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Improved Approximations of Non-Gaussian Probability, Force and Energy of a Single Polymer Chain

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The mechanical behavior of polymers such as their probability density function (PDF), strain energy and entropic force, has long been described by the non-Gaussian statistical model. Non-Gaussian models are often approximated by the Kuhn-Grün (KG) distribution function, which is derived from the first order approximation of the complex Rayleigh's exact Fourier integral distribution. The KG function is widely accepted in polymer physics, where the non-Gaussian theory is often used to describe energy of the chains with various flexibility ratios. However, KG function is shown to be only relevant for long chains and becomes extremely inaccurate for the chains with less than 40 segments. In comparison to KG model, other approximation of non-Gaussian statistical model are often less accurate, and those with higher accuracy, are usually too complex to be implemented in large-scale simulations. Here, a new accurate approximation of the Non-Gaussian PDF, entropic force and strain energy of a single chain subsequently is developed to describe the mechanics of a polymer chain. With similar level of complexity, the presented approximations of Non-Gaussian PDF, strain energy and entropic force are at least 10 times more accurate than KG approximations and thus are an excellent alternative option to be used in micro-mechanical constitutive models.

I. INTRODUCTION

In computational simulations of polymeric systems, two competing factors determine the type of the material model that should be used in the simulation; computational cost (i.e. the simulation time) and the accuracy. Optimizing the trade-off between these two factors determines the minimum requirements of the model. In mechanics of polymers, the excessive computational costs of accurate models prevents them from being used in large-scale simulations. Here, our goal is to propose a family of effective approximation functions with different range of accuracy and complexity that can address the existing trade-off problem.

In polymer physics, micro-mechanical constitutive models are mostly derived from the non-Gaussian statistical distribution of a randomly jointed molecular chain [1–4]. In these models, the elasticity of the chains is induced from the changes in the probability of chain end-to-end distance, r, in the course of deformation, and thus the change of the chain entropy [5]. The probability distribution function (PDF) of a perfectly flexible chain with fixed end positions $P(r)$ can be calculated using a solution that is first proposed to solve the random flights problem [6–8]. The concept was later used in several theoretical and experimental studies to describe the properties of dilute polymer solutions. In dilute solutions, the isolation of polymer molecules allows characterization of individual molecules. A strong correlation was found between the number of segments of a chain, n, and its end-to-end distance, r given by $r \propto \sqrt{n}$ [5]. This correlation later became the basis to consider $P(r)$ similar to that of a random-flight problem.

In most statistical polymer models, the stress-strain relation for the polymer matrix originates from molecular description of deformation of single chains. The first attempt in understanding behaviour of polymers was based on a statistical approach to derive entropic conformation of a polymer chain, which was independently proposed by Kuhn [6] and Guth and Mark[9]. Both theories successfully derived the Gaussian PDF estimation of a polymer chain from its entropy [10]. However, it can be shown that Gaussian statistics are exact only for the polymer chains with infinite length or very small deformation. Later, Kuhn and Grün proposed the inverse Langevin approximation for *'freely jointed chain'* (FJC) to address the effect of finite chain length in the network, and reached to pioneer model for single chain statistics in large deformation. The popular Kuhn-Grün (KG) model describes the statistical probability of existence of an unconstrained single chain with an entirely random orientation in space [11]. Beside simplicity, the relevance of the assumption has motivated the majority of models ever since to use the KG function to estimate non-Gaussian PDF [3, 12–14]. This estimation is the first order approximation of the Rayleigh's exact Fourier integral distribution function [15], and can describe the finite extensibility of the polymer chains even at large strains. This model is widely accepted in the field of rubber elasticity due to its accuracy to captures the ultimate strain of polymer network [2, 16, 17]. In polymer physics, most constitutive models of the polymer matrix such as 3-chain [18], 4-chain [19], 8-chain [2], the full-network models [5, 20] , and

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the micro-macro unit sphere models [21] are based on the KG approximations of non-Gaussian theory, which generally includes the inverse Langevin function [5]. However, different studies in the literature examined its relatively large error for the short chains [4, 5].

As it shown in the literature, Gaussian distribution, energy and entropic force have very good agreement with theory of rubber elasticity and experimental evidences in small deformations. As deformation increases this theory cannot predict the behavior of elastomeric material with limited extensibility accordingly. In order to overcome this shortcoming, the non-Gaussian theory of rubber elasticity proposed to improve the theory for deformations near the failure of the material. The complexity some of these theories leads to extensive application of KG theory in different area of polymer physics as a simple alternative of non-Gaussian theory. Despite the fact that KG theory is only valid for long chains, there are several studies that used this theory with less than 20 segments chains [17, 21, 22]. Arruda and Boyce (1993) [23] proposed their outstanding 8-chain model using KG theory, which is validated against experimental data assuming the chains length as low as 8. The Full network model [24] that considers the spatial uniform distribution used the KG model by chains with only 2.8 segments (the relative error of entropic force for chain with 3 segments will be shown in section IV, which is reach to more than 100% , Fig. 7).

Despite its wide acceptance, KG estimation is only valid for sufficiently large chains ($n \gg 40$) [10, 16, 25]. While KG shows good graphical agreement with Rayleigh's exact distribution in low extensibility[25], it yields significant errors in the large extensibility (see Fig.1a). Moreover, for long chains, KG approximation becomes strongly inaccurate as $\frac{r}{nl} \to 1$ as the probability approaches to zero. Figure 1-a shows that the relative errors of a short chain and a long chain almost is the same unlike the most stated in the literature [25]. In polymer physics, the strain energy of a chain W, which is correlated with $W \propto \ln(P(r,n)))$, is used more often than the $P(r)$, and thus is the subject of interest. In Fig.1-b, we have plotted the relative errors in approximating W by using KG PDF. As it can be in this figure, the maximum relative error of KG energy function is about 25% for the chain with 8 segments. However, the maximum relative error of KG energy function can reach to as much as 100% for the chain with 3 segments. It is evident that the relative error for short chains are much higher than that of long chains. To address this problem, Jerningan and Flory [25] introduced a new approximation, referred to as 'amended Kuhn-Grün' (A-KG), by adding an extra multiplicative term to the KG function. Due to its complexity, A-KG model were used in very few studies such as the work of Elias-Zuniga and Beatty [12].

Currently, almost all statistical models of chain elasticity are based on the KG PDF. Accordingly, the entropic force resulted from KG are the function of one parameter only; namely the extensibility ratio, $t = \frac{r}{L}$ where r is the end-to-end distance of a chain, $L = nl$ the contour length. However, studies suggest that the entropic force resulted from PDFs are influenced by two parameters, namely t and n. To date, most constitutive models suffer from the large errors induced by the KG function in predicting the PDF, force or energy in the case of short chains. So far, there is no other feasible approximation of PDF that can also capture the behavior of the short chains.

