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## LETTER TO THE EDITOR

# A danger of configurational averaging in constrained systems

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**Abstract.** Configurational (geometrical) averaging over all possible configurations is often used in the calculation of properties of polymer chains and branched structures. We show that for constrained systems more general consideration is needed which includes averaging over the dynamical degrees of freedom. As an example, we have found non-trivial angle distribution functions for the simplest models of rigid monomers freely joined with each other. It is shown that a Flory–Stockmayer and percolation approach can be inapplicable for the description of the equilibrium solution of polymers.

A standard approach in a study of configurational statistics of complex systems consists in calculation of their partition function. For the description of linear or branched polymers this partition function traditionally is written as a sum (or integral) over all possible configurations of the system [1–3]:

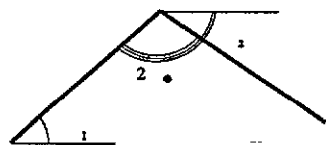
$$Z = \int D r_i e^{-U(\{r_i\})/T}. \quad (1)$$

Here  $U(\{r_i\})$  is the interaction energy of each configuration.

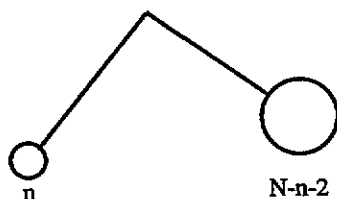
The simplest model used for the description of polymers is a model of long sticks—monomers which are freely joined at their ends with each other. In the absence of excluded volume interactions  $U(\{r_i\}) = 0$  this model is believed to be extremely simple: all angles between the adjacent sticks are considered as independent variables and each angle is assumed to be uniformly distributed.

The partition function written in the form (1), referred to as ‘geometrical’, is a starting point of the Flory–Stockmayer approach [4]. It is a basis of application of the percolation model to the problem of weight and size distribution of polymer molecules [5]. The equivalence of the statistics of the solution of the linear polymers to the thermodynamics of the  $n$ -component Heisenberg magnet in the  $n = 0$  limit [6] is also based on this formula.

The purpose of this paper is to show that in constrained systems, the simple geometrical approach based on (1) is often inapplicable. Using the above model as an example we shall show that, if calculated from first principles, the distribution of angles between two neighbouring sticks is non-trivial and depends strongly on mass distribution and internal constraints. We shall give arguments that there are serious



(a)



(b)

Figure 1. (a) Two rigid sticks connected by free joint; heavy dot indicates position of a centre of mass. The moment of inertia of the system depends on the angle  $\theta$ . (b) Two monomers (sticks) inside the long polymer chain. After the thermal average over all other degrees of freedom is done, the rest of the chain can be represented by masses  $M_1 = N-n-2$  and  $M_2 = n$  placed at the external ends of two sticks.

restrictions in the application of Flory-Stockmayer theory and percolation theory to equilibrium polymer systems.

In general the complete description of the system should include both the geometrical coordinates and their conjugate momenta. If the system is ergodic, its phase space distribution function is given by the Gibbs formula [7]:

$$Z = \int Dr_i Dp_j e^{-F(\{r_i, p_j\})/T}. \quad (2)$$

Here  $F(\{r_i, p_j\})$  is the total energy of the system, which can be written as a sum of potential and kinetic energies:  $F(\{r_i, p_j\}) = U(\{r_i\}) + E(\{r_i, p_j\})$ . If kinetic energy depends only on  $p_j$ , the integration over the momenta  $p_j$  and integration over  $r_i$  are independent and use of (1) is justified. In constrained systems the kinetic energy term is, in general, dependent on the configuration. Let us consider the planar ( $d=2$ ) configuration of two joint sticks both of unit length and mass in the absence of excluded volume effects. This system can be characterized by the position of its centre of mass  $R$  and by the rotation angles  $\alpha_1$  and  $\alpha_2$  (see figure 1(a)). It is more convenient instead of  $\alpha_1$  and  $\alpha_2$  to use their linear combinations

$$\Omega = \frac{\alpha_1 + \alpha_2}{2} \quad \text{and} \quad \theta = \frac{\pi - (\alpha_1 - \alpha_2)}{2}.$$

