

log χ^2 Distribution of Correlation Times Revisited

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Often, definitive models for molecular motion do not exist or fail to give reasonable results. And, as an approximation, an exponential decay of correlation with a distribution of correlation times is used as the correlation function. Such distributions prove to be very useful, especially for polymers and polymer solutions, at describing and quantifying the dynamics.¹⁻⁸

Heatley⁸ has summarized the successes and failures of several of the distributions used to describe polymer dynamics. Of these, the asymmetric log χ^2 distribution has had good success in fitting data from a broad range of techniques including NMR, ESR, and dielectric studies.^{1,2,5,8} We have found that the use of the log χ^2 distribution may occasionally yield parameters which should not be compared from system to system. In some cases, a proper comparison can be made with the application of a correction factor. For example, the application of the log χ^2 distribution, as proposed in the literature,¹ to NMR relaxation data of toluene in polystyrene generated a slower mean rotational correlation time for pure toluene than it did for motionally hindered toluene near polystyrene at the same temperature. It also yielded unphysical results in a dynamics study of poly(isopropyl acrylate) (PIPA).⁷ In that study, the mean correlation time predicted by the log χ^2 distribution had little correlation with polymer concentration, often being faster for more concentrated solutions than for less concentrated ones at the same temperature. Other models employed to quantify the PIPA system suffered similar problems. After examining the log χ^2 distribution, we found that the parameter τ_0 , previously interpreted as the mean correlation time, is not the true mean but rather a scaling factor which can be related to the true mean.

A normalized, scaled, base b log χ^2 distribution, $F^{\chi}(\tau_c; b, p, \theta)$, has the form of:

$$F^{\chi}(\tau_c; b, p, \theta) = \frac{\left(\frac{p}{\ln(b)}\right)^p}{\frac{1}{\theta} \frac{\Gamma(p)}{\Gamma(p)}} \left(\ln\left(\frac{\tau_c}{\theta} + 1\right)\right)^{p-1} \left(\frac{\tau_c}{\theta} + 1\right)^{-(p/\ln(b)+1)} \quad \text{for } 0 \leq \tau_c \leq \infty \quad (1)$$

with τ_c , b , p , θ , and Γ the correlation time, numerical base, width parameter, scaling parameter, and gamma function, respectively. The superscript χ denotes the log χ^2 distribution. The parameter b is often fixed at 1000, but it could be replaced with e , the natural base. The mean, $\tau_0^{\chi}(b, p, \theta)$, of $F^{\chi}(\tau_c; b, p, \theta)$ is:

$$\tau_0^{\chi}(b, p, \theta) = \int_0^{\infty} \tau_c F^{\chi}(\tau_c; b, p, \theta) d\tau_c = \theta \left[\left(\frac{p}{p - \ln(b)}\right)^p - 1 \right] \quad (2)$$

Experiments often probe the dynamics through the Fourier transform of the correlation function or spectral density, $J(\omega)$. For a distribution, $F(\tau_c)$, of exponentially

decaying correlation times, $J(\omega)$ is:

$$J(\omega) = \int_0^{\infty} \frac{2F(\tau_c)\tau_c}{1 + \omega^2\tau_c^2} d\tau_c \quad (3)$$

where ω and τ_c are the frequency and correlation time, respectively. $F^{\chi}(\tau_c; b, p, \theta)$ could be used in eq 3 and the mean correlation time calculated from eq 2 after determining the parameters b , p , and θ . However, transforming the distribution and spectral density to a reduced correlation time will allow a more direct comparison with the original work¹ and eliminate the need for eq 2 as the scaling parameter, θ , will be replaced by a mean correlation time parameter, τ_0 .

With the transformation $\tau_1 = \tau_c/\tau_0^{\chi}(b, p, \theta)$ applied to $F^{\chi}(\tau_c; b, p, \theta)$, the log χ^2 distribution of reduced correlation times, $G^{\chi}(\tau_1; b, p, \theta)$, is:

$$G^{\chi}(\tau_1; b, p) = \frac{\left(\frac{p}{\ln(b)}\right)^p}{\Gamma(p)} \tau_0^{\chi}(b, p, 1) (\ln(\tau_1 \tau_0^{\chi}(b, p, 1) + 1))^{p-1} (\tau_1 \tau_0^{\chi}(b, p, 1) + 1)^{-(p/\ln(b)+1)} \quad (4)$$

For simplicity, θ is set to one in the argument as the transformation eliminates any θ dependence. Similarly, $J(\omega)$ becomes:

$$J(\omega) = \int_0^{\infty} \frac{2G^{\chi}(\tau_1; b, p)\tau_1\tau_0}{1 + \omega^2\tau_1^2\tau_0^2} d\tau_1 \quad (5)$$

where τ_0 has replaced $\tau_0^{\chi}(b, p, \theta)$ and, consequently, represents the true mean of the distribution.