Here, we developed an approach to derive a family of approximations for the PDF, force and strain energy of polymer chains. Such an approximation model is particularly relevant in constitutive models of polymer chains that use the inverse Langevin function (ILF) $\mathcal{L}^{-1}(\frac{r}{nl})$ to describe the entropic force of a chain. Since the ILF cannot be derived explicitly, approximation functions with different degree of errors are used to represent it. Recently, due to significant improvement of our computational power for simulating the entropic energy of the whole network, accurate approximation of the ILF has become a subject of interest. In the last decade, several high accuracy approximations with errors as low as 10^{-4}% have been introduced [26–29]. While accurate approximations of the ILF can reduce the error of KG energy and force approximations, there still exists a significant error in those approximations due to the intrinsic error associated with KG PDF. Such error necessitates the future efforts to be directed toward deriving a new approximation for PDF function first before deriving force and energy.

The fundamentals of non-Gaussian statistical mechanics of polymers are first reviewed in section II. We propose new approximation functions for PDF in section III. In section IV, the error of the current approximations of entropic energy and force of a polymer chain is calculated to show the relevance of new approximation functions. Finally, in section V and VI new approximation functions for entropic force and energy of a single polymer chain is provided. The functions show negligible error even for short chains and are relevant for a long range of extensibility ratios.

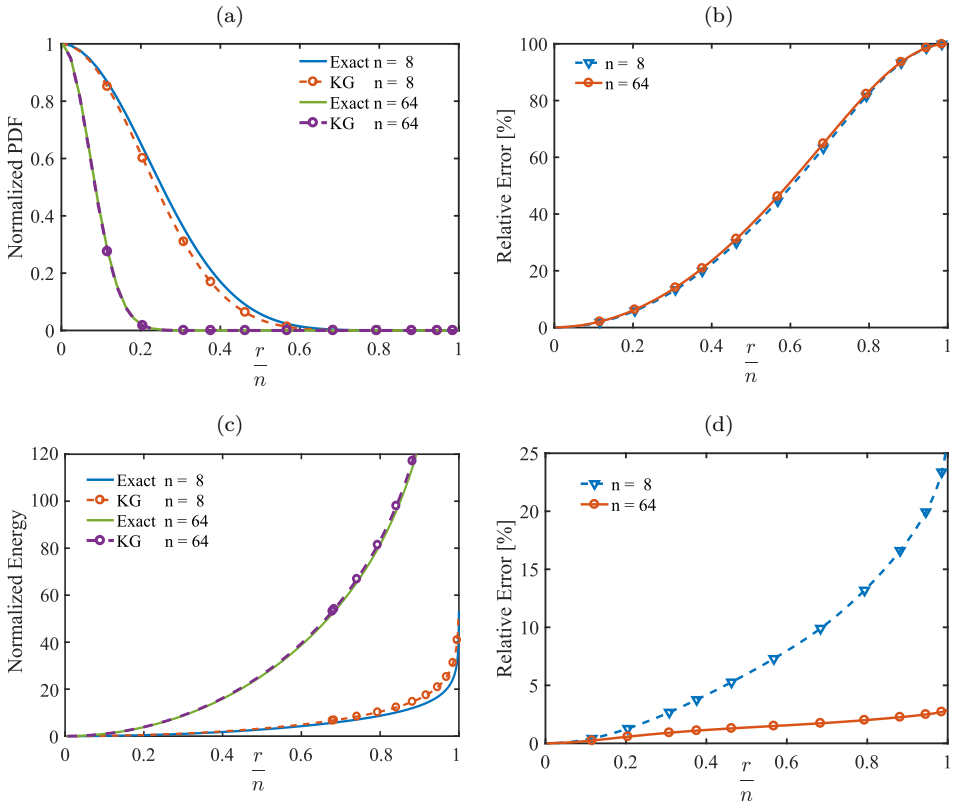

Figure 1. Comparison between Exact and KG a- Normalized PDF, b-Relative error of PDF, c- Normalized strain energies, and d- Relative error of strain energies for chains with $n = 8$ and 64

II. STATISTICAL MECHANICS TREATMENTS

In this section, the non-Gaussian PDF of existence of a chain, $P(\overrightarrow{r})$, with end-to-end vector $\overrightarrow{r}$ and contour length nl is briefly reviewed. The probability distribution of a freely jointed chain (FJC) is the same as 3-D random flight problem, which describes the probability of a chain ending at a certain point at distant r. In 1905, Pearson discussed the distribution of position of a mosquito in a forest [30]. To address this problem, several distribution functions have been developed ever-since based on the Fourier integration of the random-flight problem, first of which was developed by Rayleigh in 1919 by using the discontinuous integral of Dirichlet [15]. The probability of existence of a chain can be derived by taking the Fourier transform of characteristic function as

$$P_{exact}(r) = \frac{1}{2\pi^2 r}\int_0^\infty \rho sin(\rho r)\left(\frac{sin(\rho l)}{\rho l}\right)^n d\rho. \tag{1}$$

This equation would be difficult to solve analytically for chains with large number of segments, $n > 10$. The exact non-Gaussian distribution function for 3, 4, and 6 steps were derived by Rayleigh as sets of discontinuous polynomials [15]. The exact solution of Fourier integral of Eq.1, often referred to as **"Rayleigh exact distribution function"**, was later derived by Treloar [8] based on the theory of random sampling as

$$P_{exact}(r) = \frac{1}{2^{n+1}(n-2)!\pi l^2 r} \sum_{k=0}^{k\leq\frac{n-\frac{r}{l}}{2}} (-1)^k \binom{n}{k} \left(n-2k-\frac{r}{l}\right)^{n-2}. \tag{2}$$

Similarly, Wang and Guth [18], Nagai [31], and Hsiung et al. [32] derived similar formulations with different mathematical approaches. To avoid the high computational cost of the exact solution (due to its piece-wise nature), several approximation methods were developed for non-Gaussian distribution. The degree of mathematical difficulty of these approximations depends on the required accuracy and the covered extensibility ratio ($t = \frac{r}{nl}$). The Gaussian distribution, for example, is simple and has a good agreement with the exact distribution at small t. It can be shown that the first order approximation of 1D random walk problem yields to the Gaussian distribution (see Appendix

A). However, Gaussian distribution becomes exponentially inaccurate for the chains in their fully extended length ($t \cong 1$). Thus, a more elaborate distribution function is required to capture the non-Gaussian PDF. In general, the approximation functions that are developed to approximate the Rayleigh exact PDF, Eq.2, can be categorized into three types (i) Taylor expansion approximations which are valid for long chains with low extensibility, (ii) Statistical approximation which are valid for long chains at all extensibility ratios and (iii) Steepest decent approximations which are valid for all chains and extensibility ratios, although it has a high computational cost [18].

