On the Extraction of Diffusion Coefficients from Gravimetric Data for Sorption of Small Molecules by Polymer Thin Films

C. M. Balik

Department of Materials Science and Engineering,
Box 7907, North Carolina State University,
Raleigh, North Carolina 27695-7907

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Introduction

Diffusion coefficients of gases or vapors in polymers are conveniently measured using gravimetric methods which utilize an electrobalance or quartz spring apparatus.[1,2] The polymer sample must have a well-defined geometry (usually a thin film or monodisperse spherical particles), and the weight gain of the sample is measured vs time in an atmosphere of pure penetrant maintained at constant temperature and pressure. For the thin-film geometry in which diffusion from the edges of the film is neglected, the total mass uptake of penetrant under these conditions can be described by either of the following equations:[3]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2\pi^2 Dt}{h^2}\right) \quad (1)$$

$$\frac{M_t}{M_\infty} = \frac{4}{h}\left(\frac{Dt}{\pi}\right)^{0.5} + \frac{8}{h}(Dt)^{0.5}\sum_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\left(\frac{nh}{2(Dt)^{0.5}}\right) \quad (2)$$

Equation 1 converges rapidly at long times, whereas eq 2 converges rapidly at short times. M_t is the mass of penetrant sorbed at time t, M_∞ is the mass sorbed at $t = \infty$, h is the polymer film thickness, and D is the diffusion coefficient. Methods for obtaining a diffusion coefficient from sorption data are based on one of these two equations. Some of the more commonly used methods include the following:[1]

Method 1: measurement of the sorption half-time. The time at which $M_t/M_\infty = 0.5$ ($t_{0.5}$) can be obtained from a two-term approximation of eq 1 as

$$t_{0.5} = \frac{0.04919h^2}{D} \quad (3)$$

Method 2: measurement of the initial slope of a plot of M_t/M_∞ vs $t^{0.5}$. Using only the first term of eq 2, at sufficiently short times

$$\frac{M_t}{M_\infty} = \frac{4}{h}\left(\frac{Dt}{\pi}\right)^{0.5} \quad (4)$$

Method 3: measurement of the limiting slope of a plot of $\ln(1 - M_t/M_\infty)$ vs t. From the one-term approximation of eq 1, at sufficiently long times

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 Dt}{h^2} \quad (5)$$

Method 4: a differential variation of method 3 which may be applied in cases when the approach to equilibrium is very slow and measurement of M_∞ is difficult to achieve. Differentiating the one-term approximation of eq 1 with respect to time yields

$$\ln\left(\frac{dM_t}{dt}\right) = \ln\left(\frac{8DM_\infty}{h^2}\right) - \frac{\pi^2 Dt}{h^2} \quad (6)$$

from which D is obtained from the slope of a plot of $\ln(dM_t/dt)$ vs t.

Method 5: a moment method, due to Felder,[1] in which the quantity

$$\tau_s = \int_0^\infty\left(1 - \frac{M_t}{M_\infty}\right)dt$$

is first calculated by numerical integration of the sorption data. D is then obtained from

$$D = \frac{h^2}{12\tau_s} \quad (7)$$

Methods 1−4 are simple in application but suffer from an uncertainty in the time interval over which they apply and do not make use of all of the sorption data. Method 5 uses all of the sorption data, but the numerical integration step is subject to truncation and round-off errors, especially for slow sorption processes. Most methods also require a value for M_∞ initially, which is subject to uncertainty if the sorbed amount is small and the data is scattered or if sorption is slow and the equilibrium sorption level is not clearly delineated. Method 4 attempts to circumvent this problem but is prone to errors due to the large scatter generated by differentiating experimental data and applying an equation that is only accurate for $M_t/M_\infty \geq 0.5$ to data that is not yet approaching equilibrium.

The ready availability of data analysis software for personal computers that incorporates nonlinear regression routines adds another dimension to the treatment of sorption data. For example, a direct fit of eq 1 containing a sufficient number of terms to M_t vs t data is feasible, allowing both D and M_∞ to be extracted. This method uses all of the sorption data but can be time-consuming even on fast computers if a large number of terms is used in eq 1 or if the number of data points is large. An additional problem is that an unacceptable number of terms is required to get eq 1 to converge to zero as t approaches zero (e.g. at $t = 0$, sums containing 10 and 20 terms only yield $M_t/M_\infty = 0.017$ and 0.0089, respectively). Direct use of eq 2 is cumbersome in that some approximation or tabulation of the ierfc function is required.

