

2. A. P. SUPRUN, T. A. SOBOLEVA and G. S. KOLESNIKOV, *Vysokomol. soyed.* **5**: 630, 1963 (Not translated in *Polymer Sci. U.S.S.R.*)
3. I. A. TUTORSKII, L. V. SOKOLOVA and B. A. DOGADKIN, *Symp. Khimiya i khimicheskaya tekhnologiya* (Chemistry and Chemical Technology), 1972
4. I. A. TUTORSKII, L. V. SOKOLOVA and B. A. DOGADKIN, *Vysokomol. soyed.* **A15**: 2583, 1973 (Translated in *Polymer Sci. U.S.S.R.* **15**: 11, 2931, 1973)
5. C. PINAZZI and H. GUENIFFEY, *Compt. rend.* **261**: 3309, 1965
6. E. S. VASKONYAN, N. K. MELKONYAN, S. M. GASPARYAN and N. G. KARAPETYAN, *Arm. khimich. zh.* **30**: 349, 1977
7. TATSUE MATSUDA and SHIGETADA FUJII, *J. Polymer Sci.* **5**, A-1: 2617, 1967
8. A. P. SUPRUN, I. I. VOINTSEVA, T. A. SOBOLEVA, A. S. SHASHKOV, A. A. ASKADSKII and G. L. SLONIMSKII, *Vysokomol. soyed.* **A16**: 1106, 1974 (Translated in *Polymer Sci. U.S.S.R.* **16**: 5, 1280, 1974)
9. A. ZHUNKE, *YaMR v organicheskoi khimii* (NMR In Organic Chemistry). Izd. "Mir", 1974
10. I. I. VOINTSEVA, A. S. SHASHKOV and A. P. SUPRUN, *Vysokomol. soyed.* **A20**: 1640, 1978 (Translated in *Polymer Sci. U.S.S.R.* **20**: 7, 1851, 1978)

Polymer Science U.S.S.R. Vol. 21, pp. 1799-1807
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0032-3950/79/0701-1799\$07.50/0

CLASSICAL GIBBS DISTRIBUTION FOR A CARBON CHAIN*

N. K. BALABAYEV and E. E. SHNOL'

Institute of Applied Mathematics, U.S.S.R. Academy of Sciences
 Scientific Research Centre of Computers, U.S.S.R. Academy of Sciences

(Received 6 July 1978)

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 φ_k (φ_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 φ : $U(\varphi) = U(\varphi_1, \varphi_2, \dots, \varphi_{n-3})$.

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 Ω 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) co-ordinates, 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 $I(q) = \det\left(\frac{\partial x_i}{\partial q_i}\right)$ 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

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

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 r_1 : $q_1=x_1, q_2=x_2, q_3=x_3$; 2) spheric alcoordinates of vector $e_1=r_2-r_1$ in relation to a fixed spherical system: $q_4=r_1, q_5=\theta, q_6=\alpha$; 3) spherical coordinates $e_2=r_3-r_2$ in relation to (some) spherical system with a polar axis along e_1 : $q_7=r_2, q_8=\theta_2, q_9=\beta$; 4) spherical coordinates $e_k=r_{k+1}-r_k$ ($k \geq 2$) 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 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 φ_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 θ_k ($k \geq 2$) being established

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

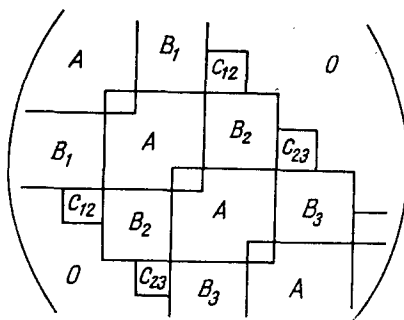
It is important to emphasize that $I(q)$ is independent of angles of internal rotation φ .

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:

$$F_1(x) = \frac{1}{2} |r_2 - r_1|^2, \quad F_3(x) = \frac{1}{2} |r_3 - r_2|^2, \dots; \\ F_2(x) = \frac{1}{2} |r_3 - r_1|^2, \quad F_4(x) = \frac{1}{2} |r_4 - r_2|^2, \dots$$

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

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

φ_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 φ . 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 and 270° (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 $\varphi=120$ and 240° . The difference of potentials at minimum values Δu 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°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: $\Omega(\varphi_1, \varphi_2) = [442 - 212.5(\cos^2 \varphi_1 + \cos^2 \varphi_2) + 70.3 \cos^2 \varphi_1 \cos^2 \varphi_2]^{0.5}$.

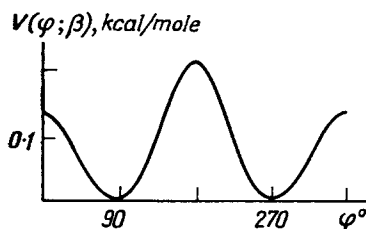


FIG. 1

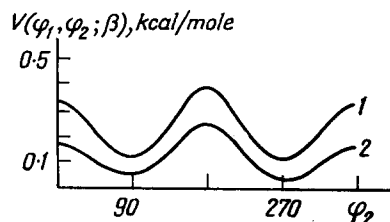


FIG. 2

FIG. 1. Dependence of the additional potential $V(\varphi; \beta)$ on the angle of internal rotation φ 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 φ_1 and φ_2 (300°K, $n=5$); $c=0$ (1) and 120° (2).

