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## CLASSICAL GIBBS DISTRIBUTION FOR A CARBON CHAIN\*

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A simplified mechanical model of a carbon chain is examined: lengths of valence bonds and valency angles are determined. The Gibbs distribution is used for this system. A further factor  $\Omega(\varphi)$  appears, which is significant. A formula is derived for  $\Omega(\varphi)$  in the form of a determinant, elements of which are in a clear form. The effect of  $\Omega(\varphi)$  is examined using low  $n$  values ( $n$  is the number of carbon atoms). The existence of a correlation between angles is emphasized even in the absence of potential interaction.

WHEN studying molecules, which are based on a chain of carbon atoms with simple bond, the following simplified mechanical model of molecules is often examined [1-3]. Carbon atoms are shown as  $n$  material points, for which given are the distances between adjacent particles:  $|r_k - r_{k+1}| = a$ ; distances between

\* Vysokomol. soyed. **A21**: No. 7, 1632-1639, 1979.

every other particle;  $|r_k - r_{k+2}| = b$  and potential  $U(r)$  which describes interaction between more distant particles. Conformations of this molecule are determined by angles of internal rotation  $\varphi_k$  ( $\varphi_k$  being the angle between planes  $(k, k+1, k+2)$  and  $(k+1, k+2, k+3)$ ). It may be considered that  $U$  is the function of  $\varphi$ :  $U(\varphi) = U(\varphi_1, \varphi_2, \dots, \varphi_{n-3})$ .

We assume now that the Gibbs distribution is used for this molecule. Then, probabilities of various molecular conformations will be determined by potential  $U(\varphi)$ . However, the density of probability will not simply be proportional to  $e^{-\beta U(\varphi)}$  ( $\beta = 1/kT$ ): in view of geometric connections there is a further factor  $\Omega(\varphi)$  [1, 3]. Rewriting the gravimetric function  $e^{-\beta U(\varphi)} \Omega(\varphi)$  in the form  $e^{-\beta U(\varphi)} \cdot e^{-\beta V(\varphi, \beta)}$  it may be said that geometric connections produce a further interaction between particles with potential  $V$  dependent on temperature:

$$V(\varphi, \beta) = -1/\beta \ln \Omega(\varphi).$$

We are concerned with the importance of this further interaction in this study. In other words, with the extent to which factor  $\Omega(\varphi)$  differs from constant. The formula for  $\Omega(\varphi)$  is a determinant, each element of which is very complicated to calculate. Using this algebraic lemma (applied for this purpose [4-5]) we write  $\Omega(\varphi)$  in the form of another determinant, all elements of which appear in a clear form (with high  $s$  value a larger part is equal to zero). As a result clear formulae may be derived for  $\Omega(\varphi_1)$  and  $\Omega(\varphi_1, \varphi_2)$  and it is much easier to derive numerically the values of  $\Omega(\varphi_1, \varphi_2, \dots, \varphi_s)$  when  $s \gg 1$ .

This paper is concerned with deriving the formula for  $\Omega$  and examining it in detail for low  $n$  values ( $n=4-6$ ). The case of  $n \gg 1$  is worthy of special examination, the authors hope to revert to it.

Those readers who are not interested in the mathematical aspect of the problem, may directly deal with the study of Gibbs distribution for the carbon chain.

#### GIBBS DISTRIBUTION IN CURVILINEAR COORDINATES

It is known that the probability density of various configurations of the system, in virtue of the Gibbs distribution in a cartesian system of coordinates, takes the form

$$\rho(x) = \frac{1}{\Phi(\beta)} e^{-\beta U(x)}, \quad (1)$$

where  $x = (x_1, x_2, \dots, x_N)$ ,  $N = 3n$ . If  $q_1, q_2, \dots, q_N$  are arbitrary (curvilinear) coordinates, instead of eqn. (1) we obtain

$$\rho(q) = \frac{1}{\Phi(\beta)} e^{-\beta U(q)} I(q), \quad \Phi(\beta) = \int e^{-\beta U(q)} I(q) dq, \quad I(q) = \det \left( \frac{\partial x_i}{\partial q_j} \right)$$

