ECEA 2019
5th International Electronic Conference on Entropy and Its Applications
18–30 November 2019

sciforum

Conference Proceedings Paper

The New Method Using Shannon Entropy to Decide the Power Exponents on JMAK Equation

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Abstract: JMAK (Johnson-Mehl-Avrami-Kolmogorov) equation is exponential equation inserted power-law behavior on the parameter, which is widely utilized to describe relaxation process, nucleation process, deformation of materials and so on. Theoretically the power exponent is occasionally associated with geometrical factor of nucleus, which gives integral power exponent. However, non-integral power exponents occasionally appear and they are sometimes considered as phenomenological in the experiment. On the other hand, the power exponent decides the distribution of step-time when the equation is considered as the superposition of step function. This work intends to extend the interpretation of power exponent by the new method associating Shannon entropy of distribution of step-time with the method of Lagrange multiplier in which cumulants or moments obtained from distribution function are preserved. This method intends to decide the distribution of step-time through power exponent, in which certain statistical values are fixed. The Shannon entropy introduced the second cumulant gives fractional power exponents that reveal symmetrical distribution function that can be compared with the experimental results. Various power exponents in which other statistical value is fixed are discussed with physical interpretation. This work gives new insight into the JMAK function and the method of Shannon entropy in general.

Keywords: stretched exponential; Shannon entropy; power-law; JMAK equation

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1. Introduction

The stretched exponential function is descrinbed as follows,

$$f\left(t, K, \beta\right) = \exp\left[-\left(\frac{t}{K}\right)^{\beta}\right]. \tag{1}$$

It is widely applied to describe relaxation processes [1–5], kinetics of crystallization [6–9], deformations of materials [10,11] so on. The name of stretched exponentials corresponds to the case for $\beta < 1$ while the opposite case of $\beta > 1$ is called compressed exponential function. The latter case corresponds to JMAK (Johnson-Mehl-Avrami-Kolmogorov) equation [6–9], and β is sometimes called Avrami constant. In the context of JMAK equation, theoretically it is occasionally associated with geometrical factor of nucleus. Avrami constant β is originated from the dimensionality in which nucleation occurs D, which has following relation $\beta = D + 1$. The surface nucleation involving effectively two-dimension gives $\beta = 3$, the homogeneous nucleation with three-dimension gives $\beta = 4$, which all should result in integral constant [12]. However, occasionally non-integer, anomalous Avrami constants are found [13–15]. This anomalousness is explained thorough the heterogeneity of dimensionality of nucleation, and distribution of pre-existing nuclei, and nucleation rate [16–19]. The limitation to associate JMAK model with dimensionality of nucleus is designated [20]. These works suggest that JMAK equations still demand interpretations.

On the other hand, Equation (1) mathematically corresponds to Weibull distribution in extreme value theory [21–23]. It is the probability distribution function of which the rate of occurrence of events varies with time, applied to the particle distribution and failure analysis for engineering. In this context, the power exponent β controls the shape of distribution of event; it is sometimes called shape parameter [24]. Time-compressed equation corresponds to Weibull distribution of which rate of occurrence of event increases with time. Hence the power exponents decide the distribution of occurrence.

It is suggested that theoretical models for Equation (1) involve the spatial-temporal heterogeneity. Hierarchical constrained model involves the constraints among Ising spins[25], Trap model involves the traps in the space in which Brownian motion occurs [26]. Evesque demonstrated that two molecules reaction in fractal geometry gives fractional power exponent for Equation (1) [27].

Based on these reports and facts that β decides the distribution, the new method to estimate the distribution is proposed, using Shannon entropy [28]. Shannon entropy [29] is utilized for the probability density function to estimate the average amount of information content of the distribution, which reflects the statistical homogeneity. Introducing Shannon entropy into the distribution function obtained from Equation (1), if was found that the Shannon entropy to which first moment is introduced has supremum at $\beta = 1$; it corresponds to single exponentials [28]. This result includes the insight on the relation between stretched exponentials and single exponentials.

This method suggestive on the application of Shannon entropy into the kinetic equations. Analyzing the method carefully, it consists of the maximum entropy estimation and Lagrange multiplier with β as a parameter. Maximum entropy method is applied to estimate the optimal distribution [31–33]. However, this method is different from general maximum entropy estimation [33] on the point that the fundamental distribution function has already fixed as Equation (1). The time compressed equation has already based then it estimate the optimal *shape* of distribution via β while the constraint condition is introduced. This method decides β that gives optimal distribution of step times, which depends on the given boundary condition.

