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An exactly soluble one-dimensional model of the thermodynamics of a rigid polymer molecule

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We construct the statistical thermodynamics of a polymer molecule in an exactly soluble one-dimensional model, which takes into account the rigidity of the macromolecule. We analyze the equation of state of the macromolecule under the action of external pressure. We show that at a fixed pressure the temperature dependence of the size of the region where the molecule is localized is nonmonotonic.

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1. INTRODUCTION. THE MODEL

An important problem in the theory of polymer macromolecules is that of spatial structure of long molecular chains of the protein or nucleic acid type. If the rigidity against bending of such a molecule is sufficiently small, the usual theoretical model to describe its statistical thermodynamical properties reduces to replacing the macromolecule by a chain with freely linked units (monomers). Confined to a closed volume or put in a sufficiently deep potential well, such a flexible and sufficiently long chain forms at a finite temperature a globule with a maximum monomer density at its center.[1,2] Of course, the structure of the globule must strongly depend on the rigidity of the macromolecule.

In the present paper we consider the effect of the rigidity of the macromolecule on the structure of the globule in an extremely simple model which allows only two configurations for the disposition of neighboring monomers. They can form only a zero angle (being directed to the same side) or an angle π between them. These two configurations have different coupling energies, and this is the manifestation of the rigidity of the chain.

The description of the state of a macromolecule is then similar to the description of the one-dimensional wandering of a point, where the probability for the direction of the next step depends on the direction of the preceding step. The system, of the type of a folding rule, is arranged along a straight line which we choose for our x-axis. The macromolecule consists of monomers of equal length a, their joints are positioned on sites with discrete coordinates $x_n = an$ ($n = 0, \pm1, \pm2, \dots$). It is convenient for us to describe the configuration of a chain in terms of the joints; therefore we introduce a numbering of the joints on the chain, starting at its beginning ($i = 0, 1, 2, \dots$), and we define a parameter σ_i that specifies the state of the i-th joint. This parameter takes the values $\sigma_i = \pm1$ and indicates the relative position of the preceding joint with respect to the given one: $x_i = x_{i-1} + a\sigma_i$. It is clear that the configuration of the chain is uniquely determined by the set $\{\sigma_i\}$. Indeed, if the start of the chain is at the point $x = 0$, we have

$$x_k = a\sum_{i=1}^{k}\sigma_i.$$

In the presence of an external field that acts upon the elements of the chain, we ascribe to each joint a potential energy $V(x_i)$. The interaction of neighboring monomers, which determines the rigidity of the chain, is in the present case described by the Ising scheme, and the interaction energy is equal to

$$U=-J\sum_{i=1}^{N}\sigma_i\sigma_{i+1}. \tag{1}$$

If $J>0$ a straightening (and not a folding) of the chain is energetically more advantageous and one can, indeed, connect this property with the idea of the rigidity of the macromolecule. However, in principle, the case $J<0$ is also possible. A stacking of the molecule on itself is then more advantageous and the parameter $|J|$ characterizes the energy for stacking one part of the pile of monomers relative to another part.

The total energy of the chain is thus equal to

$$H=\sum_{i=1}^{N}V(x_i)-J\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1}. \tag{2}$$

In contrast to the energy of the traditional one-dimensional Ising chain, in the present case the potential energy of the i-th joint in the external field $V(x_i)$ depends not only on its own state, but also on the state of all joints preceding it in the chain. Hence, the presence of an external field leads to the onset of a distinctive long-range action in a one-dimensional system, which is completely absent from the Ising model.

It is convenient for us to characterize the rigidity of the macromolecule by the quantity

$$\alpha=e^{2\beta}\equiv\exp\{2J/T\}, \tag{3}$$

which is directly connected in the present model with the persistence length l_0 ($l_0=\alpha a$).[3,4] We recall that the persistence length of a polymer chain is usually defined as that distance along the chain over which the probability of returning to the original point becomes comparable to unity.[1)] We note that a low rigidity ($J\ll T$) corresponds to $\alpha=1+2J/T$. (In the limit $J=0$ we have $\alpha=1$.)

2. PARTITION FUNCTION AND THERMODYNAMIC CHARACTERISTICS OF A MACROMOLECULE

We consider the partition function $Z_N(n,\sigma)$ of a chain of N elements, the end of which (last "joint") has a parameter σ and is at the site n. It is, by definition equal to the following sum over all possible sets $\{\sigma_k\}$:

$$Z_N(n,\sigma)=\sum_{\{\sigma_k\}}\exp\left\{-\sum_{i=1}^{N}\varphi(n_i)+\beta\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1}\right\} \tag{4}$$

under the conditions that

$$\sigma_N=\sigma,\quad \sum_{i=1}^{N}\sigma_i=n.$$

In (4) we have introduced the notation

$$\varphi(n)=V(an)/T,\quad \beta=J/T,$$

where T is the temperature.