If geometrical links are given between certain particles, the number of degrees of freedom decreases: all configurations of the system are given by coordinates

$q_1 q_2, \dots q_s$ , where  $s < N$ . Formula (2) is considerably complicated for this case: instead of factor  $I(q)$ , which is no longer meaningful when  $s < N$ , factor  $\Omega(q)$  should be written

$$\Omega(q) = [\det(g_{\alpha\beta})]^{0.5}, \quad g_{\alpha\beta} = \sum_{k=1}^N \frac{\partial h_k}{\partial q_\alpha} \frac{\partial h_k}{\partial q_\beta}, \quad \alpha, \beta = 1, 2, \dots, s \quad (3)$$

Here  $x_k = h_k(q_1, \dots, q_s)$  are formulae of Cartesian coordinates of particles  $x$  in terms of generalized coordinate  $q$ . We see that although the order of determinant was reduced ( $s < N$ ), its elements are complicated to a great deal for two reasons: 1)  $h(q)$  is normally given by complex formulae; 2) the total has to be calculated in formula (3). Using a simple algebraic lemma we overcome both these difficulties. However, difficulties naturally remain in solving the high order determinant.

*$\Omega(q)$  and geometry of bonds.* Let equations of geometric bonds take the form:  $F_j(x) = l_j$ ,  $j = 1, 2, \dots, v$ . We add to functions  $F_1, F_2, \dots, F_v$  at random  $s = N - v$  functions  $q_1(x), q_2(x), \dots, q_s(x)$  and introduce (locally)  $N$  curvilinear coordinates

$$q_1, q_2, \dots, q_s, q_{s+1} = F_1(x), \dots, q_N = F_{N-s}(x); \quad \det\left(\frac{\partial x_i}{\partial q_j}\right) \neq 0 \quad (4)$$

Let  $x_k = x_k(q_1, \dots, q_N)$  be formulae  $x_k$  via  $q_1, q_2, \dots, q_N$ . We determine matrix elements  $f_{ij}$  by the following method:

$$f_{ij} = (\text{grad } F_i, \text{grad } F_j) = \sum_{N=1}^N \frac{\partial F_i}{\partial x_i} \frac{\partial F_j}{\partial x_i}, \quad i, j = 1, 2, \dots, v \quad (5)$$

The following lemma holds good.

*Lemma.* Let  $I(q) = \det\left(\frac{\partial x_i}{\partial q_j}\right)$  be the functional determinant of transition to coordinates determined according to a previous formula (4). Then, the following formula is valid:

$$\det(g_{\alpha\beta}) = I^2(q) \det(f_{ij}) \quad (6)$$

Here in the left and right-hand side part of coordinates  $q_{s+1}, \dots, q_N$  it has been recorded that:  $q_{s+1} = l_1, \dots, q_N = l_{N-s}$ .

It is easy to confirm the lemma using the following algebraic statement [6].\* Let  $A$  and  $B$  be mutually inverse matrices  $B = A^{-1}$ ;  $A_s$ , the minor of matrix  $A$  formed of the first  $s$  rows and first  $s$  columns;  $B_{s-N}$ , the minor of matrix  $B$ , formed of the last  $N-s$  rows and  $N-s$  columns. Then

$$\det A_s = \det B_{s-N} \det A \quad (7)$$

\* Paper [4] gives a satisfactory confirmation of this lemma.

In our case  $A$  and  $B$  are

$$A_{ij} = \sum_{k=1}^N \frac{\partial x_i}{\partial q_k} \frac{\partial x_j}{\partial q_k}, \quad B_{ij} = \sum_{k=1}^N \frac{\partial q_i}{\partial x_k} \frac{\partial q_j}{\partial x_k}, \quad i, j = 1, 2, \dots, N$$

The value of  $s$  is assumed to be equal to the dimensionality of the configuration space and establishing  $q_{s+1}, \dots, q_N$  from formula (7) we obtain formula (6).