(i) Taylor expansion approximation (TE) has an acceptable accuracy for long chains at small t. In this case Eq. 1 can be rewritten as

$$P_{exact}(r) = \frac{1}{2\pi^2 r}\int_0^\infty ksin(kr)e^{\phi(k)}dk, \qquad (3)$$

where $\phi(k) = n\ln\frac{\sin(ka)}{ka}$. To further simplify the above equation, $\phi(k)$ can be substituted by its Taylor expansion $\phi(k) = -n\Sigma_{k=1}^{\infty}\frac{B_{2k-1}(2s)^{2k}}{(2k)!2k}$, where B_n is Bernoulli number. By using the first term of $\phi(k)$ Taylor series, Eq.3 yields the standard Gaussian distribution function, P_G, as [10],

$$A_n(\rho) \cong exp\left(-\frac{n(\rho l)^2}{6}\right)$$
$$\rightarrow \qquad P_G(r) = A_0\exp\left(-\frac{r^2}{2n}\right), \qquad (4)$$

where $A_0 = \left(\frac{3}{2\pi a^2 n}\right)^{\frac{3}{2}}$. By using full expansion of $\phi(k)$ a more accurate approximation of P_{exact} can be obtained as,

$$P_T(r) = A_0\left(1 - \frac{3}{20n}\left(5 - 10\frac{r^2}{n} + 3\frac{r^4}{n^2}\right) + \dots\right)\exp\left(\frac{-3r^2}{2n}\right). \qquad (5)$$

In order to further enhance the accuracy of the approximation, the Taylor expansion can be written around its saddle point [33] as,

$$P_{T-SP}(r) \cong A_0\exp\left(-n\left[\frac{3}{2}t^2(1 - \frac{1}{n} + \frac{2}{5n^2}) + \frac{9}{20}t^4(1 - \frac{11}{5n}) + \frac{99}{350}t^6\right]\right). \qquad (6)$$

To simplify Eq. 6, one can assume $\frac{1}{n} \rightarrow 0$ for long chains ($n \gg 40$), and thus reduce Eq. 6 to

$$P_{T-SP}(r) \cong A_0\, exp\left(-n\,\alpha(t)\right), \qquad (7)$$

where $\alpha(t)$ is a function of extensibility ratio only. Since Eq. 7 is equal to the distribution function resulted from Taylor expansion of ILF, one can conclude that the ILF approximations are also mainly relevant for long chains.

(ii) Statistical approximation (SA) of P_{exact} , also known as Kuhn-Grün (KG) PDF, is particularly accurate for the large chains in the highly stretched state [5]. KG PDF is introduced in 1942 through the maximum term method of statistical mechanics as

$$P_{KG}(R) = c\left\{\frac{\sinh(\beta)}{\beta\exp(t\beta)}\right\}^n, \qquad (8)$$

where c is normalization factor that can be A_0 or $P_n^{exact}\left(10^{-2}\right)$. The ILF parameter $\beta = \mathcal{L}^{-1}(t)$ can be implicitly calculated through Langevin function equation, $t = \mathcal{L}(\beta) \equiv \coth(\beta) - \frac{1}{\beta}$. Note that James and Guth (1943) [1] and Flory (1953) [34], independently derived the same formulation with different approaches. In another effort Jernigan and Flory [25] derived an amended version of KG distribution function as

$$P_{A-KG}(r) = A_0\left[\frac{\sinh(\beta)}{\beta\exp(t\beta)}\right]^n\left[\frac{\beta}{t}\right] = \frac{\beta}{t}P_{KG}. \qquad (9)$$

(iii) Steepest decent approximation (SD) is derived by Wang and Guth [18] based on the saddle point approximation of Eq.2, which gives

$$P_{WG}(r) = A_0\left[\frac{\sinh(\beta)}{\beta\exp(t\beta)}\right]^n\left[\frac{\beta}{t}\right]\left[1 - t^2 - \frac{2t}{\beta}\right]^{-\frac{1}{2}}\left[1 + \frac{q(t)}{n} + ...\right], \qquad (10)$$

where $q(t)$ is a specific function [35]. Using steepest decent approach, another approximation function is derived by Yamakawa [10]

which can be rewritten similar to P_{WG} as [1]

$$P_{SD}(r) = A_0 \left[\frac{\sinh(\beta)}{\beta \exp(t\beta)}\right]^n \left[\frac{\beta}{t}\right] \left[1 - t^2 - \frac{2t}{\beta}\right]^{-\frac{1}{2}} \tag{11}$$

Interestingly, Eq.11, P_{SD} is the first four terms of Wang and Guth approximation Eq.10 and 9, P_{A-KG} is the first three terms. As mentioned by Jerningan and Flory [25], the term $\left[\frac{\sinh(\beta)}{\beta \exp(t\beta)}\right]^n$ becomes more significant and then the other terms can be neglected for longer chains same as KG model. However, the other terms has more contribution in the accuracy of the model for shorter chains.

To date, there exists no comprehensive study to characterize the error induced by each of the aforementioned approximation methods in predicting PDF of chains with different lengths extensibility ratios. Here, a comprehensive comparison of the aforementioned approximation functions in predicting PDF and strain energy of chains with different lengths at different extensibility ratios is presented (see Fig.2).

P_G and P_T have almost similar and relatively small relative with respect to the exact distribution in only very small t. Interestingly, P_{T-SP} with only three terms has extremely low relative error with respect to exact distribution in small and moderate extensibility ratios. Note that increasing the number of terms in the expansion of this approximation can improve the relative error for larger t. As expected, $P_{KG}(R)$ has a negligible error for small t which exponentially grows as t tends to 1. Despite being the most popular approximation method, $P_{KG}(R)$ can be only a good approximation for long chains that are not stretched. Therefore, it is not suitable for models of rubber elasticity to derive force and energy due to its large error in predicting the asymptotic behavior of $\ln(P_{exact})$. The W_{KG} has a considerably large error which can become even larger in shorter chains. For example, the relative error of strain energy resulted from KG PDF for a short chain with 8 segments is at least 8 times higher than that of a long chain with 64 segments. While many other approximations such as P_{A-KG} provide slightly more accurate approximations than KG, they remain unpopular due to the extreme complexity of their first derivatives. Despite the fact that P_{SD} has an acceptable accuracy even for short chains, utilizing this distribution function is almost unfeasible due to its mathematical complexity.

[1] Original formulation presented in [10] is $P_Y(r) = 3^{\frac{3}{2}} A_0 \frac{\beta^2}{t\left[1-\left(\frac{\beta}{\sinh(\beta)}\right)^2\right]^{\frac{1}{2}}} \left\{\frac{\sinh(\beta)}{\beta \exp(t\beta)}\right\}^n$, which can be rewritten as P_{SD} by considering $1 - t^2 - \frac{2t}{\beta} = \frac{1}{\beta^2} - \frac{1}{\sinh^2(\beta)}$.