The moment of inertia of two sticks, is dependent on the angle  $\theta$ . Then the kinetic energy of these system can be written as a function  $\theta$ ,  $\dot{\Omega}$ ,  $\dot{\theta}$ ,  $\dot{R}$ :

$$E = \left( \frac{1}{12} + \frac{\sin^2 \theta}{4} \right) \dot{\Omega}^2 + \left( \frac{1}{12} + \frac{\cos^2 \theta}{4} \right) \dot{\theta}^2 + \dot{R}^2. \quad (3)$$

The momenta  $p_j = \partial E / \partial r_j$ , conjugated to the centre of mass coordinate  $R$  and to the angles  $\Omega$  and  $\Theta$  are

$$p_R = 2\dot{R}; p_\Omega = \left(\frac{1}{6} + \frac{\sin^2 \theta}{2}\right) \dot{\Omega}; p_\theta = \left(\frac{1}{6} + \frac{\cos^2 \theta}{2}\right) \dot{\theta}.$$

After integration over  $p_R$ ;  $p_\Omega$ ;  $p_\theta$  we obtain the configuration space distribution function

$$f(\theta) = \left(\frac{1}{3} + \sin^2 \theta\right)^{1/2} \left(\frac{1}{3} + \cos^2 \theta\right)^{1/2} \quad (4)$$

(the normalization factor is omitted here and in expressions given below). This distribution shows a substantial reduction for probability of stretched ( $\theta=0$ ) or folded ( $\theta=\pi/2$ ) configurations. Nevertheless the average distance between the ends of two link chains is the same as in the 'geometric' picture:  $\langle R^2 \rangle = 2$ .

It is easy to check that this result is sensitive to any additional restrictions on the two sticks. The energy functional (3) will have a different form if we assume that the position of one of the ends is fixed, or one of its coordinates is fixed, for example the  $x$ -coordinate. This will result in distribution functions different from (4). In the above calculations we suggested the mass of the sticks is uniformly distributed along their length so the moment of inertia of the stick is  $1/12$ . If we assume that the mass is concentrated mainly at the ends of the sticks (necklace model) the moment of inertia of each particular stick will be  $\frac{1}{4}$ . In this case the numerical coefficients  $\frac{1}{3}$  in (4) should be replaced by 2. The anisotropy of the distribution is much lower in this case [10]. It is clear that the difference in masses of adjacent sticks will also change the angle distribution functions in the above examples. In the limiting case, when the ratio of masses tends to zero, the distribution function is constant.

We can study the internal structure of polymer chain of length  $N \gg 1$  considering the simplified picture of two monomers (sticks) somewhere inside the chain (figure 1(b)). There is a subchain of  $n$  monomers attached to one external end of these two monomers and a subchain of  $N-n-m$  monomers attached to the other end. After thermal averaging over all other degrees of freedom is done, the rest of the chain can be represented by masses  $M_1 = N-n-2$  and  $M_2 = n$  placed at the external ends of two sticks. If both  $N-n-2$  and  $n$  are much larger than 1, the centre of mass of the whole system will be somewhere on the line connecting  $M_1$ ,  $M_2$ , and this line can be considered as a symmetry axis of the system. For the distribution function we obtain:  $f(\theta) = |\sin 2\theta|$  for  $d=2$ , and  $f(\theta) = |\sin 2\theta|^2$  for  $d=3$ . This means that the perpendicular configuration of adjacent monomers is the most probable one. Nevertheless, asymptotically, the mean square distance between the ends of the chain remains nearly the same as in the 'geometrical' model:  $\langle R^2 \rangle = N + O(1)$ , where  $O(1)$  is a finite contribution from the ends of the chain.

It is interesting to consider the configurational properties of a star-like structure of three rigid sticks jointed by their ends (figure 2). After some simple algebra, the result for the distribution function of the angles between the ends is ( $d=2$ )

$$f(\theta) = (4 - \cos^2 \theta_{32} - \cos^2 \theta_{21} - \cos^2 \theta_{13})^{1/2} \delta(\theta_{32} + \theta_{21} + \theta_{13} - 2\pi). \quad (5)$$

Here  $\theta_{ij}$  are the angles between sticks  $i$  and  $j$ . The most probable configuration in this case is one with all three sticks pulled apart from each other.