Presented here is a method for obtaining D from sorption data which overcomes the problems associated with the above methods. It is a nonlinear regression method that uses all of the data, converges to zero at $t = 0$, and runs much faster than a direct application of eq 1.

Description of the Method

The first terms of eq 1 and 2 provide very good approximations to their infinite series at sufficiently long and short times, respectively. This is illustrated in Figure 1, which represents the percentage error between the values of M_t/M_∞ calculated with the first-term approximations and calculated with a 500-term version of the infinite series in eq 1, i.e.

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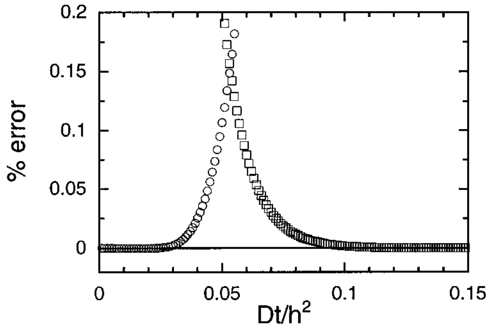

Figure 1. Percentage error in M_t/M_∞ values obtained from the first terms of the short-time (circles) and long-time (squares) infinite series solutions (eqs 1 and 2, respectively), relative to a 500-term version of eq 1.

$$\% \text{ error} = 100 \times \frac{\dfrac{M_t}{M_\infty}(\text{first term}) - \dfrac{M_t}{M_\infty}(\text{500 terms})}{\dfrac{M_t}{M_\infty}(\text{500 terms})}$$

The error associated with the short-time approximation is negligible at $Dt/h^2 \leq 0.03$ and begins to increase rapidly at $Dt/h^2 > 0.04$ ($M_t/M_\infty > 0.45$). The error associated with the long-time approximation is negligible at $Dt/h^2 > 0.1$ and begins to increase rapidly at $Dt/h^2 < 0.08$ ($M_t/M_\infty < 0.63$). These two approximations cross at $Dt/h^2 = 0.05326$ ($M_t/M_\infty \approx 0.52$), at which point the relative error is less than 0.15% and the absolute error is less than 0.0008. Thus, the combination of these two first-term approximations provides an excellent approximation to eq 1 over the entire sorption time domain. This forms the basis of our method for determining D, which is hereafter referred to as the *hybrid 1-term method*. A weighted sum of the two first-term approximations is used, with the weighting function designed to switch rapidly between the short-time term and the long-time term at $Dt/h^2 = 0.05326$. Mathematically, this can be represented as

$$\frac{M_t}{M_\infty} = \phi(x)\, f(x) + [1 - \phi(x)]\, g(x) \qquad (8)$$

where $x = Dt/h^2$, $f(x) = 4(x/\pi)^{0.5}$ (the short-time approximation), $g(x) = 1 - (8/\pi^2)\exp(-\pi^2 x)$ (the long-time approximation), and $\phi(x)$ is the weighting function. Ideally, the weighting function should be defined as

$$\phi(x) = 1, \quad x \leq 0.05326$$

$$\phi(x) = 0, \quad x > 0.05326$$

A discontinuous function such as this is cumbersome if not impossible to incorporate into many data analysis software packages, although it can easily be added to a nonlinear regression program that is written exclusively for this purpose. In most cases, a continuous analytical function is more desirable. A function that fulfills this need is the well-known Fermi function:[4]

$$\phi(x) = \frac{1}{1 + \exp\left(\dfrac{x - a}{b}\right)} \qquad (9)$$

This function is plotted in Figure 2 using the a and b values listed below. The midpoint of the transition from $\phi(x) = 1$ to $\phi(x) = 0$ occurs at $x = a$, and the width of the transition region is related to b. Ideally, b should be as small as possible, but extremely small values will result in large values for the exponential terms in eq 9, which may lead to overflow errors during regression. b values from 0.001 to 0.004 were found to be acceptable, and the value chosen did not change the regressed parameters (D and M_∞) significantly. $b = 0.001$ was used for the results reported here. The optimum value for a depends somewhat on b for $b > 0.004$ but is very insensitive to b for $b \leq 0.004$. For $b \leq 0.004$, the optimum value for a is 0.05326, which is the point at which the one-term approximations intersect in Figure 1.