III. APPROXIMATION OF NON-GAUSSIAN DISTRIBUTION

The accuracy-complexity trade-off problem in current PDF approximation functions (see section II) necessitate to develop a family of precise and simple approximation that are particularly relevant for shorter chains. Comparing P_{KG} with P_{exact} for different chain lengths shows a repeating error profile which can be considered almost independent of n. In view of this profile as a multiplicative error functions, one can consider all of the previous approximation functions such as P_{WG}, P_{SD} and P_{A-KG} as special sub-classes of a master approximation function $\tilde{P}$ which can be written with respect to P_{KG} as

$$\tilde{P}(r) \simeq P_{KG}(r, n)\, \phi(t), \tag{12}$$

where $\phi(t)$ is a multiplicative correction function defined to reduce the error of P_{KG}. Here, we hypothesize that $\phi(t)$ can be chosen to control the accuracy- complexity trade off for different applications. In view of good agreement of P_{WG}, P_{SD} and P_Y with exact distribution for short chains, one can conclude $\phi(t)$ should have same properties as the ratio of these distribution and P_{KG}. As discussed in the Section II, P_{WG}, P_{SD} and P_Y have almost same formulation. Thus among them, P_Y is selected to calculate an estimation of $\phi(t)$ as

$$\phi(t) \simeq \frac{P_Y}{P_{KG}} = \frac{\beta^2}{t\left[1 - \left(\frac{\beta}{\sinh(\beta)}\right)^2\right]^{\frac{1}{2}}}. \tag{13}$$

The first feature of this estimation is its limit when t approaches to 1 tends to infinity. By considering the first order pole of ILF at $t = 1$ and $\lim_{t\to 1} 1 - \left(\frac{\beta}{\sinh(\beta)}\right)^2 = 1$, one can conclude that $\phi(t)$ has second order pole at this point and its residue can be calculated as

$$\mathcal{R}(\phi) = \lim_{t\to 1} (t-1)^2 \phi(t) = 1. \tag{14}$$

By fitting $\phi(t)$ an approximation $\tilde{P}$ with good accuracy with respect to P_{exact} can be obtained. In this regard, the approximation function should have same properties as $\phi(t)$, second order pole

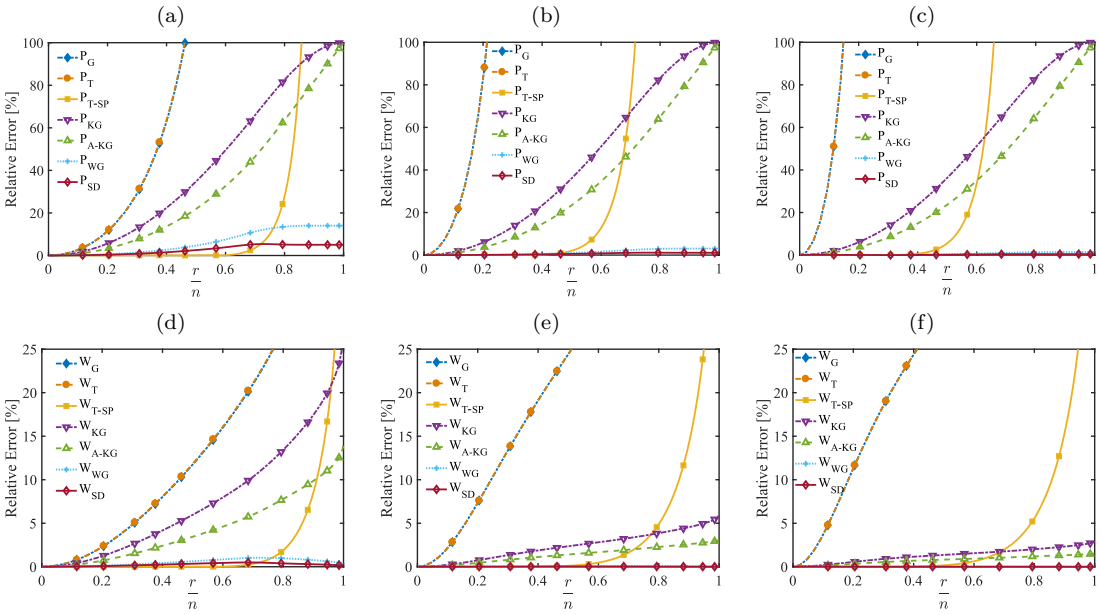

Figure 2. Comparison between Gaussian, KG, Amended KG and Eq. 11 distribution function with the exact PDF (Relative error of PDF *a-c* and Relative error of $\ln(P_n)$ *d-f*)of ideal chains with different lengths a and d) $n = 8$, b and e) $n = 16$ and c and f) $n = 64$

with residue of 1. The simplest function with second order pole is $(1-t)^{-2}$. In view of the second order pole of $\phi(t)$ and $(1-t)^{-2}$, it can be written as a rational function such as,

$$\phi(t) = \frac{a(t)}{(1-t)^2}, \tag{15}$$

where $a(t)$ is approximation function which is used to adjust the approximation function with the exact distribution. There are different alternative forms for estimations of $a(t)$ such as polynomial, exponential and ... . In this study exponential function ($\exp\left[\sum_{i=1}^{m} a_i t^{2i-1}\right]$, where m is the number of terms used in the approximation) is selected to approximate $a(t)$, which will result simple strain energy functions. In order to obtain best approximation with least maximum relative error in whole domain $[0-1]$, predefined min−max solver (fminimax) in MATLAB is used to minimize the maximum relative error of $\tilde{P}(r)$ respect to exact distribution function. The coefficient of approximation function with one and two terms is obtained as

$$P^{m=1}_{approx}(r) = P_{KG}(r,n)\left[\frac{\exp(-1.75\,t)}{(1-t)^2}\right] \tag{16a}$$

$$P^{m=2}_{approx}(r) = P_{KG}(r,n)\left[\frac{\exp\left(-2t+0.29t^3\right)}{(1-t)^2}\right]. \tag{16b}$$

The max relative errors of these approximations for chains with different length are presented in Table I and summarized in Fig. 3. They illustrate good agreement with the exact PDF for chains with different lengths in the whole range of t.

IV. ENTROPIC FORCE OF A SINGLE CHAIN

In polymer physics, the elastic retraction force of a single polymer chain is associated with changes in the entropy of the chains in the course of deformation. Accordingly, the strain energy $W = -TS$ of a single chain is calculated through Boltzmann's entropy relation, $S = k\ln(P(r))$, where S is the entropy of the chain, T the absolute temperature, and k the Boltzmann constant. Thus, the entropic force, $f_n(r)$, required to perturb the chains end-to-end distance is given by

$$f_n(r) = \frac{\partial W(r)}{\partial r} = -kT\frac{\partial \ln(P_n(r))}{\partial r}. \tag{17}$$

In view of the complicated formulation of the exact PDF, the approximates are often used to describe the force of the chain in the course of deformation. The simplest approach is to derive the force based on the Gaussian PDF P_G (Eq. 4) which yields the force as a linear function of deformation ($f_G(t) = \frac{kT}{l}t$). However, P_G is valid for long chains and at small deformation regimes, only. In large deformations, P_{KG} is the most popular ap-

Table I. Relative error of approximated distribution function by considering 1 and 2 terms for chains with different length

	max. relative error [%]			
m	$n=8$	$n=16$	$n=32$	$n=64$
KG	100	100	100	100
1	11	8	9	10
2	3	4	5	5