Herein, this work intends to extend the previous method and attempt to explore the distributions of Equation (1) in which certain statistical quantities are fixed. Then we attempt to discuss the physical interpretation for obtained distributions.

2. Method: Maximum Entropy Estimation Method Based on JMAK Equation

The point that it is different from general maximum entropy estimation [33] is that the form of equation has already fixed on Equation (1), JMAK equation. Thus, here we call this method Maximum entropy estimation method based on JMAK equation. The method consists of two procedure. First is introduction of Shannon entropy into the compressed exponential equation Equation (12). Second is introduction to statistical quantity which corresponds to restricted condition.

At first, the integral equation is assumed as,

$$\exp\left[-\left(\frac{t}{K}\right)^{\beta}\right] = \int_0^{\infty} D(\tau)\, F(t-\tau)\, d\tau \tag{2}$$

where $F(t-\tau)$ is step function. Then distribution function $D(\tau)$ is obtained as follows,

$$D(\tau, K, \beta) = \frac{\beta}{K}\left(\frac{\tau}{K}\right)^{\beta-1} \exp\left[-\left(\frac{t}{K}\right)^{\beta}\right]. \tag{3}$$

Shannon entropy is defined as,

$$H(K,\beta) = \int_0^\infty D(\tau,K,\beta)\ln\frac{D(\tau,K,\beta)}{C}d\tau \quad (4)$$

where C is the constant for nondimensionalization. Then Shannon entropy of Equation (3) is given as follows,

$$H(K,\beta) = \gamma\left(1-\frac{1}{\beta}\right) + \ln\frac{CK}{\beta} + 1 \quad (5)$$

where γ is Euler constant. Now $H(K,\beta)$ is function with two parameters K and β. To introduce the constraint condition, K is now related with parameter β. Certain statistical quantity $\langle\xi\rangle$, which is obtained using Equation (3) is given as

$$\langle\xi\rangle = \Phi(K,\beta). \quad (6)$$

For example, $\langle\xi\rangle$ is first moment when $\Phi(K,\beta) = \int_0^\infty \tau D(\tau,K,\beta)\,d\tau$. As $\langle\xi\rangle$ is constant, Equation (6) can be reformalized as

$$K = K(\langle\xi\rangle,\beta). \quad (7)$$

Now $K = K(\langle\xi\rangle,\beta)$ is a function with one parameter β. Following Lagrange multiplier method, then we have

$$H(K,\beta) = H[K(\langle\xi\rangle,\beta),\beta] = H(\beta,\langle\xi\rangle). \quad (8)$$

Equation (8) is Shannon entropy of which statistical quantity $\langle\xi\rangle$ is fixed. In order to get optimal distribution, supremun of Equation (8) is identified as follows,

$$H(\beta^*,\langle\xi\rangle) = \sup_\beta H(\beta,\langle\xi\rangle). \quad (9)$$

β^* gives the optimal distribution in which $\langle\xi\rangle$ is fixed.

3. Result and Discussion

3.1. Constraint Condition of *n*-th Moment

In the previous work, first moment was introduced to Shannon entropy Equation (5) to find $\beta^* = 1$ [28]. Here we discuss the case in which other moments (e.g., third moment, n-th moment) are fixed. Moment gives the information of shape of function. First moment is mean value, second moment is related with variance and so on.

N-th moment of Equation (3) is given as

$$\langle K^n\rangle = \int_0^\infty \tau^n D(\tau,K,\beta)\,d\tau = \frac{K^n}{\beta}\Gamma\left(\frac{n}{\beta}\right) \quad (10)$$

where $\Gamma(x)$ is Gamma function.

By introducing n-th moment of Equation (3) into Equation (5), we have

$$H(\beta,\langle K^n\rangle) = \gamma\left(1-\frac{1}{\beta}\right) - \frac{1}{n}\ln\Gamma\left(\frac{n}{\beta}\right) + \left(\frac{1}{n}-1\right)\ln\beta + \ln C\langle K^n\rangle^{1/n} + 1 \quad (11)$$

We can easily estimates β^* by differentiating above Equation (12) as follows,

$$\frac{dH(\beta,\langle K^n\rangle)}{d\beta} = \frac{1}{\beta^2}\left[\gamma + \psi\left(\frac{n}{\beta}\right) + \beta\left(\frac{1}{n}-1\right)\right] \quad (12)$$

where $\psi(x)$ is Digamma function. β^* of each n-th moments are listed in Table 1. β^* increases with n and they are fractional number except for $n = 1$ and 3. These results seem trivial but third moment can be related with volume in the case that t has space dimension. Rosin-Rammler distribution [34], which corresponds to Equation (1), is applied for particle distributions. Rosin Rammler distribution has $\beta > 1$. These moments can be related with physical quantity through distribution function.