In the sum (4) we split off the factor

$$Z_N=(2\operatorname{ch}\beta)^{N-1}\tilde{Z}_N \tag{5}$$

which is characteristic for the Ising model. In that case $\tilde{Z}_N$ satisfies the following recursion relation

$$\tilde{Z}_N(n,\sigma)=e^{-\varphi(n)}\sum_{s=\pm1}\tilde{Z}_{N-1}(n-\sigma,s)g(\sigma,s), \tag{6}$$

where $g(\sigma,\sigma)=\alpha/(1+\alpha)$, and $g(\sigma,-\sigma)=(1+\alpha)^{-1}$.

To isolate the dependence of $\tilde{Z}_N(n,\sigma)$ on the large parameter N we use the standard method of expanding $\tilde{Z}_N(n,\sigma)$ in the eigenfunctions of the following set of difference equations:

$$\psi_k(n,\sigma)=e^{\lambda_k-\varphi(n)}\sum_{s}\psi_k(n-\sigma,s)g(\sigma,s), \tag{7}$$

where k enumerates the eigenfunctions ψ_k and eigenvalues λ_k of this equation. Through direct substitution one verifies easily that the expansion for $\tilde{Z}_N(n,\sigma)$ has the following form:

$$\tilde{Z}_N(n,\sigma)=\sum_{k}C_ke^{-\lambda_kN}\psi_k(n,\sigma), \tag{8}$$

where the C_k are some coefficients. If the spectrum of λ_k starts with discrete values, for sufficiently large N we can restrict ourselves in Eq. (8) to only the basic term with the smallest discrete value λ_0:

$$\tilde{Z}_N(n,\sigma)\approx C_0e^{-\lambda_0N}\psi_0(n,\sigma). \tag{9}$$

Using Eq. (5) we then get for the free energy of the macromolecule ($N\gg1$)

$$F=-T\ln Z=-NT\ln(2\operatorname{ch}\beta)+NT\lambda_0. \tag{10}$$

Introducing the symbols $u(n)=\psi_0(n,1)$ and $v(n)=\psi_0(n,-1)$ we rewrite Eq. (7) in the form

$$\begin{aligned}\alpha u(n-1)+v(n-1)&=(\alpha+1)e^{\varphi(n)-\lambda_0}u(n),\\ \alpha v(n+1)+u(n+1)&=(\alpha+1)e^{\varphi(n)-\lambda_0}v(n).\end{aligned} \tag{11}$$

One checks easily that the functions $u(n)$ and $v(n)$ determine the monomer density distribution along the x-axis. Indeed, the eigenvalue of Eq. (11) is a functional of the potential $V(x_n)$ of the external field, and by definition the density $\rho(n)$ of the joints is equal to

$$\rho(n)=\delta F/\delta V=N\delta\lambda_0/\delta\varphi(n). \tag{12}$$

By varying Eq. (11) we establish that the density of the joints is proportional to

$$\rho(n)\propto\{u^2(n)+v^2(n)+2\alpha u(n)v(n)\}e^{-\varphi(n)}. \tag{13}$$

This formula generalizes the expression for the monomer density in a chain without rigidity ($\alpha=1$).[1]

When the external potential is symmetric, $\varphi(n)=\varphi\times(-n)$, we have the following relation between u and v: $u(n)=\pm v(-n)$. The set (11) can thus easily be reduced to an equation for $u(n)$ only:

$$\begin{aligned}&\alpha e^{-\lambda_0}\{e^{\varphi(n+1)}u(n+1)+e^{\varphi(n-1)}u(n-1)\}\\ &=\{(\alpha-1)+(\alpha+1)e^{\varphi(n)+\varphi(n-1)-2\lambda_0}\}u(n).\end{aligned} \tag{14}$$

We shall assume that the external field $\varphi(n)$ vanishes at infinity $[\varphi(\pm\infty)=0]$ and produces a potential well with a finite width and depth. We shall be interested in a compact form (globule) of the macromolecule, such that its size is determined by the shape of the potential well.