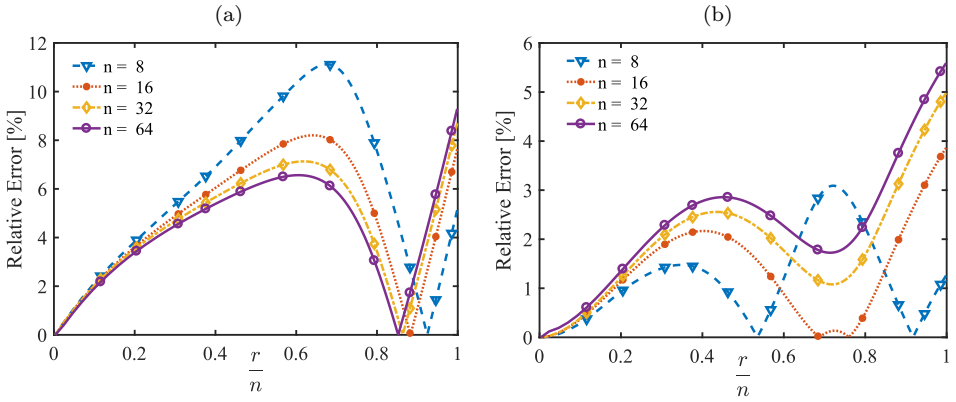

Figure 3. The relative error of approximated distribution function respect to the exact PDF for chains with different number of segment a) $m=1$ and b) $m=2$.

proximation function, which yields the following equation for polymer force

$$f_{KG}(t) = \frac{kT}{l}\beta. \tag{18}$$

Other approximations of the force can be simply derived by implementing any of the aforementioned PDF approximations into Eq. 17. For example using the P_{SD} (Eq. 11), the entropic force can be estimated as

$$f_{SD}(n,r) = \frac{kT}{l}\left\{\beta + \frac{1}{n}\left(\frac{1}{t} - \frac{\gamma}{2t}\frac{t\beta(\beta-\gamma)+2\left(\beta-\frac{5}{4}\gamma\right)}{(\beta-\gamma)^2}\right)\right\}, \tag{19}$$

where $\gamma = \frac{2t}{1-t^2}$. Similar to PDFs, the complexity of accurate approximations such as Eq. 19 prevent them from wide acceptance (e.g. compare Eq. 18 with Eq. 19).

The entropic force derived based on P_G, P_{KG}, P_{A-KG} and P_{SD} are compared with the force of the exact PDF and shown in Fig. 4-a and$b$ for short and long chains, respectively. As illustrated in Fig. 4-a , the force resulted from the KG has large relative errors with respect to the exact entropic force for a small chain. In longer chains, the KG force has good agreement with the exact one. Furthermore, the force associated with P_{SD} has the best agreement with the exact entropic force (see Fig. 4-a-b). The Fig. 4-c-d show that the relative error of the steepest decent approximation is the minimum in both short and long chains.

V. APPROXIMATION OF THE ENTROPIC FORCE

A new approximation for the force of a chain is developed based on the following observation. The profile of the relative error, E_n, of the force derived by P_{KG} is almost identical for the chains with different lengths, n. As shown in Fig.5, the relative error can be normalized by $\frac{1}{n}$, $e(t) = -nE_n$, the value of which is varying approximately between 100% and 220% ($\pm 5\%$). Accordingly, a new approximation function can be derived simply by multiplying a correction function, $\frac{1}{1-E_n}$, into f_{KG}.

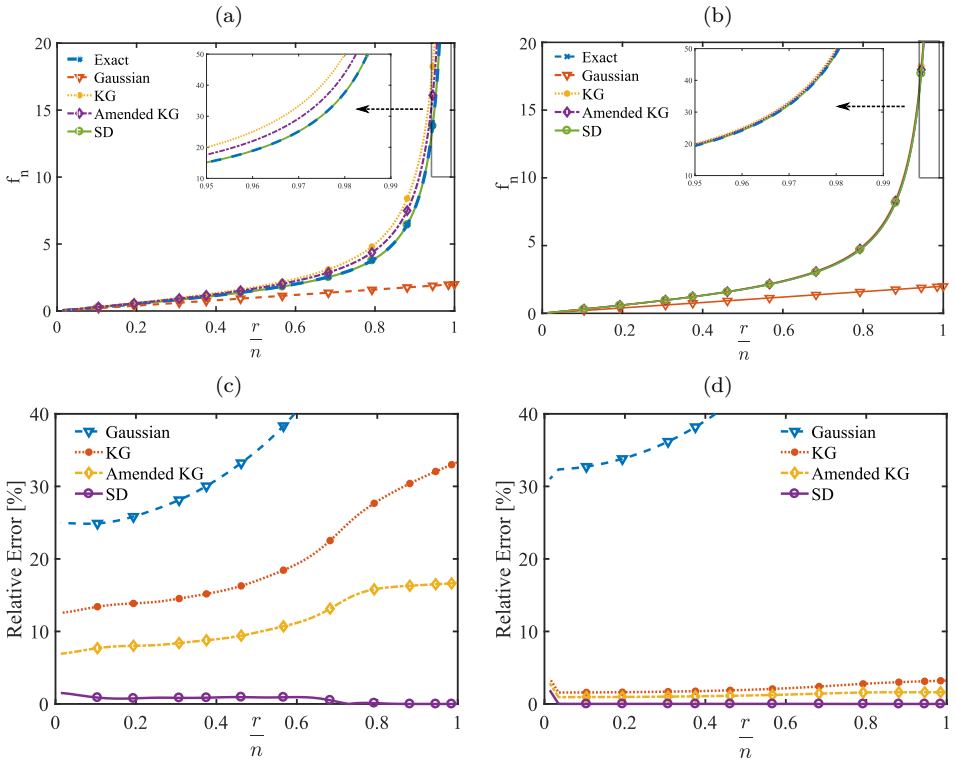

Figure 4. Comparison of the entropic force of a single chain resulted from exact non-Gaussian distribution function and its approximations, steepest decent approximation, and inverse Langevin function (a-b), and their relative errors with respect to the exact function (c-d) for a and c) $n = 8$ and b and d) $n = 64$,.

Then, by expanding the correction function using the geometric series and using the first two terms, the approximation of exact force is written as

$$E_n = \frac{f_{exact} - f_{KG}}{f_{exact}} \implies$$
$$f_{exact} = f_{KG}\frac{1}{1-E_n} \simeq f_{KG}\sum_{i=0}^{n}(E_n)^i \simeq f_{KG}(1+E_n). \tag{20}$$

By replacing the error, E_n, by its normalized value $-\frac{e(t)}{n}$, the proposed function becomes

$$f_{approx}(n,R) = \frac{kT}{l}\mathcal{L}^{-1}(t)\left(1-\frac{e(t)}{n}\right), \tag{21}$$

The approximation can be optimized by fitting a more general function for the normalized error shown in Fig.5, which can make the approximation too complex for practical applications. Here, $e(t)$ can be estimated through a fitting procedure of a polynomial with degree of m (see Fig.5), which yields

- **Order 0**: using $e(t) = 1$ reduces the Eq.19 into

$$f^{m=0}_{approx}(n,R) = \frac{kT}{l}\mathcal{L}^{-1}(t)\left(\frac{n-1}{n}\right), \tag{22}$$

which has a relative error varying from 0% to $\frac{120}{n}$% as shown in Fig. 5. The relative error of $f^{m=0}_{approx}$ is around half of the relative error of f_{KG}.[2] This simple modification can strongly improve the constitutive models [39–41], that use a probability of chains existence with different lengths. In these models, the force of the matrix is determined by summing up the forces of chains with different lengths.