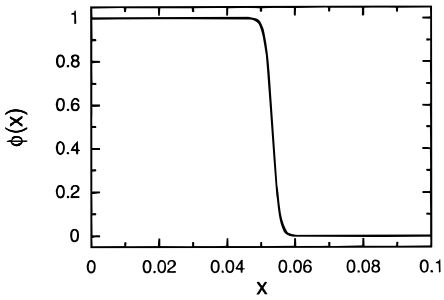

Figure 2. Plot of the weighting function (Fermi function) for $a = 0.05326$ and $b = 0.001$.

Test of the Method

To evaluate the hybrid 1-term method and to compare it with other methods for extracting diffusion coefficients, artificial data sets with a known diffusion coefficient were generated using a 500-term version of eq 1 and adding random errors (noise) to the M_t/M_∞ values to simulate experimental scatter. The error distribution was designed to be approximately Gaussian, and the error was weighted equally for each data point as would be the case in an actual gravimetric sorption experiment. Five data sets were generated with large errors (extrema ≈ ±10%, standard deviation = ±4.4% of full scale, taken as $M_t/M_\infty = 1.0$), five with intermediate errors (extrema ≈ ±5%, standard deviation = 2.4%), and five with small errors (extrema ≈ ±2%, standard deviation = ±1.1%). One data set was generated with zero noise to evaluate the accuracy of the various methods in the absence of experimental scatter. All regression analyses were run on a Macintosh personal computer using Kaleidagraph 3.0 software which utilizes the Marquardt nonlinear regression algorithm.[5] Initial parameter “guesses” input to the regression routine were $D = 10^{-8}$ cm²/s and $M_\infty = 3$ in each case. The program always converged to the same final parameters, regardless of the initial guesses.

Representative plots from each group of sorption data generated with $D = 10^{-9}$ cm²/s, $h = 0.01$ cm, and $M_\infty = 1.0$ are displayed in Figure 3. For the various methods, average values of D and M_∞ (where applicable) obtained from each group of five data sets are listed in Table 1, along with their standard deviations, average errors, and 99% confidence intervals. The hybrid 1-term method was tried as a 2-parameter and a 1-parameter nonlinear fit (M_∞ was fixed at 1.0 in the latter case). A 6-term version of eq 1 was also evaluated as 1- and 2-parameter nonlinear fits (6 terms were sufficient to determine D to four significant figures). The initial slope method used eq 4 and data from $M_t/M_\infty \leq 0.5$. $t_{0.5}$ for the half-time method was taken from the line obtained with the initial slope method in order to avoid errors that may result from visual interpolation of the

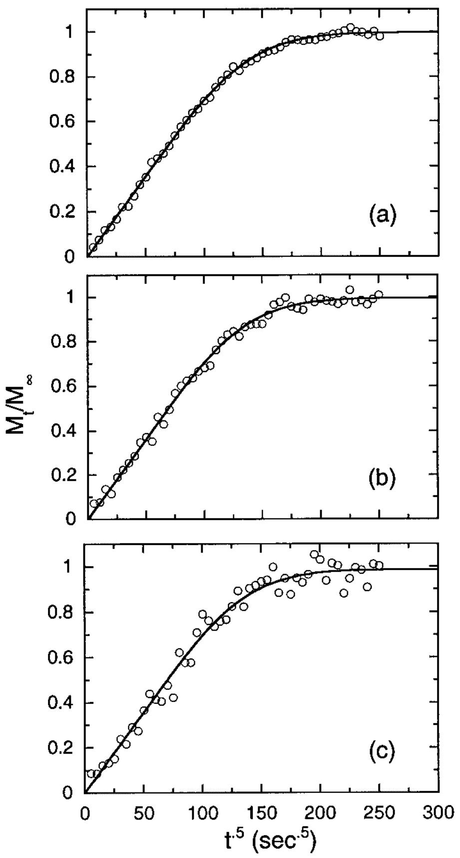

Figure 3. Representative data sets generated with (a) low, (b) intermediate, and (c) high amounts of noise added. The solid lines are fits obtained with the hybrid 1-term method.

data. The limiting slope method used eq 5 and data from $M_t/M_\infty \geq 0.5$. Due to problems cited above, the method which uses eq 6 was not evaluated.