#### COFACTOR $\Omega(q)$ FOR THE CARBON CHAIN

*Introduction of curvilinear coordinates.* Let  $r_k$  be the radius vector of  $k$ -th particle,  $k=1, 2, \dots, n$ . We introduce  $q_1, q_2, \dots, q_N$  ( $N=3n$ ) by the following standard method: 1) three Cartesian coordinates  $\mathbf{r}_1$ :  $q_1=x_1$ ,  $q_2=x_2$ ,  $q_3=x_3$ ; 2) spherical coordinates of vector  $\mathbf{e}_1=\mathbf{r}_2-\mathbf{r}_1$  in relation to a fixed spherical system:  $q_4=r_1$ ,  $q_5=\theta$ ,  $q_6=\alpha$ ; 3) spherical coordinates  $\mathbf{e}_2=\mathbf{r}_3-\mathbf{r}_2$  in relation to (some) spherical system with a polar axis along  $\mathbf{e}_1$ :  $q_7=r_2$ ,  $q_8=\theta_2$ ,  $q_9=\beta$ ; 4) spherical coordinates  $\mathbf{e}_k=\mathbf{r}_{k+1}-\mathbf{r}_k$  ( $k>2$ ) in relation to a "mobile" spherical coordinate system:  $q_{3k+1}=r_k$ ,  $q_{3k+2}=\theta_k$ ,  $q_{3k+3}=\varphi_{k-2}$  (polar axis along vector  $\mathbf{e}_{k-1}$ ,  $\varphi_{k-2}=0$  corresponds to the maximum removal of  $k-2$  and  $k+1$  particles).

In these coordinates the constancy of lengths of valence bonds is described in the form  $r_k=\text{const}$ ,  $k=1, 2, \dots, n-1$ ; the constancy of valency angles  $\theta_k=\text{const}$ , where  $k=2, 3, \dots, n-1$ . Angles of internal rotation we are interested in are angles  $\varphi_k$ . It is easy to show that the functional determinant of transition from Cartesian coordinates  $x_1, x_2, \dots, x_{3n}$  to values of  $q_1, q_2, \dots, q_{3n}$  selected by the authors has the same external appearance as if all spherical systems had been established

$$I(q)=\det\left(\frac{\partial x}{\partial q}\right)=\prod_{k=1}^{n-1} r_k^2 \sin \theta_k$$

With values of  $r_k$  and  $\theta_k$  ( $k \geq 2$ ) being established

$$I(q)=\text{const} \sin \theta_1 \quad (8)$$

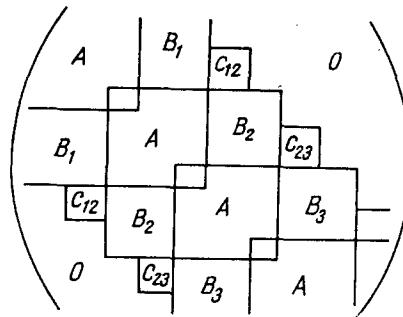
It is important to emphasize that  $I(q)$  is independent of angles of internal rotation  $\varphi$ .

*Matrix  $(f_{ij})$ .* Geometrical relations  $F_j(x)$  are numbered by the following method:  $F_1, F_3, F_5, \dots$  are the valence bonds,  $F_2, F_4, F_6, \dots$  the valency angles. More accurately:

$$\begin{aligned} F_1(x) &= \frac{1}{2} |\mathbf{r}_2 - \mathbf{r}_1|^2, & F_3(x) &= \frac{1}{2} |\mathbf{r}_3 - \mathbf{r}_2|^2, \dots; \\ F_2(x) &= \frac{1}{2} |\mathbf{r}_3 - \mathbf{r}_1|^2, & F_4(x) &= \frac{1}{2} |\mathbf{r}_4 - \mathbf{r}_2|^2, \dots. \end{aligned}$$

We note that the  $f_{ij}$  values only differ from zero when  $F_i$  and  $F_j$  have a common point. For example, when  $i=5$ , values of  $f_{52}, f_{53}, f_{54}, f_{56}$  and  $f_{57}$  are different from zero. When angles between segments illustrating the bonds are fixed, corresponding values of  $f_{ij}$  are constant. Thus,  $f_{13}=f_{35}=\dots=-\cos \omega$ , where  $\theta_2=\theta_3=\dots=\pi-\omega$  are fixed valency angles. Similarly,  $f_{12}=f_{32}=\dots=1+\cos \omega$ . It is easy to calculate formulae for other  $f_{ij}$  values and this will be omitted here. The

general form of the matrix  $f_{ij}$  is as follows



Here  $A$  is a third order constant matrix.