If $F^{\chi}(\tau_c; b, p, \theta)$ had been scaled by the parameter τ_0 , as in ref 1, instead of $\tau_0^{\chi}(b, p, \theta)$, τ_0 of eq 5 would not be the true mean, but a scaling parameter. The mean correlation time could then be calculated from:

$$\langle \tau_c \rangle = \int_0^{\infty} \tau_c F^{\chi}(\tau_c; b, p, \theta) d\tau_c = \tau_0 \int_0^{\infty} \tau_1 G^{\chi}(\tau_1; \tau_0, b, p, \theta) d\tau_1 \quad (6)$$

where $G^{\chi}(\tau_1; \tau_0, b, p, \theta)$ is $F^{\chi}(\tau_c; b, p, \theta)$ scaled about the parameter τ_0 . Being scaled about $\tau_0^{\chi}(b, p, \theta)$ simplifies matters by canceling any previous scaling and making the mean of $G^{\chi}(\tau_1; b, p) = 1$ and, so, $\langle \tau_c \rangle = \tau_0$.

For comparison, the spectral density (eq 5) can be put into a form similar to eq 25 of ref 1:

$$J(\omega; \tau_0, b, p) = \int_0^{\infty} 2\chi^2(s, p) [e^s - 1] \tau_0 / \left\{ \left[\left(\frac{p}{p - \ln(b)}\right)^p - 1 \right] \left[1 + \omega^2\tau_0^2 \left([e^s - 1] / \left[\left(\frac{p}{p - \ln(b)}\right)^p - 1 \right] \right)^2 \right] \right\} ds \quad (7)$$

where p , b , and ω are as defined previously, s is an integration variable,

$$\chi^2(s, p) = \frac{p^p}{\Gamma(p)} s^{p-1} e^{-sp} \quad (8)$$

and τ_0 is the mean correlation time of the distribution.

The relationship between the true mean, τ_0 , of eq 5 and 7 and the originally reported mean,¹ τ_0^{org} , can be calculated from eq 6 and is:

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$$\tau_0 = \tau_0^{\text{org}} \frac{\left(\frac{p^{\text{org}}}{p^{\text{org}} - \ln(b^{\text{org}})} \right)^{p^{\text{org}}} - 1}{b^{\text{org}} - 1} \quad (9)$$

where the superscript org indicates parameters that were fitted from the original distribution. Depending on b and p , this could be a large correction and, consequently, responsible for the $\log \chi^2$'s previously reported unphysical behavior. Also, this equation and the distribution itself are only valid for $p > \ln(b)$ where the distribution is normalizable. The possible limitations of the distribution and its dependencies on p and b are clarified by examining the moments of $G^x(\tau; b, p)$ which are:

$$\langle \tau^n \rangle = \int_0^\infty \tau^n G^x(\tau; b, p) d\tau = \sum_{i=0}^n \binom{n}{i} (-1)^{n-i} \left(\frac{p}{p - i \ln(b)} \right)^p \left(\left(\frac{p}{p - \ln(b)} \right)^p - 1 \right)^{-n} \quad (10)$$

where $\binom{n}{i}$ is the binomial coefficient. The original distribution has a similar form for its moments. For large values of p , the moments are essentially independent of b . For the intermediate values, $\ln(b)$ scales p to smaller values, making the distribution wider for a given $p/\ln(b)$ ratio. Finally, for small values of p , the dependence is unclear as the moments are infinite. This behavior suggests that the natural base e should work as well as any other, i.e., 1000, as long as p is not restricted to integer values. Indeed, with noninteger p values, all data tested fit equally well and with the same predicted τ_0 using either e or 1000 as the base.