From Table 1 it can be seen that all of the methods accurately reproduce the target *D* value in the absence of experimental scatter (zero noise). The hybrid 1-term, 6-term series, and initial slope methods systematically produce slightly low *D* values while the other methods produce slightly high values; however, in all cases the differences are entirely negligible. The hybrid 1-term method consistently ran faster than the 6-term series by a factor of at least 2.1.

Larger differences in the regressed *D* values begin to appear when noise is added to the data. Generally, the deviation from the target value increases with increasing noise, although there are some inconsistencies due to limited sampling of only 5 data sets at each noise level. The hybrid 1-term and 6-term series methods consistently produced *D* values that were nearly identical and closest to the target value, even with very noisy data (Figure 3c). The accuracy of these two methods increased in most cases when M_∞ was fixed and a 1-parameter regression for *D* was carried out. This was especially evident in the data sets with higher noise. M_∞ values obtained from the 2-parameter nonlinear regressions were consistently very close to the target value.

The moment method proved to be nearly as accurate as the hybrid 1-term and 6-term series methods. The initial slope and half-time methods produced similar *D* values but were significantly less accurate than the previous three methods. At higher levels of noise, the target *D* value often did not fall within the 99% confidence interval with the latter two methods.

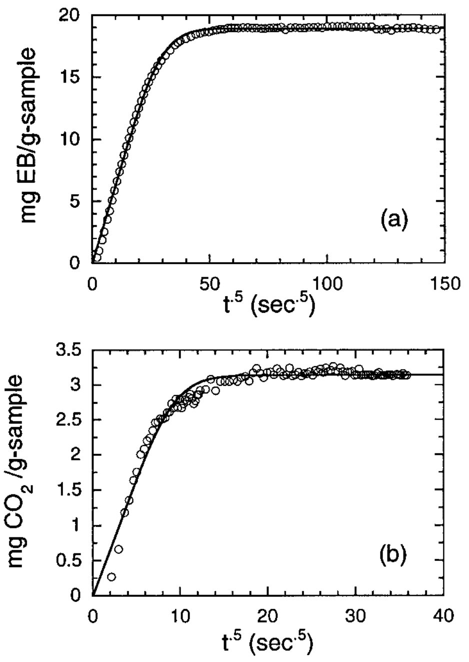

Figure 4. Experimental data for (a) vacuum desorption of ethyl butyrate (EB) from low-density polyethylene at 30 °C and (b) sorption of CO_2 by polystyrene at 30 °C and 447 Torr. The solid lines are fits obtained with the hybrid 1-term method.

For all of the data sets, the limiting slope method proved to be the least accurate way to extract *D*. The error in *D* with this method increased very rapidly with increasing noise, and the target *D* value was well outside the 99% confidence interval at higher noise levels. $\ln(1 - M_t/M_\infty)$ becomes highly scattered for noisy data when M_t/M_∞ approaches 1.0, and the accuracy of this method could be improved by removing outlying points from the data sets. This was not done here to avoid bias in comparing this method with the others which always utilized all of the data.

Application to Experimental Data

The various methods were also applied to two different experimental sets, to assess the variation in *D* obtained from actual data. The data was collected in our laboratories at 30 °C using a recording electrobalance interfaced with a computer data acquisition system. The systems evaluated are vacuum desorption of ethyl butyrate from low-density polyethylene (h = 0.00975 cm) and sorption of CO_2 in polystyrene (h = 0.00525 cm) at 447 Torr. Both systems follow Fickian kinetics. The data is plotted in Figure 4, and *D* values extracted with the various methods are listed in Table 2. The M_∞ values from the 2-parameter nonlinear fits were used for the other methods which required M_∞. The polyethylene data is very smooth, while the polystyrene data is rather scattered and lacks data points in the initial region due to the low solubility of CO_2 and rapid equilibration in a thin sample, respectively.