$$A = \begin{pmatrix} 2 & 1+\cos\omega & -\cos\omega \\ 1+\cos\omega & 4(1+\cos\omega) & 1+\cos\omega \\ -\cos\omega & 1+\cos\omega & 2 \end{pmatrix}$$

$B_k$ , multiple of a second order unit matrix

$$B_k = -(\cos\omega + \cos^2\omega + \sin^2\omega \cos\varphi_k) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},$$

$\varphi_k$ , angles of internal rotation. Finally,  $c_{k,k+1} = -\cos\omega (1+\cos\omega)^2 - \sin^2\omega \cdot (1+\cos\omega) (\cos\varphi_k + \cos\varphi_{k+1}) + \sin^2\omega (\cos\omega \cos\varphi_{k+1} - \sin\varphi_k \sin\varphi_{k+1})$ .

Now using formulae (6) and (8) we can write for the carbon chain:  $\Omega(q) = \text{const.} \cdot \sin\theta_1 [\det(f_{ij})]^{0.5}$ , where matrix elements  $f_{ij}$  were given previously. Factor  $\sin\theta_1$  is unimportant for calculating varying average configuration values and  $\Omega(q) = [\det(f_{ij})]^{0.5}$  will be calculated later.

#### GIBBS DISTRIBUTION FOR CARBON CHAIN CONSISTING OF A FEW UNITS

$n=4$ . In this case (4 carbon atoms) there is only one angle of internal rotation  $\varphi$ . Cofactor  $\Omega(\varphi)$  may clearly be written as:  $\Omega(\varphi) = [74.152 + 4.375 \cos\varphi - 34.657 \cos^2\varphi + 1.248 \cos^3\varphi + 1.250 \cos^4\varphi]^{0.5}$  (Numerical coefficients were given for  $\theta = 109^\circ 28'$ ). In a general formula these coefficients take the form of eight order polynomials of  $\cos\theta$ .

Function  $\Omega(\varphi)$  has maximum values near  $90^\circ$  and  $270^\circ$  (Fig. 1). If internal rotation were therefore completely free ( $U(\varphi)=0$ ), angles between two planes close to right angles would be more probable.

Internal rotation is not really free. It is usually assumed that potential  $u(\varphi)$  has three minimum values: a lower one at  $\varphi=0^\circ$  and less low ones near angles  $\varphi=120^\circ$  and  $240^\circ$ . The difference of potentials at minimum values  $\Delta u$  is  $\sim 0.7-0.9$  kcal/mole [6]. Supplementary potential  $V(\varphi, \beta) = -1/\beta \ln \Omega(\varphi)$  does not markedly change  $u(\varphi)$ , but overall potential  $u(\varphi) + V(\varphi, \beta)$  is a more continuous value. At a temperature of  $300^\circ\text{K}$  the difference between minimum values decreases

by about 0.1 kcal/mole (i.e. by 10–15%). With an increase in temperature the role of  $V(\varphi, \beta)$  increases. At 600°K the reduction of the difference reaches 20–30%.

$n=5$ . The function  $\Omega^2(\varphi_1, \varphi_2)$  is a trigonometric polynomial consisting of over 40 components. We only write here terms with the highest coefficients:  $\Omega(\varphi_1, \varphi_2) = [442 - 212.5 (\cos^2 \varphi_1 + \cos^2 \varphi_2) + 70.3 \cos^2 \varphi_1 \cos^2 \varphi_2]^{0.5}$ .