To test the corrected $\log \chi^2$ distribution's ability to fit polymer data and yield physically meaningful results, we used it to fit four data sets: polystyrene, polyisoprene, and polybutadiene ^{13}C $T_1 - T_2$ (20.6 MHz) data from the original paper,¹ polyisoprene ^{13}C T_1 (20.1 and 100.6 MHz) data,⁵ poly(isopropyl- d acrylate) in chloroform ^2H $T_1 - T_2$ (13.8 MHz)⁷ data; and toluene- d_6 in polystyrene ^2H $T_1 - T_2$ (30.7 MHz) data.⁸ These systems represent a wide variety of polymer dynamics, namely, bulk polymer dynamics, solution-state polymer dynamics, and solvent dynamics in polymer solutions.

For the polymer data in the original paper, the mean correlation times, τ_0 's, from both the original and modified $\log \chi^2$ seem physically reasonable for polystyrene in o -dichlorobenzene and bulk polyisobutene. However, the original distribution yielded an unusually fast τ_0 of 0.1 ns for bulk polybutadiene. Using eq 9, this τ_0 became 5 ns, the same value fit from the modified distribution. This seems more reasonable. In general, the modified $\log \chi^2$

distribution generates larger τ_0 's than the original. But, with the use of eq 9 both distributions yield the same τ_0 , with smaller values of p requiring larger corrections. These results are typical of all the data fit in this paper.

Unlike $T_1 - T_2$ data investigated, both the modified and original (in conjunction with eq 9) $\log \chi^2$ distributions generate unrealistically long τ_0 's from the polyisoprene ^{13}C T_1 data.⁵ Table 1 lists the results from the ^{13}C data. The reason the $\log \chi^2$ distribution fails for the ^{13}C data is not clear. It may be linked to its undefined moments and that the ^{13}C data only samples the distribution in the megahertz region. As can be seen from Table 1, the modified $\log \chi^2$ compares well until p becomes less than $2 \ln(b)$, below which only the $\log \chi^2$'s first moment exists. For these values of p , the distribution's tail is poorly parameterized and large correlation times may be unduly weighted. To successfully fit data to such a distribution, some constraints on the tail, as the zero frequency T_2 data imposes, would probably help give more reasonable results.

As an alternative to low-frequency data, the log normal distribution might be used. Its moments exist; so, its tail and skew are well-defined.⁹ In general, it has simple dependencies on its parameters (easy to fit), is well-behaved with well-defined moments, and is more skewed than the $\log \chi^2$. It also affords a simple physical interpretation of the underlying processes.¹⁰⁻¹² The distribution of reduced correlation times, $G(\tau; \sigma)$, for the log normal distribution is:

$$G(\tau; \sigma) = \frac{1}{\pi^{1/2} \sigma \tau} e^{-(\ln(\tau) / \sigma + \sigma/4)^2} \quad (11)$$

which would replace $G^x(\tau; b, p)$ in eq 5). Its second moment is:

$$\langle \tau^2 \rangle = e^{\sigma^2/2} \quad (12)$$

and its mean is 1, as expected from the scaling.

The log normal distribution fit both the $T_1 - T_2$ and ^{13}C T_1 data discussed earlier with vanishing error and few iterations of the fitting algorithm.¹³ For these data, except for where $\log \chi^2$ failed, the τ_0 's were essentially identical between the modified $\log \chi^2$ and the log normal, differing from the original $\log \chi^2$ according to eq 9. As mentioned previously, the predicted magnitudes and trends of the τ_0 's were more realistic than those of the original $\log \chi^2$ and, for the PIPA data, also more realistic than other models employed⁷ (compare Figure 1 to similar plots in ref 7). That is, the τ_0 's increased with increasing polymer concentration or decreasing temperature, realistic in an intuitive sense.

Table 1. Fits to the C_1 Methylene ^{13}C T_1 Data of Reference 5 ($M_n = 7000$) ($b = 1000$)