- **Order 2**: a two term polynomial, $e(t) = 1 + t^i$, is used to represent $e(t)$. By minimizing the approximation error, the second

[2] In another study, Horgan and Saccomandi [36, 37] and later Beaty [38] derived almost the same formulation as Eq. 22 by comparing an estimation of non-Gaussian theory with the averaged stretch in the macroscopic level ($\beta = \frac{2t}{1-t^2}$) with Gent phenomenological model. Interestingly, it can be shown that Gent model has better agreement with non-Gaussian theory than KG for short chains.

order polynomial ($i = 2$) is selected in this study due to its simplicity and lower relative errors. The proposed approximation can be written as

$$f_{approx}^{m=2}(n,R) = \frac{kT}{l}\mathcal{L}^{-1}(t)\left(1 - \frac{1+t^2}{n}\right). \quad (23)$$

This approximation has extremely high accuracy, comparable to that of f_{SD} (Eq. 19), as shown in Fig. 6. The maximum relative error of the proposed approximation for $n = 8$ is equal to 1.7%, which is significantly lower than 33% error of the f_{KG}. In addition the maximum relative error of proposed entropic forces (Eq. 22 and 23) for the chains with different lengths are plotted in comparison with the maximum relative error of Langevin entropic force in Fig 7. It can be seen in Fig 7 that the maximum relative error of KG entropic force with 40 segment is about 5%. Considering this limit as an error tolerance for the approximation of Non-Gaussian entropic force, the proposed simple modification of entropic force is valid for the chains with 4 segments. Note that both proposed approximation functions can be easily implemented in most of the current elasticity models by replacing ILF.

In most physical-based models of rubber elasticity, breakage of the chain occurs when the chains deformation exceeds their allowed extensibility limit, which is determined by strength of C-C bonds. Therefore, it is important that models use an acceptable prediction of the force and the energy at high extensibility ratios, particularly when t is approaching 1. While for long chains there are few models to provide force and energy with enough accuracy around $t = 1$, for short chains no model exists that can accurately predict force around $t = 1$.

VI. APPROXIMATION OF THE ENTROPIC ENERGY

In view of the proposed approximations for the distribution function and the entropic forces, one can derive a set of approximations for the strain energy function. Accordingly, in view of the PDFs derived in Eq. 16a and 16b, the strain energy, W, can be obtained through $W = -kT\ln(P(r))$ as

$$W_{P-app}^{m=1}(r) = W_{KG}(r,n) + kT\left(1.75\,t + 2\ln(1-t)\right), \quad (24a)$$

$$W_{P-app}^{m=2}(r) = W_{KG}(r,n) + kT\left(2t - 0.29t^3 + 2\ln(1-t)\right). \quad (24b)$$

The relative errors of the proposed approximations of Eq. 24a and 24b, as shown in Fig 8, are significantly more accurate in comparison to KG strain energy function (see Table II). We also propose a second approach to estimate the strain energy functions directly from the proposed entropic forces in Eq. 23 by integrating them over R. Since direct integration of force approximation is not feasible due to the complex nature of the ILF, the integration is carried out after replacing the ILF by its approximation. Recently, many accurate ILF approximations with relative error less than 0.1% have been proposed in the literature (e.g. [26, 27]) and thus using each of those, one can derive the strain energy of the chains from Eq. 23 as follows

$$W_{f-app}^{m=2}(n,r) = n\int_0^t \frac{kT}{l}\beta(t)\left(1 - \frac{1+t^2}{n}\right)dt \quad (25)$$

For example, using $\mathcal{L}^{-1}(y) = \frac{x}{1-x} + 2x - \frac{8}{9}x^2$ (max relative error 1%)[26], the internal energy can be written as,

$$W_{f-app}^{m=2}(n,r) = kT\left[\frac{8}{45}t^5 - \frac{t^4}{2} - \frac{8n-17}{27}t^3 + \left(n - \frac{1}{2}\right)t^2 - (n-2)\left[t + \ln(1-t)\right]\right] + c \quad (26)$$

As shown in Fig 8, the relative errors of Eq 26 are significantly lower than that of W_{KG}. The relative error and the complexity of strain energy can be easily adjusted by using simpler or more accurate ILF.

VII. CONCLUSION

Currently, the probability distribution function, force and energy of a polymer chain is mostly derived based on the Kuhn and Grün model. However, the KG model is only valid for long chains ($n \gg 40$) and induces a significantly high error as the length of chain decrease [3, 4, 25]. How-

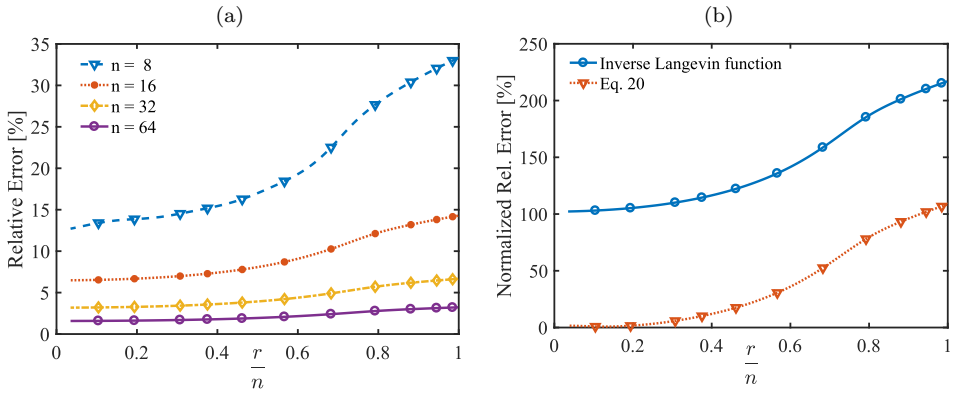

Figure 5. The relative error of the inverse Langevin function (ILF) a) with respect to the length of chain and b) Averaged normalized for all lengths