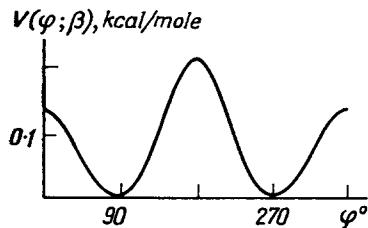


FIG. 1

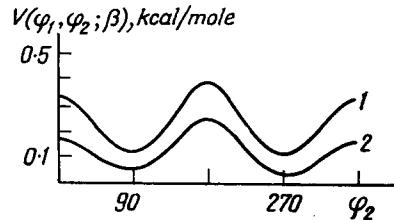


FIG. 2

FIG. 1. Dependence of the additional potential  $V(\varphi; \beta)$  on the angle of internal rotation  $\varphi$  at 300°K ( $n=4$ ).

FIG. 2. Curves of  $V(\varphi_1, \varphi_2; \beta)$  with different fixed values of  $\varphi_1=c$ . The difference in the form of curves indicates a correlation between  $\varphi_1$  and  $\varphi_2$  (300°K,  $n=5$ );  $c=0$  (1) and  $120^\circ$  (2).

The combined density of distribution of probabilities of angles  $\varphi_1$  and  $\varphi_2$  is given by the formula

$$\rho(\varphi_1, \varphi_2) = \frac{1}{\Phi(\beta)} e^{-\beta U(\varphi_1, \varphi_2)} \Omega(\varphi_1, \varphi_2), \quad \Phi(\beta) = \int_0^{2\pi} \int_0^{2\pi} e^{-\beta U(\varphi_1, \varphi_2)} \Omega(\varphi, \varphi_2) d\varphi_1 d\varphi_2 \quad (9)$$

Representation concerning the role of  $\Omega(\varphi_1, \varphi_2)$  may be obtained by examining potential  $U$  of the form

$$U(\varphi_1, \varphi_2) = u(\varphi_1) + u(\varphi_2) \quad (10)$$

If  $u(\varphi)$  is minimum near  $\varphi=0$  and  $\varphi=\pm 120^\circ$ , values of  $\Omega$  are most significant near minimum values (Table 1). For example, when  $\varphi=0^\circ$ , let the minimum of  $u(\varphi)$  be lower by 0.75 kcal/mole ( $\Delta u=0.75$  kcal/mole). Then, without considering factor  $\Omega$  at 300°K we obtain:  $\rho(0, 0)/\rho(0, 120)=3.49$ ;  $\rho(0, 0)/\rho(120, 120)=12.18$ . When considering factor  $\Omega$  we obtain:  $\rho(0, 0)/\rho(0, 120)=2.65$ ;  $\rho(0, 0)/\rho(120, 120)=8.07$ . Therefore, the same way as for  $n=4$ , factor  $\Omega$  moderates the difference between probabilities of various conformations.

*Correlation between angles  $\varphi_1$  and  $\varphi_2$ .* When  $U(\varphi_1, \varphi_2) = u(\varphi_1) + u(\varphi_2)$ :  $e^{-\beta U(\varphi_1, \varphi_2)} = e^{-\beta u(\varphi_1)} e^{-\beta u(\varphi_2)}$ . If we ignore factor  $\Omega$  in formula (9), then  $\rho(\varphi_1, \varphi_2) = \rho(\varphi_1) \rho(\varphi_2)$ , angles  $\varphi_1$  and  $\varphi_2$  will vary independently. However, factor  $\Omega(\varphi_1, \varphi_2)$  is not represented in the form of  $a(\varphi_1) a(\varphi_2)$  with any function of  $a(\varphi)$ . Therefore, considering this factor forms a correlation between angles even for  $U$

values of type (10). Figure 2 shows the dependence of additional potential  $V(\varphi_1, \varphi_2; \beta)$  on angle  $\varphi_2$  with different fixed values of  $\varphi_1=c$ . A difference in the form of curves indicates a correlation between  $\varphi_1$  and  $\varphi_2$ . With potentials type (10) with narrow potential wells  $u(r)$  the correlation produced by  $\Omega$  is, evidently,

