes of the curves in the graph. For example, curve 4 indicates that the spherulite grew with linear radial velocity from a radius of 50 μm at 7000 s to a radius of 300 μm at 41 000 s, so the radial velocity is:

$$V = \frac{300 - 50}{41\,000 - 7000} = \frac{250}{34000} = 0.0074\,\mu\text{m}\,\text{s}^{-1}$$

The authors report this velocity, in the caption, as $V = 0.1255\,\mu\text{m s}^{-1}$. There are comparable discrepancies between the slopes of the other graphs and the reported velocities.

CONCLUSION

Readers who plan to use the model developed in the paper should establish, for the particular cases in which they are interested, whether the quasi-stationary approximation is valid before they apply it. If they decide that this approximation is valid, they should use the correct formula, given above in equation (10′).

My recommendation is that anyone interested in using this model simply solve the equations by a finite-difference method or a finite-element method. These are more accurate. And, given the speed of the current generation of computers and the sophistication and availability of mathematical software, it is probably simpler to use these methods than it is to estimate the error introduced by the quasi-stationary approximation.

REFERENCES

1 Huang, T., Rey, A. D. and Kamal, M. R. *Polymer* 1994, **35**, 5434

2 Kamal, M. R., personal communication
3 Spanier, J. and Oldham, K. B. 'An Atlas of Functions', Hemisphere, Washington, 1987, Ch. 37

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