T (K)	T_1 (100 MHz) (s)	T_1 (20 MHz) (s)	$\log \chi_{\text{org}}^2$ ^a		$\log \chi_{\text{org}}^2$ ^b		$\log \chi_{\text{mod}}^2$ ^c		$\log \text{normal}$ ^d	
			τ_0 (ns)	p	τ_0 (ns)	p	τ_0 (ns)	p	τ_0 (ns)	σ
293	0.152	0.035	2.00	7	1.90	7.3	340×10^3	7.5	20.0	3.45
303	0.156	0.043	1.00	7	0.67	8.0	5500	8.0	7.10	3.36
313	0.168	0.053	0.40	8	0.31	9.4	71.2	9.5	3.30	3.27
323	0.185	0.068	0.17	11	0.17	11.5	6.48	11.5	1.40	3.07
333	0.210	0.090	0.10	14	0.10	14.0	1.41	14.0	0.660	2.86
343	0.239	0.135	0.073	24	0.076	23.3	0.272	23.5	0.240	2.25
353	0.275	0.192	0.062	34	0.064	35.7	0.139	35.7	0.130	1.80
363	0.323	0.255	0.053	45	0.054	45.6	0.097	45.6	0.095	1.57
373	0.378	0.310	0.043	47	0.044	45.7	0.079	45.7	0.078	1.58
	E_a high temp (kJ)		18.6		19.6		43.6		38.7	
	E_a low temp (kJ)		63.0		59.2		257 ^e		68.5	

^a Fit by Denault and Prud'homme using original $\log \chi^2$. ^b Recalculated data using original $\log \chi^2$ and noninteger p 's. ^c Modified $\log \chi^2$ (eq 4). ^d Log normal distribution (eq 11). ^e See text for explanation.

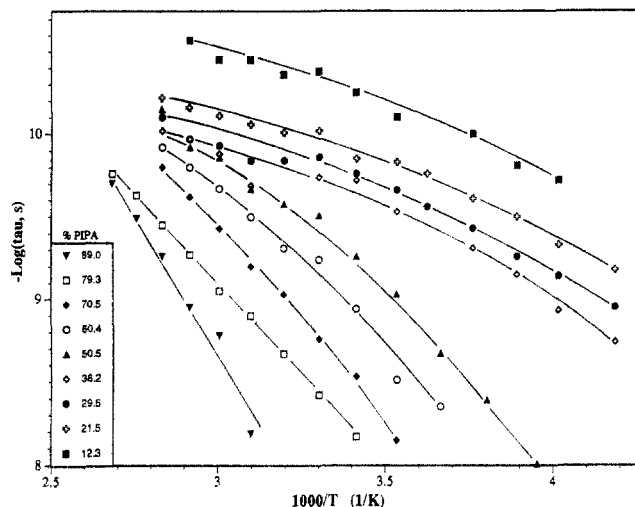


Figure 1. τ_0 values from the log normal distribution's fit to ^2H T_1 and T_2 data (ref 7) as a function of temperature and PIPA concentration. The curves drawn are for visual clarification.

For ref 5, the main difference between the log normal and the original $\log \chi^2$ is that the log normal predicts a higher apparent activation energy for the high-temperature data and a 10-fold increase in τ_0 at low temperatures. As in the ref 5, the NOEF's were not used in the fitting procedure. They offer an independent test of each distribution's predictive ability. Unfortunately, the calculated NOEF's follow the experimental values for all the distributions and no distinction can be made. For extremely broad distributions, however, the log normal has a limiting, τ_0 -independent, NOEF value of 1.33 compared to the $\log \chi^2$'s value of 0.9 (at 20 MHz). This increase is presumably due to the larger skew of the log normal distribution. None of the experimental data required broad enough distributions to test this difference.

In conclusion, τ_0 of the original $\log \chi^2$ distribution is a scaling parameter which is often, but not always, representative of the mean. Comparisons and predicted trends may be on different scales unless a correction to the true mean (eqs 6 and 9) is made. Modifying the distribution yields a new distribution in which τ_0 is the true mean. However, both the original and modified $\log \chi^2$ distribution have limited use as their moments can be ill-defined and careful sampling of the frequency space is required. We

prefer the log normal distribution as it is better skewed and has well-defined moments and simple derivatives. Its ability to fit and give physically reasonable results from low- and high-frequency $T_1 - T_2$ data as well as solely high-frequency T_1 data indicates that it may be useful where the $\log \chi^2$ appears unphysical.^{6-8,14,15}

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$$\% \text{ error} = \sum_{i=1}^2 \left(\frac{T_i^{\text{exp}} - T_i^{\text{calc}}}{T_i^{\text{exp}}} \right)^2$$
 were 10^{-6} for both Schaefer's original distribution and the modified $\log \chi^2$ and 10^{-30} for the log normal. For all $\log \chi^2$'s, the number of iterations ranged from 20 to 2000, depending on the quality of the initial guesses. For the log normal, the number of iterations was always less than 50, independent of the initial guess.
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