In that case the density (13) of the globule and the function $u(n)$ describing it must vanish at infinity. We verify first that localized solutions of Eq. (14) (which vanish at infinity) are possible only when $\lambda_0<0$. Indeed, we substitite $\varphi=0$ in Eq. (14):

$$u(n+1)+u(n-1)=2\{\operatorname{ch}\lambda_0-\alpha^{-1}\operatorname{sh}\lambda_0\}u(n). \tag{15}$$

If we rewrite this equation in the form

$$u(n+1)+u(n-1)-2u(n)=2\{\operatorname{ch}\lambda_0-\alpha^{-1}\operatorname{sh}\lambda_0-1\}u(n),$$

it becomes clear that solutions of (14) that decrease exponentially with $|n|$ are possible only when

$$\operatorname{ch}\lambda_0-\alpha^{-1}\operatorname{sh}\lambda_0-1>0. \tag{16}$$

The equation $\cosh\lambda_0-\alpha^{-1}\sinh\lambda_0=1$ has two roots: $\lambda=0$ and $\lambda=\lambda_m\sim\alpha^{-1}$. The condition (16) is satisfied either when $\lambda_0<0$ or when $\lambda_0>\lambda_m$. However, only the smallest discrete value λ_0 is of interest to us and it must be negative.

3. GLOBULE IN A RECTANGULAR POTENTIAL WELL

We consider as an example the rectangular potential well

$$V(x)=\begin{cases}-V_0, & |x|<d/2\\ 0, & |x|>d/2'\end{cases} \tag{17}$$

assuming that $d\gg a$.

If $[d/2a]=m$, there can fit inside the well $2m+1$ sites on which there can be joints. For such an external field Eq. (14) has different functional forms outside the well, inside the well, as well as at the points adjacent to its boundaries.

For negative λ_0 the general form of the solution is:

$$\begin{gathered} u=Ae^{k_1n},\quad -\infty<n<-(m+1),\\ u=B\operatorname{ch}k_2n+C\operatorname{sh}k_2n,\quad -(m-1)<n<(m-1),\\ u=De^{-k_1n},\quad (m+1)<n<\infty; \end{gathered} \tag{18}$$

$$\operatorname{ch}k_1=\operatorname{ch}\lambda_0-\alpha^{-1}\operatorname{sh}\lambda_0, \tag{19}$$

$$\operatorname{ch}k_2=\operatorname{ch}(\lambda_0+\varphi_0)-\alpha^{-1}\operatorname{sh}(\lambda_0+\varphi_0), \tag{20}$$

$$\operatorname{th}k_2(2m+1)=\operatorname{sh}k_1\operatorname{sh}k_2\{1-\operatorname{ch}k_1\operatorname{ch}k_2-(1-\alpha^{-2})(1-\operatorname{ch}\varphi_0)\}^{-1}, \tag{21}$$

where $\varphi_0=V_0/T$.

From Eq. (14) with $n=-(m+1)$, $-m$, m, $m+1$, corresponding to the boundaries, we easily find B, C, and D (the coefficient A can be determined from the normalization condition). The set (19) to (21) enables us to find the eigenvalue λ_0 as function of α and of the parameters of the potential well. We now analyze these equations.

We note first that k_1 is real only if condition (16) is satisfied, i.e., when $\lambda_0<0$. One can check that for finite values of α the eigenvalue λ_0 is always negative. If $V_0d\ll Ja$, λ_0 approaches zero with increasing rigidity. An analysis of Eq. (19) to (21) for small λ_0 and $\alpha\to\infty$ leads to the result

$$\lambda_0=\alpha^{-1}[1-\operatorname{ch}\{\varphi_0(2m+1)\}]. \tag{22}$$

It then turns out that

$$k_1=\alpha^{-1}\operatorname{sh}\{\varphi_0(2m+1)\}\ll 1. \tag{23}$$

We see that in the limit as $\alpha\to\infty$ the region where the globule is localized broadens to infinity. However, a macromolecule of arbitrarily large but finite rigidity is confined to the potential well. This conclusion is analogous to the quantum-mechanics conclusion that a particle is captured by even a very small one-dimensional potential well.

It follows from (23) that if $2m\varphi_0\gg 1$ there occurs a competition of two large parameters: α and $e^{2m\varphi_0}$. It is clear that $k_1\ll 1$ when $V_0d\ll 2Ja$. If, however, we have the inequality $V_0d\gg 2Ja$, then k_1 and λ_0 cease to be small in the limit as $\alpha\to\infty$.