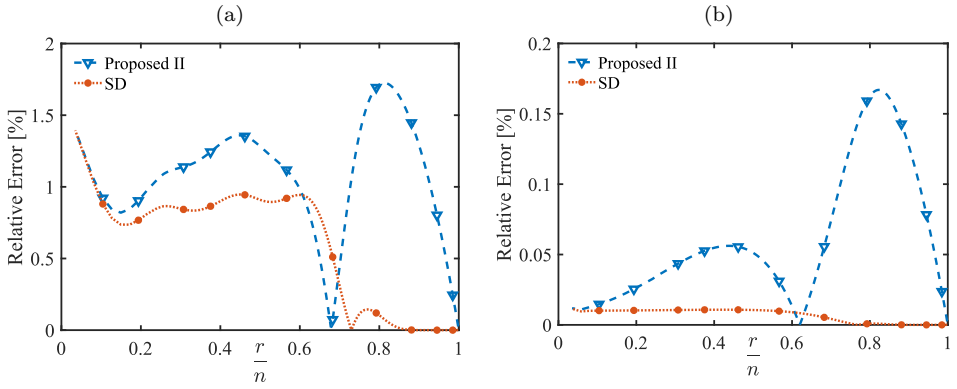

Figure 6. The relative error of the proposed entropic force for a) $n = 8$ and b) $n = 64$ along with the relative error of full steepest decent approximation

ever, long isolated polymer molecules is often does not exist in reality. They are in the interaction with other molecules. In theory of rubber elasticity, the segment between two cross-link or entanglement is considered as a non-Gaussian chain. Thus, the networks mostly contain short chains in the polymers with high cross-linking, which account for their limited extensibility. While there are some other approximation models with considerably higher accuracy, their complex nature prevents their wide implementation in large-scale models. In this work, we presented a generic approach to derive a family of approximation functions for the probability distribution function, entropic force and strain energy of a polymer chain with adjustable accuracy and complexity level, which are summarized in Table III. We show that with same level of complexity, our proposed functions are considerably more accurate than current functions. Particularly for short chains or chains under large deformations, our approximation functions are at least 10 times more accurate than KG approximations and thus are excellent options to replace them in constitutive models. We hope that the proposed family of approximations can help other researchers to improve the modeling accuracy in polymer physics. In addition to help engineers to optimize the accuracy-cost trade-off in large-scale simulations by allowing them to select the approximation functions based on the application.

Having a family of approximations with different accuracy-complexity would be particularly helpful in some specific applications where one certain form of the approximation function can reduce the computational loads or increase accuracy significantly. Some of application of proposed approximation of theory of rubber elasticity includes bi-modal polymeric networks, constrained swelling, stress induced orientation of the polymer chains and etc.. The proposed Non-Gaussian theory can directly affect the contribution of short and long chains in a bi-modal polymeric networks, which contains various proportions of relatively short and long chains specially in high elongations [42–44]. The contribution of free energy in the total change of chemical potential of a solvent resulting from swelling of a network contain short chains

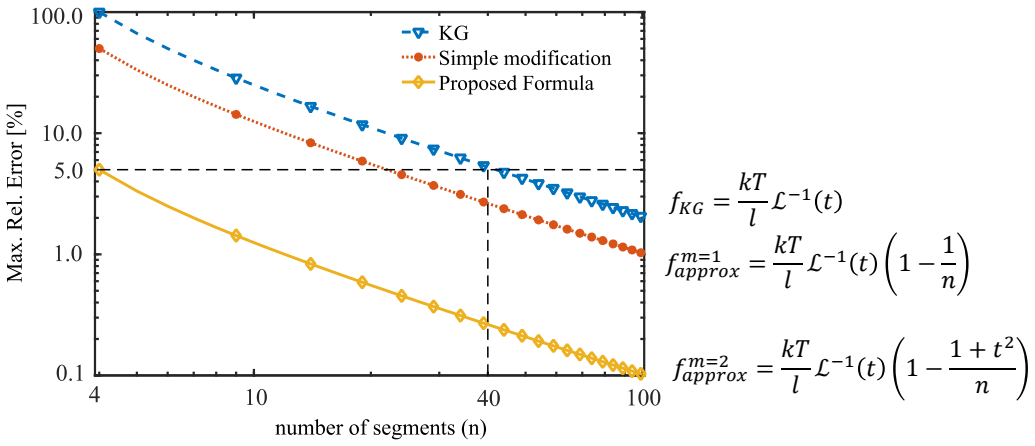

Figure 7. The maximum relative error of the proposed entropic force for chains with different length along with the maximum relative error of KG approximation

Table II. Max. relative error of approximated distribution functions for chains with different length

	max. relative error [%]			
m	$n = 8$	$n = 16$	$n = 32$	$n = 64$
KG	26	13	6	3
1 (Eq. 24a)	1.2	0.6	0.45	0.3
2 (Eq. 24b)	0.28	0.25	0.2	0.14
(Eq. 26)	1	0.68	0.65	0.67

can be affected by considering more realistic non-Gaussian distribution instead of Wall−White end-to-end distribution function, which cannot taking to account the finite extensibility limitations and only approximate the excluded volume effect in the compact conformations region [45, 46]. The KG distribution function and entropic force of chains is used to develop a model to predict the stress induced orientation of the polymer chains [47, 48]. Another possible application of current theory is studying molecular orientation of polymers chain due to fast elongational flow.

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DISCLAIMER

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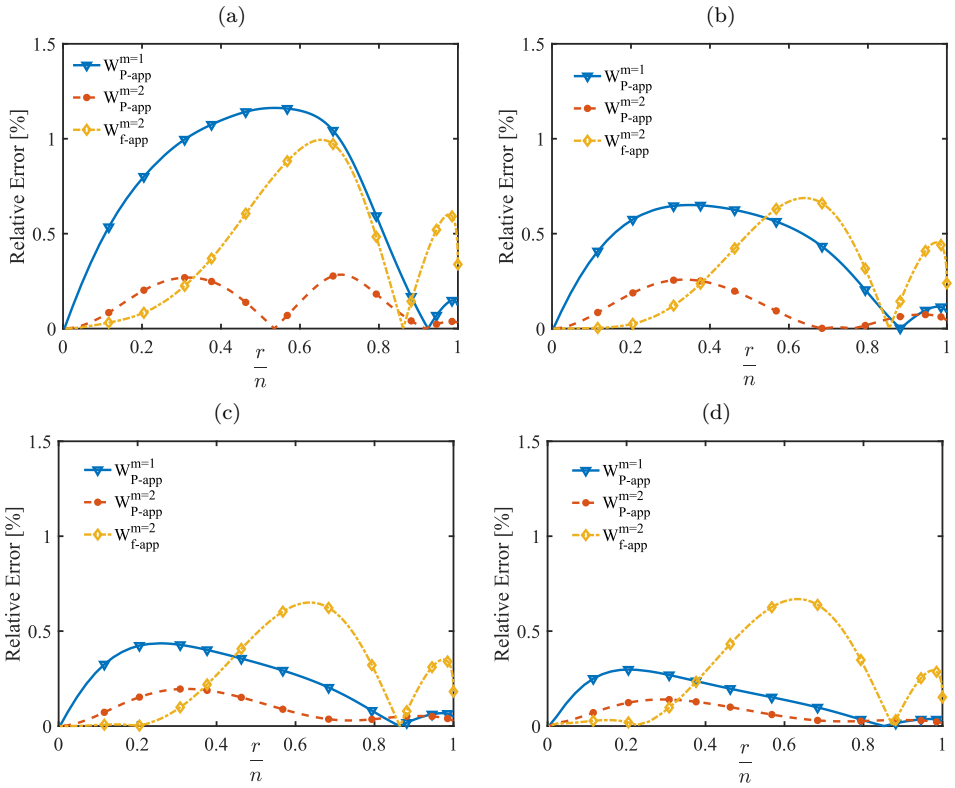

Figure 8. The relative errors of approximations of entropic energy (Eq. 24a, 24b and 26) respect to the exact entropic energy for chains with different number of segments a) $n = 8$, b) $n = 16$, c) $n = 32$ and d) $n = 64$.