The rigidity of sticks is important in the above examples. In fact due to the rigidity, the motion of the centre of mass of one particular sticks along  $x$ -,  $y$ - and  $z$ -directions is

coupled and depends on the position of the adjacent sticks. Thus the effective masses in the expression for kinetic energy are anisotropic and configuration dependent. After integration over the momenta this results in inhomogeneous probability weights for different configurations.

Another delicate issue is the definition of a joint between the ends of two monomers. In classical mechanics if two ends are connected by a free joint, it is assumed that both the relative velocities of the ends and their relative displacements are zero:  $v_1 - v_2 = 0$ ;  $r_1 - r_2 = 0$ . It is remarkable that it is possible to introduce another definition of the free joint [8]. Let us assume that there is a strong attraction between the end points of two sticks  $r_1$  and  $r_2$  with a potential  $V(r_1 - r_2)$ , and this potential has a minimum at  $r_1 - r_2 = 0$ . In the limit of infinitely strong potential we have a constraint on the relative position of these ends  $r_1 - r_2 = 0$ , but their velocities  $v_1, v_2$  remain uncorrelated. The instantaneous momenta of the two sticks  $p_1, p_2$  are also uncorrelated. If this definition of a free joint is used, the integration over  $p_i$  in partition function (2), is decoupled from integration over  $r_i$  and use of (1) is justified. It appears that two definitions of the joint lead to two different distribution functions for the angle between rigid sticks! Two models are characterized by different average kinetic energies and different entropies. However, the difference between the two models exists only in classical mechanics. Considering the limit of infinitely strong attraction  $V(r_1 - r_2)$  between the two ends we should take into account limitations introduced by quantum mechanics. The problem is equivalent to the problem of a 'particle' with a coordinate  $r = r_1 - r_2$  in a potential  $V(r)$ . The motion of the particle in the potential is quantized and the distance between the energy levels is inversely proportional to the strength of the binding potential. If the distance between energy levels is less than the temperature, many energy levels contribute to the motion of the particle. In this case the classical description is valid and the motion of the particle is uncorrelated with its position. When the strength of the binding potential is increased, the distance between the energy levels of a 'particle' increases and becomes larger than the temperature. In the limit of infinitely strong potential only the ground-state level remains important. In other words the additional degree of freedom, which in the classical limit correspond to uncorrelated velocity, becomes 'frozen out' in the limit of large  $V(r)$ . The difference between the two above models of a free joint then disappears.

The covalent chemical bonds between monomers in a polymer chain are rather rigid: the typical excitation energy of a carbon-carbon or silicon-silicon bond is of the order 0.1 eV, and at room temperature it should be in the ground state. This allows us to use, for a description of a polymer chain, the above picture of sticks connected by a rigid joint. It is known from infrared spectroscopy that the excitation energy of rotational degrees of freedom of a covalent bond can vary from 0.01 to 0.1 eV. This

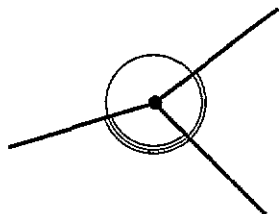


Figure 2. Three rigid sticks connected by a free joint ( $D=2$ ).

means that in one case the joint can be considered as a free one, in the other case as an absolutely rigid joint.

The above effects of coupling of the configurational and dynamical degrees of freedom can substantially restrict the applicability of Flory–Stockmayer theory and percolation theory to equilibrium polymer systems. The distribution function of the connected clusters—molecules in these theories are controlled only by the energy of formation of chemical bonds and by configurational entropy. This distribution function of the connected clusters has the form  $P_S \sim S^{-\tau} e^{-S/\bar{S}}$ . Here  $\bar{S}$  is the average cluster size and  $\tau$  is a critical exponent;  $\tau = \frac{5}{2}$  in the Flory–Stockmayer theory and  $\tau = 2.2$  for the percolation model. We can repeat all the arguments of the above theories but start, not from (1), but from (2). If we assume that the clusters formed from monomers are rigid, i.e. they do not have any internal vibrational or rotational degrees of freedom the final result will be