The condition $V_0d\gg Ja$ requires a reconsideration of the limit $\alpha\to\infty$. First of all, it is clear that this limit is feasible only because $T\to 0$. In other words, it assumes that the temperature is a small energy parameter, in particular, $T\ll Ja/d\ll J$.

We let T tend to zero, assuming that $\lambda_0+\varphi_0\ll\varphi_0$. Equations (19) to (21) then lead us to the conclusion that

$$\lambda_0=-\varphi_0+\beta/d=-\varphi_0+2Ja/Td. \tag{24}$$

As it follows from Eq. (24) that $k_1\approx|\lambda_0|\gg 1$, the globule fits practically completely in the potential well, and one needs speak only about the monomer distribution in the region $-(m+1)<n<m+1$. We have thus verified that the shape of the globule depends very considerably on the relation between the characteristic aJ of the macromolecule and the characteristic V_0d of the well.

If $V_0d\gg Ja$, when the entire globule is in the potential well, it makes sense to study its structure assuming that $\varphi_0=\infty$, i.e., assuming the well be be infinitely deep. Inside an infinitely deep potential well Eq. (14) reduces to

$$u(n+1)-2u(n)+u(n-1)=2\{\operatorname{ch}\lambda-\alpha^{-1}\operatorname{sh}\lambda-1\}u(n),\quad |n|<m, \tag{25}$$

where $\lambda=\lambda_0+\varphi_0$. Putting further in (14) $|n|=m$ and $|n|=m+1$, we get the boundary conditions for Eq. (25):

$$u(-m)=0,\quad \frac{u(m-1)}{u(m)}=\frac{1+\alpha}{\alpha}e^{-\lambda}-\frac{1}{\alpha(1+\alpha)}e^{\lambda}. \tag{26}$$

All $u(n)$ with $|n|>m$ vanish identically. We note that the eigenvalue λ entered not only in the equation, but also in the boundary condition. The asymmetry of the boundary conditions (26) is connected with the fact that they are written down for the function $u(n)=\psi_0(n,1)$, i.e., for a quantity which is completely characterized by a well defined value of σ. The boundary condition (26) is satisfied by the solution

$$u=u_0\operatorname{sh}k_2(n+m), \tag{27}$$

where k_2 is determined by condition (20)

$$\operatorname{ch}k_2=\operatorname{ch}\lambda-\alpha^{-1}\operatorname{sh}\lambda \tag{28}$$

and the relation

$$\operatorname{th}k_2(2m+1)=\alpha\operatorname{sh}k_2\{(\alpha-1)e^{\lambda}-\alpha\operatorname{ch}k_2\}^{-1}. \tag{29}$$

We note first that from Eqs. (28) and (29) we get an equation that directly determines the quantity k_2 that characterizes the behavior of the solution inside the well:

$$\operatorname{sh}^2k_2(2m+1)=\alpha^2\operatorname{sh}^2k_2. \tag{30}$$

From this it follows that the solution (18) inside the well is strongly restructured when the persistence length becomes comparable with the size d of the well. Indeed, when $\alpha=\alpha^*\equiv 2m+1\approx d/a$, when $l_0=\alpha a=d$, the quantity $k_2=0$. If $\alpha>\alpha^*$, then k_2 is real, but if $\alpha<\alpha^*$, the quantity k_2 is purely imaginary.

One sees easily that k_2 becomes of order unity when $\alpha\sim e^{d/a}$, which is equivalent to the condition $2Ja\sim Td$. When $2Ja\ll Td$ we have $a|k_2|\ll 1$ and a long-wavelength consideration of the problem is thus possible. For such values of the rigidity, λ also turns out to be small at the same time. Indeed, it follows from Eqs. (28) and (29) that as $k_2 \to 0$, the eigenvalue λ tends to the value $\lambda_* \approx 2/\alpha^* = 2a/d \ll 1$.

We take in Eqs. (25) and (26) the limit to the long-wavelength approximation, restricting ourselves to the first terms in the expansion in powers of λ. In that case case Eq. (25) and the boundary conditions (26) take the simple form:

$$a^2\frac{d^2u}{dx^2}+\frac{\lambda(2-\alpha\lambda)}{\alpha}u=0, \tag{31}$$

$$u|_{x=-d/2}=0, \quad a\frac{du}{dx}\Big/u\Big|_{x=d/2}=\frac{\alpha\lambda-1}{\alpha+1}. \tag{32}$$