TABLE 1. FUNCTIONS  $\Omega(\varphi_1, \varphi_2)/\Omega(0, 0)$  ( $n=5$ ) FOR VARIOUS  $\varphi_1$  AND  $\varphi_2$  VALUES

| $\varphi_2$ | $\varphi_1^\circ$ |      |      |      |      |      |
|-------------|-------------------|------|------|------|------|------|
|             | 0                 | 10   | 100  | 110  | 120  | 130  |
| -10         | 1.02              | 1.04 | 1.47 | 1.42 | 1.35 | 1.27 |
| 0           | 1.00              | 1.02 | 1.45 | 1.41 | 1.34 | 1.26 |
| 10          | 1.02              | 1.03 | 1.45 | 1.41 | 1.35 | 1.27 |
| 100         | 1.45              | 1.45 | 1.74 | 1.70 | 1.64 | 1.64 |
| 110         | 1.41              | 1.41 | 1.79 | 1.66 | 1.60 | 1.52 |
| 120         | 1.34              | 1.35 | 1.64 | 1.60 | 1.53 | 1.46 |
| 130         | 1.26              | 1.27 | 1.57 | 1.52 | 1.46 | 1.37 |
| -130        | 1.26              | 1.27 | 1.59 | 1.54 | 1.48 | 1.41 |
| -120        | 1.34              | 1.35 | 1.67 | 1.62 | 1.56 | 1.48 |
| -110        | 1.41              | 1.42 | 1.74 | 1.69 | 1.62 | 1.54 |
| -100        | 1.45              | 1.47 | 1.78 | 1.74 | 1.67 | 1.59 |

not very significant. As far as real molecules are concerned,  $U(\varphi_1, \varphi_2)$  cannot apparently be given by formula type (10) [8]. Factor  $\Omega$  them creates a correlation between angles, which is in addition to that formed by force interaction.

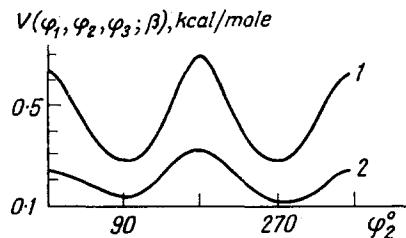


FIG. 3. Curves of  $V(\varphi_1, \varphi_2, \varphi_3; \beta)$  with different fixed values of  $\varphi_1 = \varphi_3 = c$  (300°K,  $n=6$ );  $c=0$  (1) and  $120^\circ$  (2).

$n=6$ . There are three angles of internal rotation here:  $\varphi_1$ ,  $\varphi_2$  and  $\varphi_3$  (unequal). The effect of factor  $\Omega(\varphi_1, \varphi_2$  and  $\varphi_3$ ) on the depth of potential wells and the correlation between angles is illustrated by Table 2 and Fig. 3 (compared with Table 1 and Fig. 2).

#### FINAL OBSERVATIONS

1. An accurate formula was derived for  $\Omega(\varphi_1)$  ( $n=4$ ) and an approximate formula for  $\Omega(\varphi_1, \varphi_2)$  ( $n=5$ ). When  $n \geq 6$  clear formulae become immensely complicated and therefore, useless. We note that for a chain for which

only valence bonds are absolutely rigid, formulae for the additional weighting factor are considerably simpler.\*

2. Complementary potential  $V(\varphi, \beta) = 1/\beta \ln \Omega(\varphi)$  differs considerably from constant. At a temperature of 300°K and a single angle of internal rotation ( $n=4$ )  $\Delta V = \max V(\varphi, \beta) - \min V(\varphi, \beta) \approx 0.22$  kcal/mole; when  $n=5$   $\Delta V \approx 0.6$  kcal/mole; when  $n=6$   $\Delta V \approx 1$  kcal/mole. On further increasing  $n$ ,  $\Delta V$  increases [3].

TABLE 2. FUNCTIONS  $\Omega(\varphi_1, \varphi_2, \varphi_3)/\Omega(0, 0, 0)$  WITH DIFFERENT  $\varphi_1$ ,  $\varphi_2$  AND  $\varphi_3$  VALUES

| $\varphi_2$ | $\varphi_1^*$ |      |      | $\varphi_1^\dagger$ |      |      |
|-------------|---------------|------|------|---------------------|------|------|
|             | 0             | 120  | 240  | 0                   | 120  | 240  |
| 0           | 1.00          | 1.46 | 1.46 | 1.46                | 1.97 | 1.97 |
| 120         | 1.66          | 1.92 | 1.95 | 1.92                | 2.17 | 2.25 |
| 240         | 1.66          | 1.95 | 1.92 | 1.95                | 2.24 | 2.25 |

\* $\varphi_3 = 0^\circ$ ;  $\dagger \varphi_3 = 120^\circ$ .