Diffusion coefficients obtained with all methods for the ethyl butyrate/polyethylene system were in relatively good agreement, as expected from this well-behaved data set. The hybrid 1-term and 6-term series methods produced identical *D* values to three significant figures, and the moment method *D* was also quite close to this value. The limiting slope and initial slope methods produced *D*'s that were respectively smaller and larger than the hybrid 1-term method by about 30%.

Table 1. Diffusion Coefficients Obtained with Various Methods from Artificial Data Sets

method	$D^a \times 10^9$ (cm^2/s)	error in D (%)	99% confidence interval for D	M_∞
		0% Noise		
hybrid 1-term (2-parameter)	0.9996	−0.04		1.0000
hybrid 1-term (1-parameter)	0.9997	−0.03		
6-term series (2 parameter)	0.9999	−0.01		1.0000
6-term series (1 parameter)	0.9999	−0.01		
initial slope	0.9996	−0.04		
half-time	1.0039	+0.39		
moment	1.0040	+0.40		
limiting slope	1.0002	+0.02		
		±1.1% Noise		
hybrid 1-term (2-parameter)	0.9933 ± 0.0017	−0.67	±0.0035	0.9992 ± 0.0018
hybrid 1-term (1-parameter)	0.9912 ± 0.0057	−0.88	±0.0117	
6-term series (2-parameter)	0.9937 ± 0.0018	−0.63	±0.0036	0.9992 ± 0.0018
6-term series (1-parameter)	0.9915 ± 0.0057	−0.85	±0.0117	
initial slope	0.9829 ± 0.0391	−1.71	±0.0805	
half-time	0.9822 ± 0.0145	−1.78	±0.0299	
moment	0.9954 ± 0.0109	−0.46	±0.0225	
limiting slope	0.9554 ± 0.1291	−4.46	±0.2656	
		±2.4% Noise		
hybrid 1-term (2-parameter)	0.9947 ± 0.0350	−0.53	±0.0720	1.0024 ± 0.0101
hybrid 1-term (1-parameter)	1.0019 ± 0.0200	+0.19	±0.0411	
6-term series (2-parameter)	0.9961 ± 0.0353	−0.39	±0.0726	1.0022 ± 0.0103
6-term series (1-parameter)	1.0020 ± 0.0199	+0.20	±0.0409	
initial slope	0.9574 ± 0.0853	−4.26	±0.1754	
half-time	0.9654 ± 0.0127	−3.46	±0.0262	
moment	1.0140 ± 0.0457	+1.40	±0.0940	
limiting slope	0.7922 ± 0.0643	−20.78	±0.1323	
		±4.4% Noise		
hybrid 1-term (2-parameter)	0.9791 ± 0.0729	−2.09	±0.1501	1.0072 ± 0.0159
hybrid 1-term (1-parameter)	0.9991 ± 0.0413	−0.09	±0.0850	
6-term series (2-parameter)	0.9795 ± 0.0729	−2.05	±0.1500	1.0070 ± 0.0160
6-term series (1-parameter)	0.9996 ± 0.0417	−0.04	±0.0859	
initial slope	0.9032 ± 0.1837	−9.68	±0.3780	
half-time	0.8992 ± 0.0900	−10.08	±0.1851	
moment	1.0255 ± 0.0555	+2.55	±0.1141	
limiting slope	0.6134 ± 0.1282	−38.66	±0.2637	

[a] Average from five data sets, except for 0% noise values.

Table 2. Diffusion Coefficients Obtained with Various Methods from Experimental Data

method	$D \times 10^8$ (cm^2/s)	M_∞ (mg/g of sample)
Ethyl Butyrate/Low-Density Polyethylene (Desorption)		
hybrid 1-term (2-parameter)	2.10	18.9
hybrid 1-term (1-parameter)	2.10	
6-term series (2-parameter)	2.10	18.9
6-term series (1-parameter)	2.10	
initial slope	2.74	
half-time	2.23	
moment	1.98	
limiting slope	1.54	
CO_2/Polystyrene (Sorption)		
literature value (ref 6)	7.4	
hybrid 1-term (2-parameter)	5.98	3.14
hybrid 1-term (1-parameter)	5.77	
6-term series (2-parameter)	5.98	3.14
6-term series (1-parameter)	5.77	
initial slope	15.1	
half-time	6.51	
moment	5.41	
limiting slope	2.55	

No literature values are available for comparison with these data.