For small rigidities ($\alpha < \alpha^*$), when $k_2 = i\varkappa$ the solution of Eq. (27) becomes

$$u(x)=u_0\sin\varkappa(x+d/2), \quad \varkappa=[\lambda\alpha^{-1}(2-\alpha\lambda)]^{1/2}, \tag{33}$$

where

$$\mathrm{tg}(\varkappa d)/\varkappa=(\alpha+1)/(\alpha\lambda-1). \tag{34}$$

The boundary condition (34) admits of the existence of different values of λ which are, in fact, the eigenvalues of Eq. (7). The number of such values equals $p=[d/\pi+\frac{1}{2}]$. It is very important for the method used by us that the smallest value λ_0 be separated by a finite gap from the other values of λ for all values of the rigidity ($\alpha \geqslant 1$). The function $\lambda=\lambda(\alpha)$ for the lowest eigenvalue is single-valued and monotonic (it corresponds to curve 1 in Fig. 1). The remaining $p-1$ graphs of the function $\lambda_s=\lambda_s(\alpha)$ lie above the lowest one and are double-valued (the first ones of them are shown in Fig. 1 with the numbers 2, 3, 4). For not too large values of s the upper branches of these graphs approach asymptotically, in the limit as $\alpha \to 0$, the function $\lambda = 2/\alpha$ indicated by the dashed line in Fig. 1.

We now track the behavior of the graph for the lowest value of λ. In the limit of very small rigidity ($\alpha \ll \alpha^*$) the lowest eigenvalue is proportional to α:

$$\lambda={}^1/_2(\pi a/d)^2\alpha. \tag{35}$$

When there is no rigidity ($\alpha = 1$) this expression is, of course, the same as the corresponding result from the paper by I.M. Lifshitz[1] but recalculated for the one-dimensional case. Relation (35) for $\alpha \neq 1$ also follows from from the results of that paper. Indeed, Khokhlov has shown[4] that as far as its statistical properties are concerned a macromolecule is equivalent to an absolutely flexible fiber in which the role of the length of the freely joined monomers is played not by a, but by the persistence length $l_0 = \alpha a$. At the same time the number of links N must necessarily be replaced by $\tilde{N} = Na/l_0 = N/\alpha$. Of course, λ then changes to an effective eigenvalue $\tilde{\lambda}$. As $\tilde{\lambda}\tilde{N} = \lambda N$, we have $\tilde{\lambda} = \alpha\lambda$. Using the relation $\lambda = \frac{1}{2}(\pi a/d)^2$ for the absolutely flexible chain and replacing in it $\lambda \to \tilde{\lambda} = \alpha\lambda$ and $a \to l = \alpha a$, we get Eq. (35).

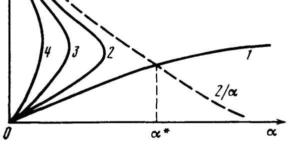

FIG. 1. The eigenvalues $\lambda_s (s=1, 2, 3, 4)$ as functions of the rigidity coefficient.

The next values λ_s (the lower branches of the curves 2, 3, 4 in Fig. 1) correspond to the expressions

$$\lambda_s=\frac{1}{2}\frac{\pi^2a^2s^2}{d^2}\alpha \quad (s=2,3,4,\dots). \tag{36}$$

For an appreciable rigidity, when $\alpha \gg \alpha^*$, but with the long-wavelength approximation still valid, i.e., $\alpha \ll e^{d/a}$, we have

$$\lambda \approx \frac{a}{d}\ln\left(\frac{a}{d}\alpha\right). \tag{37}$$

Finally, for very large ridigity ($\alpha \gg e^{d/a}$), when the long-wavelength approximation breaks down, it is necessary to use the exact relations (25) and (26), from which follows that

$$\lambda \approx \frac{a}{d}\{\ln\alpha-\alpha^{-2a/d}\}. \tag{38}$$

Equations (35) to (38) give us the function $\lambda = \lambda(\alpha)$ for the whole range of rigidity changes.

4. THERMODYNAMIC PROPERTIES OF A GLOBULE IN A DEEP POTENTIAL WELL

When one studies the thermodynamics of a globule in a potential well, two formulations of the problem are possible. Firstly, one can study the distribution of the monomers of the globule in a well of fixed width at various temperatures. Secondly, one can analyze the equation of state of the globule, assuming that the size of the well is not fixed, but that the external pressure on the "walls" of the well is given.