3. If the potential of internal rotation takes the form:  $U(\varphi_1, \dots, \varphi_s) = u(\varphi_1) + \dots + u(\varphi_s)$ , considering  $V(\varphi, \beta)$  reduces the energy barrier between various conformations and produces a relation between angles of internal rotation.

If  $u(\varphi)$  is determined experimentally, it has to be considered, apparently, that  $V(\varphi, \beta)$  has already been taken into account. In this case, the experimental potential depends on temperature.

For long molecules ( $n \gg 1$ ) the problem of correlation between angles of internal rotation is the most interesting. This correlation rapidly decreases with an increase in distance (along the chain). Considering the relation between angles in statistical mechanics of polymer molecules does not, in our view, change the main conclusions: the coefficient of (linear) correlation may be zero (or very low) [9]. Nevertheless, we emphasize that if valence bonds and valency angles are regarded as absolutely rigid values, angles of internal rotation,  $\varphi_1, \varphi_2, \dots, \varphi_s$  cannot with any potentials  $U(\varphi)$  be regarded as varying independently.

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#### SUPPLEMENT

##### 1. The case of different masses.

In the main text we regarded the masses of particles as identical ( $m_k = 1, k = 1, 2, \dots, n$ ).

\*This factor takes the form:  $D_1 = \left(1 - \frac{1}{4} \cos^2 \theta\right)^{0.5}$ ,  $D_2 = \left[1 - \frac{1}{4} (\cos^2 \theta_1 + \cos^2 \theta_2)\right]^{0.5}$ ,  $D_3 = \left[1 - \frac{1}{4} (\cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3) + \frac{1}{16} \cos^2 \theta_1 \cos^2 \theta_3\right]^{0.5}$  and recurrent ratio  $D_{k+2}^2 = D_{k+1}^2 - \frac{1}{4} \cos^2 \theta_{k+2} D_k^2$  [4], [5] is valid.

In the general case of different masses formula (3) takes the form

$$g_{\alpha\beta} = \sum_{k=1}^n m_k \frac{\partial \mathbf{r}_k}{\partial q_\alpha} \frac{\partial \mathbf{r}_k}{\partial q_\beta}, \quad \alpha, \beta = 1, 2, \dots, s$$

Here  $\mathbf{r}_k = (x_{3k-2}, x_{3k-1}, x_{3k})$ . When calculating matrix  $f_{ij}$  scalar products with weight factors

$$f_{ij} = (\text{grad } F_i, \text{ grad } F_j) = \sum_{k=1}^n \frac{1}{m_k} \frac{\partial F_i}{\partial \mathbf{r}_k} \frac{\partial F_j}{\partial \mathbf{r}_k}, \quad i, j = 1, 2, \dots, v$$

should be used. In this case

claims of the argument hold good.

## 2. Factor $\Omega(\phi)$ and curvature of configuration space.

Factor  $\Omega(\phi)$  has the obvious geometrical significance:  $dV = \Omega(\phi) \prod_{k=1}^s d\phi_k$  which is a volumetric element of the configuration space of the system. From this point of view  $\Omega(\phi)$  is quite similar to functional determinant  $I(q)$ , formed when using curvilinear coordinates  $q$ . There is, however, a fundamental difference. In the absence of absolutely rigid bonds the configuration space is plane and coordinates may be selected so that  $I(q) = \text{const}$ .

With geometrical bonds configuration space  $M$  is distorted. (In our case  $M$  is the intersection of  $2n-3$  spheres in  $3n$ -dimensional Euclidean space).

In view of the non-zero curvature of  $M$  no choice of coordinates  $q$  can remove factor  $\Omega(q)$ , which gives an additional "potential"  $V(\phi, \beta)$ .

This conclusion may be compared with the initial Einstein theory of gravitation: gravitational interaction is the manifestation of curvature of space (more accurately, four-dimensional space-time).

*Translated by E. SEMERE*

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