$$P_S \approx (J_1 \dots J_d)^{-1/2} S^{-d/2 - \tau} e^{-S/\bar{S}}. \quad (6)$$

Here  $J_a$   $a = 1, \dots, d$  are the principal values of the moment of inertia of the cluster. For tree-like structures  $J_a \approx S^{1+2/d_f}$  with  $d_f = 4$  (Flory–Stockmayer); in percolation theory  $d_f \approx 2.5$ . This classical consideration of external rotational degrees of freedom is possible only if the distance between the energy levels of the rotator is less than the temperature; otherwise only the ground state of the rotator contributes to the partition function. This means that rotational degrees of freedom are ‘frozen out’ and  $P_S$  is independent of  $J_a$ . The situation becomes more complicated if the clusters are not completely rigid, but have some internal rotational degrees of freedom.

For large clusters the internal rotational and vibrational degrees of freedom should be taken into account. For a linear chain made from  $S$  monomers the lowest vibrational frequency is of the order  $\omega \approx S^{-1}\omega_0$  where  $h\omega_0$  is the excitation energy of the joint (of the chemical bond). For a random branched structure of the same mass the lowest vibrational frequency is of the order  $\omega \approx S^{-3/4}\omega_0$ . For large enough fragments of the structure such that  $h\omega = kT$  the structure cannot be considered rigid any more. On this scales the dynamical and configurational degrees of freedom can be separated and the Flory–Stockmayer formula becomes valid.

We have shown that in systems with internal constraints the geometrical approach is inapplicable and more general considerations are needed. The results of consideration of particular simple cases happens to be sometimes counterintuitive, but qualitatively can be summarized as follows: The most probable are the configurations which have the largest product of all moments of inertia with respect to principal axes, and the largest masses associated with the internal modes.

In a long polymer chain the most probable are the configurations of adjacent monomers perpendicular to each other. Due to the central limit theorem this does not affect the Gaussian statistics of an unperturbed polymer coil. Nevertheless, if the coil is strongly stretched the internal correlations give the additional mechanism of nonlinear rigidity. In the branched polymer structures we found the effective dynamical repulsion of adjacent monomers at the branching points. This results in an effective increase of the elementary length in the problem. The presence of closed loops in a branched polymer may produce strong non-trivial correlations. We expect effects of coupling of configurational and dynamical degrees of freedom to be the strongest in the systems with a maximum number of constraints, such as a rigid-stick model of membranes, surfaces [9] or models of gel [10].

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## References

- [1] Flory P 1969 *Statistics of Chain Molecules* (New York: Interscience Publishers)
- [2] Doi M and Edwards S F 1986 *The Theory of Polymer Dynamics* (Oxford: Oxford University Press)
- [3] Bird R B, Curtiss C F, Armstrong R C and Hassager O 1977 *Dynamics of Polymeric Liquids* vol 2 (New York, John Williams)
- [4] Flory P 1953 *Principles of Polymer Chemistry* (Cornell University)  
Edwards S F and Goodyear A G 1972 *J. Phys. A: Math. Gen.* **5** 965–80, 1188–95
- [5] Stauffer D 1985 *Introduction to Percolation Theory* ed Taylor and From (Philadelphia)
- [6] de Gennes P G 1972 *Phys. Lett.* **38A** 339  
Daoud M *et al* 1975 *Macromolecules* **8** 804  
des Cloiseaux J 1975 *J. Physique* **36** 281
- [7] Landau L D and Lifshitz E M 1980 *Statistical Physics* (Pergamon)
- [8] des Cloiseaux J Private communication
- [9] Nelson D, Piran T and Weinberg S (eds) 1989 *Statistical Mechanics of Membranes and Surfaces* (Singapore: World Scientific)
- [10] Rubinstein M, Leibler L and Bastide J 1992 *Phys. Rev. Lett.* **68** 405
- [11] Kramers H A 1946 *J. Chem. Phys.* **14** 415

† After this work was completed and circulated as a preprint, P G de Gennes brought to my attention that an equation for a necklace model similar to (4) was obtained by H A Kramers. Kramers concluded that anisotropy of the distribution function in this model is small. Probably this is the reason why 'geometrical' averaging procedure became self evident for next generations. All textbooks which I have seen just take it for granted.