Table 1. Table of each β^* in which the entropy is maximized in each n-th moments.

n	β^*
1	1
2	1.2994
3	1.5
4	1.6533
5	1.7784
10	2.1981
100	3.8527
1000	5.7403

3.2. *Constraint Condition of Second Cumulant: Variance*

Now let us see the Shannon entropy to which the variance of Equation (1) is introduced. The variance of Equation (1) is

$$\sigma^2 = K^2 \left[\Gamma\left(1 + \frac{2}{\beta}\right) - \Gamma\left(1 + \frac{1}{\beta}\right)^2 \right]. \tag{13}$$

Introducing Equation (13) into Equation (5), we have Shannon entropy of which variance is fixed,

$$H\left(\beta, \sigma^2\right) = \gamma\left(1 - \frac{1}{\beta}\right) - \ln\beta - \frac{1}{2}\ln\left[\Gamma\left(1 + \frac{2}{\beta}\right) - \Gamma\left(1 + \frac{1}{\beta}\right)^2\right] + \ln C\sqrt{\sigma^2} + 1. \tag{14}$$

The relation of H and β is described in Figure 1(a). The absolute value of H is relative depending on C. Continuous Shannon entropy is relative to the coordinate system. Here we're interested in the relative value of entropy, particularly supremum value. β that gives supremum of H is $3.7673\cdots$ though H shows plateau over $\beta \simeq 3$. Interestingly, β that have large values of entropy seems to be related with symmetry of distribution as Figure 1(b) shows. The β having lower entropy (e.g., $\beta = 0.5 \sim 1.5$) give asymmetric distribution of τ while β having larger values ($\beta = 3.76 \sim 10$) give symmetric distribution.

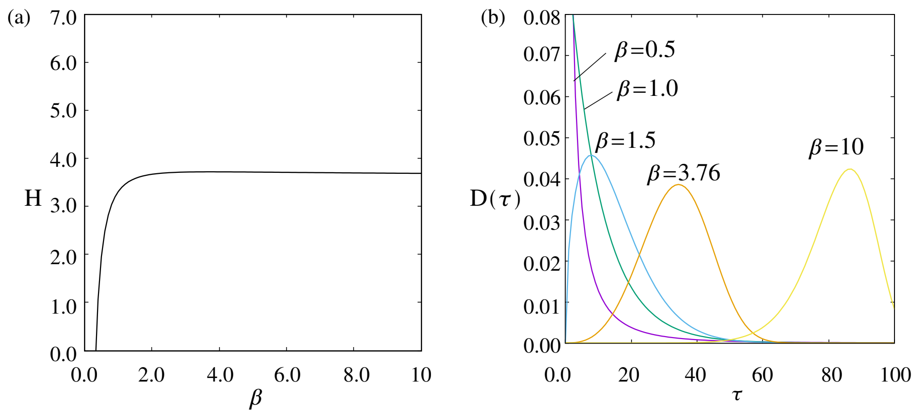

Figure 1. (Color online) (a) Dependece of H introduced variance with β. (b) Comparison of distribution of step time for different β vaules ($\beta = 0.5, 1.0, 1.5, 3.76, 10$). $\sigma^2 = 100$, $C = 1$.

The relation between distribution and variance was suggested in the relaxation of shrink of PNIPA gels [30]. The relaxation process of PNIPA gels involves two-steps shrinking. First shrink undergoes diffusion process that was described with a single exponential while second shrink can be described compressed exponential having $\beta = 2 \sim 4.5$. These reported β have largest Shannon entropy, which suggests the correspondence. In the shrinkage of PNIPA gels, each part of gels undergoes the step-like shrinkage, which corresponds to step-function. However, it is expected that the timing of shrinkage has variations, which results in symmpetric distribution. This interpretation reinforce that the JMAK relaxation of PNIPA gels involves the process in which the variance is fixed.