The combined density of distribution of probabilities of angles φ_1 and φ_2 is given by the formula

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

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 Ω 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 Ω at 300°K we obtain: $\rho(0, 0)/\rho(0, 120)=3.49$; $\rho(0, 0)/\rho(120, 120)=12.18$. When considering factor Ω 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 Ω moderates the difference between probabilities of various conformations.

Correlation between angles φ_1 and φ_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 Ω in formula (9), then $\rho(\varphi_1, \varphi_2) = \rho(\varphi_1) \rho(\varphi_2)$, angles φ_1 and φ_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 φ_2 with different fixed values of $\varphi_1=c$. A difference in the form of curves indicates a correlation between φ_1 and φ_2 . With potentials type (10) with narrow potential wells $u(r)$ the correlation produced by Ω is, evidently,

TABLE 1. FUNCTIONS $\Omega(\varphi_1, \varphi_2)/\Omega(0, 0)$ ($n=5$) FOR VARIOUS φ_1 AND φ_2 VALUES

| φ_2 | φ_1° | | | | | |
|-------------|-------------------|------|------|------|------|------|
| | 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 Ω then creates a correlation between angles, which is in addition to that formed by force interaction.

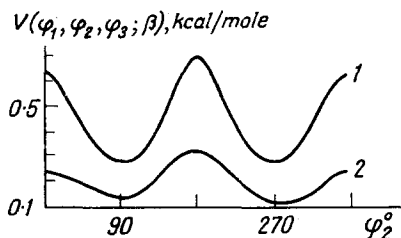


FIG. 3. Curves of $V(\varphi_1, \varphi_2, \varphi_3; \beta)$ with different fixed values of $\varphi_1=\varphi_3=c$ (300°K, $n=6$); $c=0$ (1) and 120° (2).

$n=6$. There are three angles of internal rotation here: φ_1 , φ_2 and φ_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 , ΔV increases [3].

TABLE 2. FUNCTIONS $\Omega(\varphi_1, \varphi_2, \varphi_3)/\Omega(0, 0, 0)$ WITH DIFFERENT φ_1, φ_2 AND φ_3 VALUES

| φ_3° | φ_1^* | | | φ_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.

The authors are grateful to I. P. Pavlotskii for providing valuable literature references, L. V. Lunevskaya for her considerable help in preparing the manuscript for printing and participants of the seminar "Mathematical Methods for Investigating Polymers" for the valuable discussions.

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

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

claims of the argument hold good.

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

Factor $\Omega(\varphi)$ has the obvious geometrical significance: $dV = \Omega(\varphi) \prod_{k=1}^s d\varphi_k$ which is a volumetric element of the configuration space of the system. From this point of view $\Omega(\varphi)$ 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" $V(\varphi, \beta)$.

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. SEMERÉ

REFERENCES

1. **M. V. VOL'KENSHTEIN**, Konfiguratsionnaya statistika polimernykh tsepei (Configuration Statistics of Polymer Chains). Izd. AN SSSR, 1956
2. **P. FLORY**, Statisticheskaya mekhanika tsepykh molekul (Statistical Mechanics of Chain Molecules). Izd. "Mir", 1971
3. **N. GÖ** and **H. A. SCHERAGA**, J. Chem. Phys. **51**: 4751, 1969
4. **M. FIXMAN**, Proc. Nat. Acad. Sci. USA **71**: 3050, 1974
5. **N. K. BALABAYEV** and **E. E. SHNOL'**, Ob uglakh vnutrennego vrashcheniya uglerodnoi tseepochki (Angles of Internal Rotation of a Carbon Chain). Preprint NTsBI U.S.S.R. Academy of Sciences, Pushchino, 1974
6. **F. R. GANTMAKHER**, Teoriya matrits (Matrix Theory). Izd. "Nauka", 1966
7. **T. M. BIRSHTEIN** and **O. B. PTITSYN**, Konformatsii makromolekul (Macromolecular Conformations). Izd. "Nauka", 1964
8. **N. P. BORISOVA**, Vysokomol. soyed. **6**: 135, 1964 (Translated in Polymer Sci. U.S.S.R. **6**: 1, 160, 1964)
9. **D. A. SVETOGORSKII**, Klassicheskaya statisticheskaya mekhanika polimerov s golonomnymi svyazyami. Soobshcheniya Ob'yedinennogo instituta yadernykh issledovaniy (Classical Statistical Mechanics of Polymers with Holonomic Bonds. Reports of the Joint Institute of Nuclear Research). R17-11116, 11117, 11118, Dubna, 1977