We consider first the density of the units of the macromolecule in a well of fixed dimensions. We substitute into (13) the lowest eigensolution of (27) for which $v(n) = u(-n)$ and use the normalization

$$\sum_{n=-m}^{m}\rho(n)=N.$$

It then turns out that

$$\rho(n)=N\frac{\mathrm{ch}\,k_2(2m+1)-\mathrm{ch}\,k_2\,\mathrm{ch}\,2k_2n}{(2m+1)\,\mathrm{ch}\,k_2(2m+1)-\mathrm{cth}\,k_2\,\mathrm{sh}\,k_2(2m+1)}, \tag{39}$$

where k_2 is determined from Eqs. (28) and (29). In the limit of a small rigidity the coordinate-dependence of the density of the globule takes its usual form[1]: the density is maximal in the center and vanishes at the boundaries:

$$\rho(n) \approx \frac{N\pi a}{2d}\cos\frac{\pi na}{d}. \tag{40}$$

When the rigidity increases the density decreases in the center and increases at the boundaries. When $\alpha \gg e^{d/a}$ the graph of the function $\rho(n)$ flattens and there appears a finite density jump $\rho(m-1)-\rho(m)$ at the boundary points. In the limit of infinite rigidity ($\alpha \to \infty$, $k_2 \to \infty$) it follows from (39) that

$$\rho(\pm m)=Na/2d, \quad \rho(n)=Na/d \quad \text{when} \quad |n| \neq m. \tag{41}$$

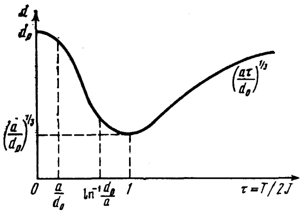

FIG. 2. Temperature dependence of the localization region of a macromolecule for a fixed pressure.

This natural result means that for large rigidity the molecule remains straight inside the well and is broken only at its boundaries. We note that the persistence length l_0 is then equal to the size of the system d and the simple relation $l_0 = \alpha a$ is not satisfied.

We now turn to the equation of state of a macromolecule. Assuming that the parameter J is temperature-independent, the pressure P on the walls is defined in the usual way:

$$P = -\left(\frac{\partial F}{\partial d}\right)_T = -NT\frac{\partial}{\partial d}\lambda(\alpha, d). \tag{42}$$

From this relation we can find the function $P = P(d, T)$. For arbitrary P and T it is rather difficult to find it in explicit analytical form, but one can indicate the form of the equation of state at the limiting temperatures when Eqs. (35) and (38) hold:

$$Pd^2 = 2aNJ, \quad T \ll J, \tag{43}$$

$$Pd^3 = (\pi a)^2 NT, \quad T \gg J. \tag{44}$$

The temperature dependence of the size of the globule at sufficiently low pressures ($aP \ll 2NJ$) is:

$$d \approx d_0 \text{ when } T \ll 2Ja/d_0, \tag{45}$$

$$d \approx d_0\left\{1 - \frac{T}{4J}\ln d_0/a\right\} \text{ when } 2J\frac{a}{d_0} \ll T \ll 2J\ln^{-1}\left(\frac{d_0}{a}\right), \tag{46}$$

$$d \approx (a\pi^2)^{1/3} d_0^{2/3} (T/2J)^{1/3} \text{ when } T > 4J, \tag{47}$$

where $d_0 = (2JNa/P)^{1/2}$.

The limiting size of the globule d_0 at $T = 0$ is obvious: all kinks occur at the boundaries of the well, their total number equals Na/d, and the energy connected with them is $E = F = 2JNa/d$. Therefore

$$P = -\partial E/\partial d = 2JNa/d^2,$$

from which follows $d = (2JNa/P^{1/2})$. When $T \sim 2J$ the size of the globule reaches its minimum value

$$d_{min} \sim (NJa^2/P)^{1/3}. \tag{48}$$

Figure 2 shows the function $d = d(T)$ for a fixed pressure on the well walls.

At high temperatures, when we can neglect the rigidity, the size of the globule increases with temperature: $d \sim (NTa^2/P)^{1/3}$. At low temperatures in the range

$$Ja/d_0 \ll T \ll J|\ln^{-1}(a/d_0)|$$

the size of the globule decreases with increasing temperature. This fact has a simple explanation: when the temperature increases the role of the rigidity diminishes and the external pressure compresses the molecule more.

In conclusion we note that the assumption of an infinitely deep well, which we used reduces in fact to the weaker assumptions:

$$\varphi_0 = V_0/T \gg 1 \text{ and } V_0 \gg J/\ln(d/a).$$

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[1)] Generally speaking the relation $l_0 = \alpha a$ is not universal. Cases of a more complicated dependence of the persistence length l_0 on the rigidity α are possible (we consider one of them in what follows).

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