The D values obtained for the CO_2/polystyrene data were considerably more scattered, with the extremes (initial and limiting slope methods) differing by almost an order of magnitude. Once again, the hybrid 1-term and 6-term series produced identical D's, although there was a slight variation between the 2-parameter and 1-parameter nonlinear fits. A literature value for the diffusion coefficient of CO_2 in polystyrene at 30 °C has also been included in Table 2 for comparison.[6] It is difficult to draw definite conclusions from this comparison since the polystyrene samples are not identical and the method used to obtain D from the experimental data was not cited in the reference. However, the date of the reference would suggest that a non-computer method was used (probably the half-time method). It is nevertheless satisfying to note that all methods except the limiting slope and initial slope yield D values within 27% of the literature value. Based on the results with the artificial data sets, we would conclude that the D obtained from the hybrid 1-term or 6-term series method is probably more accurate for CO_2 in polystyrene at 30 °C.

Application to Incomplete Data

Often the approach to equilibrium is very slow for systems exhibiting a low D or with thick samples, and it is not experimentally feasible to obtain a value for M_∞. For these cases, it is of interest to test the accuracry of the hybrid 1-term method for estimating M_∞ and D. A limited study of this was conducted by truncating the five intermediate noise data sets at values of M_t/M_∞ from 0.9 to 0.2 and applying the hybrid 1-term method in each case. Average D and M_∞ values with 1σ error bars are plotted in Figure 5 against the value of M_t/M_∞ above which the data were deleted. D diverges rapidly for data truncated at $M_t/M_\infty \leq 0.6$. M_∞ also begins to diverge at this truncation value but remains closer to the target value than D. Error bars predictably increase as fewer data are included in the fits. The parameter uncertainties (computed by the

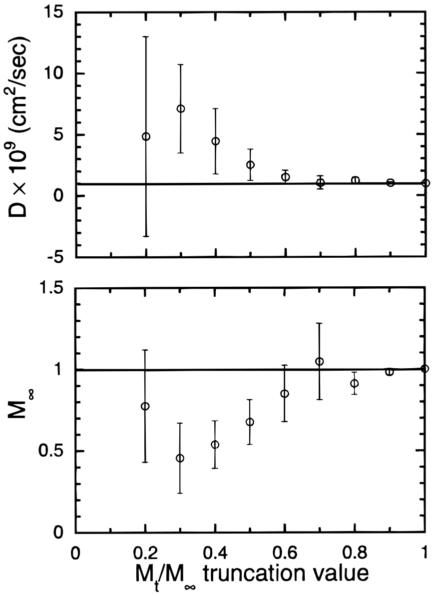

Figure 5. Average D and M_∞ values obtained from applying the hybrid 1-term method to intermediate noise data sets which have been truncated at the M_t/M_∞ values shown on the abscissa (1σ error bars). The horizontal lines represent the target values of D and M_∞.

nonlinear regression routine) become approximately the same size as the parameters themselves at a truncation value of 0.7 and increase by as much as 1−2 orders of magnitude at lower values. The regressed values obtained in this way are also somewhat dependent on the initial "guesses" supplied to the nonlinear regression routine. Note that for truncation values less than 0.5, the hybrid 1-term method essentially reduces to a 2-parameter nonlinear regression using eq 4. These limited results suggest that reasonable estimates of D and M_∞ can be made from incomplete data that has reached $M_t/M_\infty \geq 0.7$.

Conclusions

Diffusion coefficients of small molecules in polymers cover many orders of magnitude. Often one is only interested in an order-of-magnitude estimate of D for a particular system. If so, any of the methods described here for obtaining D from sorption data will suffice, provided that equilibrium is reached during the experiment and the data are not too scattered. Among the methods described here, the hybrid 1-term and 6-term series methods have the advantages of using all of the data, not requiring a value for M_∞ initially, and providing the most accurate estimate of D from data showing significant scatter. Compared with the 6-term series, the hybrid 1-term method offers the additional advantages of being analytically simpler, converging faster, and having a true zero intercept at $t = 0$.

References and Notes

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