3.3. Constraint Condition of Third Cumulant: Skewness

The third cumulant, skewness reflects the asymmetry of distribution. The thrid cumulant is obtained as follows,

$$c^3 = K^3 \left[\frac{1}{\beta}\Gamma\left(\frac{3}{\beta}\right) - \frac{3}{\beta^3}\Gamma\left(\frac{2}{\beta}\right)\Gamma\left(\frac{1}{\beta}\right) + \frac{2}{\beta^3}\Gamma\left(\frac{1}{\beta}\right)^3 \right]. \tag{15}$$

By introducing Equation (15) into Shannon entropy Equation (5) in the same way, we can estimate the Shannon entropy of which skewness is fixed as

$$H\left(\beta, c^3\right) = \gamma\left(1 - \frac{1}{\beta}\right) - \frac{1}{3}\ln\beta^3 \left[\frac{1}{\beta}\Gamma\left(\frac{3}{\beta}\right) - \frac{3}{\beta^3}\Gamma\left(\frac{2}{\beta}\right)\Gamma\left(\frac{1}{\beta}\right) + \frac{2}{\beta^3}\Gamma\left(\frac{1}{\beta}\right)^3 \right] + \ln C\sqrt[3]{c^3} + 1. \tag{16}$$

Figure 2(a) is the dependence of Shannon entropy introduced skewness with β. β^* has value around 1.20 and decreases monotonically. The distributions of τ having $\beta = 0.5, 1.2, 3.76$ are compared in Figure 2(b).

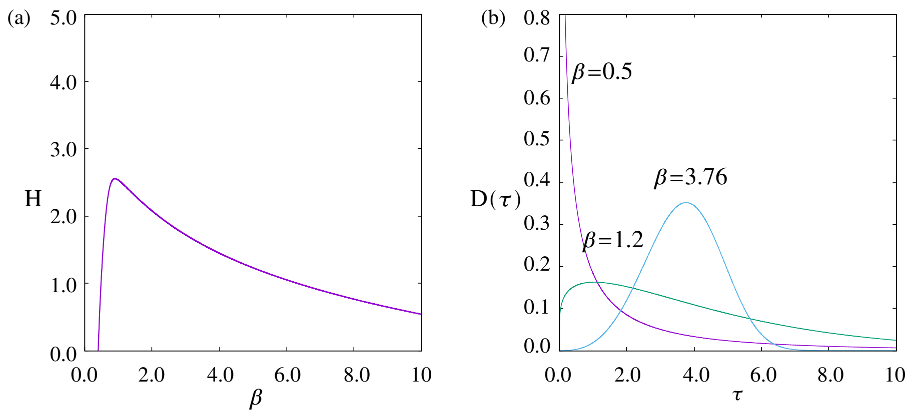

Figure 2. (Color online) (a) Dependence of Shannon entropy of which skewness is fixed with β. (b) Comparison of distribution of step-times τ for $\beta = 0.5, 1.2, 3.76$. $c^3 = 100$, $C = 1$.

β^* seemingly gives positive skewed distribution. Negative skew distribution has to be asymmetric for left side but it is not possible for Equation (3).

4. Conclusions

In this work, the new method to obtain the distribution is attempted using Shannon entropy. The point that it is different from general maximum entropy estimation [33] is that the form of equation has already fixed on Equation (1), JMAK equation. The Shannon entropy of JMAK equation was firstly estimated using distribution function $D(\tau)$, which is obtained by integral equation of which Kernel $F(t - \tau)$ is step function. Introducing the certain statistical quantity, the Shannon entropy of which the

the quantity is fixed was estimated. The optimal distributions are obtained by identifying β^*, which is β that gives supremum of H.

The Shannon entropies introduced n-th moments gives β^* fractional power exponents except for first and third moments. The Shannon entropy which variance is introduced shows plateau over $\beta = 3$. The value of entropy seems to reflect the symmetry of distribution of step times. The power exponents observed in the shrinking of PNIPA gels have the value around $2 \sim 4.5$, which corresponds to the distribution of largest entropies. Shannon entropy which third cumulant, skewness is introduced has supremum at $\beta^* = 1.20$, which gives the positive-skewed distribution.

The Shannon entropies which variance or skewness is introduced are quite interesting as its β^* seems to give the distribution in which its constraint condition, variance and skewness is typically fixed. There is a interpretation of maximum entropy. Kolmogorov-Sinai theorem [35] says that the partition obtained by maximum entropy gives smallest subsets of generator. The distribution of τ corresponds to the partition of step-times. If we follow the theorem, these distributions gives the generator in which each constraint conditions, variance or skewness are fixed. The relation and interpretation based on the Kolmogorov-Sinai theorem should be pursued for further development.

The method to decide β using Shannon entropy with Lagrange multipliers give the optimal distribution of which physical quantity is fixed. The phenomnena which are described by JMAK type equations may involve these constraint conditions.

Funding: This research received no external funding.

Acknowledgments: The author wish to thank prof. K. Osaki and K. Shigeoka for discussion of this research.

Conflicts of Interest: The author declares no conflict of interest.

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