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Table III. Summary of the proposed approximates for PDF, entropic force and strain energy along with their relative errors with respect to exact ones

	Eq.	Formula	Max. Rel. Error [%] for n			
			8	16	32	64
PDF	8	$P_{KG} = c\left\{\frac{\sinh(\beta)}{\beta\exp(t\beta)}\right\}^n$			100	
	16a	$P^{m=1}_{approx} = P_{KG}\left[\frac{\exp(-1.75\,t)}{(1-t)^2}\right]$	11	8	9	10
	16b	$P^{m=2}_{approx} = P_{KG}\left[\frac{\exp\left(-2t+0.29t^3\right)}{(1-t)^2}\right]$	3	4	5	5
Entropic Force	23	$f_{KG} = \frac{kT}{l}\beta$	33.3	14.27	6.45	3.22
	23	$f^{m=2}_{approx} = \frac{kT}{l}\beta\left(1-\frac{1+t^2}{n}\right)$	1.73	0.74	0.35	0.17
Strain Energy		$W_{KG} = nkT\left(t\beta + \ln\frac{\beta}{\sinh\beta}\right) + c$	26.6	12.2	5.9	2.9
	24a	$W^{m=1}_{P-app} = W_{KG} + kT\left(1.75\,t + 2\ln\left(1-t\right)\right)$	1.2	0.6	0.45	0.3
	24b	$W^{m=2}_{P-app} = W_{KG} + kT\left(2t - 0.29t^3 + 2\ln\left(1-t\right)\right)$	0.28	0.25	0.20	0.14
	26	$W^{m=2}_{f-app} = kT\{\frac{8t^5}{45} - \frac{t^4}{2} - \frac{8n-17}{27}t^3 + \left(n-\frac{1}{2}\right)t^2 - (n-2)\left[t+\ln\left(1-t\right)\right]\} + c$	1	0.68	0.65	0.67

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Appendix A: Appendix

The random flights' problem was one of the interesting topics in the early 20^{th} century. The random flight problem first introduced by Pearson in a letter to Nature 1905 [30, 49]. He tried to solve the distribution of position of a mosquito in a forest. Various distribution functions have been developed in the literature based on the Fourier integration of the random-flight problem, which is first presented by Rayleigh in 1919 [15]. In order to review the solutions of random flights' problem, different approach is presented as below.

1D Random Walk

In 1-D random walk problem, the probability of arriving to a point with distance x from the origin by n equal step can be written as binomial distribution

$$P_n(x) = \frac{1}{2^n} \frac{n!}{\left(\frac{n+x}{2}\right)!\left(\frac{n-x}{2}\right)!} \tag{A.1}$$

Considering $x \ll N$ and using Stirling's formula ($a! = \sqrt{2\pi a}\left(\frac{a}{e}\right)^a$), the probability distribution function will be simplified to Gaussian distribution[3]. The most well-known solution of end-to-end distance distribution is expressed by the Gaussian distribution, which is the probability of 1-D random links at

$$P_n(x) = \frac{1}{\sqrt{2\pi n}} \exp\left(-\frac{x^2}{2n}\right) \tag{A.2}$$

The efforts for enhancing the Gaussian theory of rubber elasticity to a more exact theory sacrifice the generality and simplicity. The non-Gaussian treatment of rubber elasticity is developed to account for the limiting extensibility of the single chain. This leads to a more accurate deformation-force relationship in the whole range of end-to-end distance up to its limiting value. The entropic force resulted from 1D random walk distribution (A.1) can be written as

$$f_{1D}(x) = \frac{kT}{2l}\left(\Psi\left(\frac{n+x+2}{2}\right) - \Psi\left(\frac{n-x+2}{2}\right)\right), \tag{A.3}$$

where Ψ is the Digamma function. As it can be seen in Eq. A.3, the entropic force has a asymptotic behavior around $r = n+2$ instead of $r = n$.

3D Random Walk

The probability distribution of a freely jointed chains (FJC) is same as 3-D random flight problem, which describes the probability of a chain ending at a certain point at distant $\overrightarrow{r}$ can be solved by 3-D random flight problem. The probability of one step with length l in an arbitrary direction is equal to probability of existence of a point on a sphere, $\frac{\delta(r-l)}{4\pi l^2}$. Applying the Fourier integration of this probability, "*characteristic function*" of a single random step is derived as $\frac{\sin(\rho l)}{\rho l}$, where l is the length of a segment in FJC chain (Kuhn length), and ρ the Fourier integral parameter. Due

[3] Using Gaussian PDF to calculate entropic strain energy is the basis of the Neo-Hookean constitutive model.

to the independent nature of bonds, $P_n(r)$ can be written by the multiplication of the probabilities of each bond. Considering an equal probability for all steps, the "*characteristic function*" of FJC, $A_n(\rho)$ is given as

$$A_n(\rho) = \prod_{i=1}^{n} (\rho l_i)^{-1} \sin(\rho l_i) \overset{l_i = l}{\rightarrow}$$
$$A_n(\rho) = \int exp(i\rho.r)\, P_n(r)\, dr = \left(\frac{\sin(\rho l)}{\rho l}\right)^n \tag{A.4}$$

In the next step, the probability function a chain can be derived by taking the Fourier transform of characteristic function, which first derived by Rayleigh by using the discontinuous integral of Dirichlet [15]. He used the inverse Fourier transformation of Eq.A.4 to derive the non-Gaussian PDF as

$$P_n(r) = \frac{1}{2\pi^2 r} \int_0^\infty \rho sin(\rho r) \left(\frac{sin(\rho l)}{\rho l}\right)^n d\rho, \quad (1)$$

which would be difficult to solve analytically for large number of steps, $n > 10$. The exact non-Gaussian distribution function for 3, 4 and 6 steps are derived by Rayleigh as sets of discontinues polynomials [15]. The exact solution of Fourier integral of Eq.1, often referred to as **"Rayleigh exact distribution function"**, was first derived by Treloar [8] based on the theory of random sampling. Later, Wang and Guth [18], Nagai [31], and Hsiung et al. [32] reached to the same expression with different mathematical approach.

$$P_n^{exact}(r) = \frac{1}{2^{n+1}(n-2)!\pi l^2 r} \sum_{k=0}^{k \le \frac{n-\frac{r}{l}}{2}} (-1)^k \binom{n}{k} \left(n - 2k - \frac{r}{l}\right)^{n-2} \tag{2}$$