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Quantum fluctuations of flexible chain molecules and rods and molecular nanotechnology

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The *classical* ground state of a flexible chain molecule (polymer) is well known to be simple, just a straight line. Here we consider *quantum* fluctuations of flexible chains. In their presence, the straight ground (zero-temperature) state becomes rough, whereas the Hookean, linear elastic theory breaks down: For a *weak* tensile force applied to the chain ends, the increment of the chain length is $\sim(\text{force})^{1/2}$. In non-self-avoiding chains, quantum fluctuations *alone* may induce a zero-temperature phase transition from the straight to a *crumpled ground state.* Self-avoiding chains, however, appear to have only straight ground states. We discuss these phenomena in physical systems of interest for molecular nanotechnology.

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I. INTRODUCTION

In recent years, the study of *thermal fluctuations* of membranes and surfaces has advanced considerably, not only because of its technological importance [1], but also because of its manifestation of interesting statistical physics on fundamental levels [2]. Much of the attention has been devoted to fluid and crystalline membranes that are two-dimensional (2D) generalizations of ordinary polymers. In these systems, thermal fluctuations may produce a number of striking effects, such as strong entropic intermembrane interactions [3], anomalous elasticity [4], and crumpling transitions [5]. All these effects can be understood in the framework of the classical statistical physics. *Quantum fluctuations,* however, ubiquitously dominate low-temperature behavior of physical systems. In ordinary crystalline solids, quantum phonon effects become important below the Debye temperature T_D, which is, in many practical instances, above the room temperature [6]. So the well known T^3 specific heat law of crystals is associated with a classical-to-quantum crossover: well below T_D, phonon fluctuations are purely quantum in nature in a broad range of length scales shorter than a crossover scale, which diverges as $T \rightarrow 0$. A similar crossover exists in realistic membranes and polymers, and their analogs, such as flexible thin shells and rods. This has already been realized in newly emerging *molecular nanotechnology* dealing with remarkable mechanical elements (rods, shells, springs, etc.) of extremely small sizes [7]. We remark that quantum effects are also important, or even dominant, in other systems involving fluctuating manifolds, such as the Abrikosov flux-line lattices in high-T_c superconductors ("quantum melting" [8]). Manifolds analogous to membranes and flexible rods may exist in *quark-nuclear matter,* even at $T=0$, in the form of periodic phases of stacked quark shells or rods imbedded in a nuclear matter background [9]. These phases are analogs of lamellar and columnar phases of fluid membranes [1]. Whereas the lamellar fluid membrane phases are stabilized by Helfrich's entropic repulsion induced by thermal fluctuations [3], analogous phases of quark membranes or rods may be stabilized at $T=0$ by a similar interaction induced by quantum fluctuations of the kind we consider here.

This paper yields deep theoretical insight into quantum fluctuations of flexible manifolds such as polymers and membranes [2]. We consider the fundamental problem of ground-state properties of a single *long* chain molecule (flexible polymer) or a flexible rod of practical interest for molecular nanotechnology [7]. The classical ground state of these systems is well known to be simple—just a straight line configuration. This is the unique configuration minimizing chain bending energy. Here, we show that quantum fluctuations substantially modify this picture. The straight ground state is actually *rough,* with transverse chain fluctuations growing as $\sqrt{N}$ for a chain of N monomers. A striking effect of these quantum fluctuations is a *breakdown* of the classical, Hookean elastic behavior: One would classically expect that a *weak* tensile force f applied to polymer ends stretches its ground-state configuration by an amount simply proportional to f, i.e., *strain* $\sim f$. We find, however, that this Hooke law, usually expected to hold in the limit $f \rightarrow 0$, is replaced by an *anomalous* elastic response to a weak f of the form

$$\text{strain} \sim \sqrt{f} \ ,$$

which originates from the long length-scale quantum fluctuations of long chains (Sec. III). So, the Hooke law of the conventional mechanical engineering breaks down in the quantum-mechanical engineering of nanosystems [7]. This anomalous elastic behavior occurs for $f \ll f_G$ where f_G is a crossover ("Ginzburg") force scale (see

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Secs. III and V). For $f > f_G$ one has ordinary Hookean behavior with *strain* $\sim f$. For the common hydrocarbon polyethylene chain $(\text{—CH}_2\text{—})_M$, in Sec. V we find that $f_G \sim 10^{-3}$ nN. Thus, at least for hydrocarbon chains, the forces required to observe the anomalous elastic response are some three orders of magnitude smaller than the forces required to manipulate atoms and build practical nanosystems [7]. If these systems are to be used for performing accurate measurements (e.g., as accelerometers), then one must go to low temperatures, where the quantum effects we consider are ubiquitously present. The main objective of this technology is to suppress fluctuations, *not* to hunt for fascinating fluctuations phenomena. On this route, thermal fluctuations can be a serious problem. Once they are eliminated by going to sufficiently low T, quantum fluctuations still remain and pose the ultimate limit to molecular nanotechnology. Our paper explores this ultimate limit.

We remark that a similar anomalous elastic response to weak external forces is well known to occur in crystalline membranes [4]. There, the anomalous elasticity is purely classical phenomenon induced by *thermal* fluctuations. On the other hand, here we show that anomalous elastic behavior can be present even at $T=0$, i.e., in the absence of thermal fluctuations. The source of this ground-state anomalous elasticity is quantum fluctuations ubiquitously present even at $T=0$.

Another interesting purely quantum effect we find in chains with bending rigidity constant κ smaller than a critical value $\kappa_c \sim \hbar^2$. For $\kappa < \kappa_c$, a non-self-avoiding (self-intersecting) chain has a *crumpled ground state* having the appearance of a highly collapsed polymer configuration (Sec. IV). Its radius of gyration grows very slowly with N as $R_g \sim [\log(N)]^{1/2}$. Such a disordered ground state is induced purely by quantum fluctuations—the classical ground state is straight for any $\kappa > 0$. However, repulsive interactions preventing chain self-intersection may significantly affect the existence of the crumpled ground state. We find, from quantum Monte Carlo simulations, that they are likely to suppress the occurrence of the crumpled ground state (Sec. IV). Similar suppression of crumpled phases was found to occur in tethered membranes [10].

This paper is organized as follows. In Sec. II we discuss flexible chains and their quantum statistical physics. Section III discusses quantum fluctuations around the straight ground state and its anomalous elastic response to weak tensile forces. Section IV deals with the crumpled ground state. In Sec. V we apply our results to polyethylene chains. The Appendix describes an alternative derivation of the results presented in Sec. III.

II. MODEL

We start by discussing models for non-self-avoiding flexible chain molecules. For a chain of $N+1$ molecules (monomers) with positions $\mathbf{R}_0, \mathbf{R}_1, \ldots, \mathbf{R}_N$ in a d-dimensional space ($d=2,3,\ldots$), the chain potential energy is, generally, of the form

$$U(\mathbf{R}_0, \mathbf{R}_1, \ldots, \mathbf{R}_N) = U_{\text{nn}} + U_{\text{bend}} \; . \tag{1}$$

Here

$$U_{\text{nn}} = \sum_{s=0}^{N-1} V(|\mathbf{R}_{s+1} - \mathbf{R}_s|^2) \; ,$$

where V is a nearest-neighbor potential binding monomers together. V typically has a deep minimum keeping neighbors at some preferred distance l_0 ($|\mathbf{R}_{s+1} - \mathbf{R}_s| \approx l_0$). U_{bend} in (1) is a bending energy of the form

$$U_{\text{bend}} = \frac{\kappa l_0^2}{2} \sum_{s=0}^{N-2} (\mathbf{T}_{s+1} - \mathbf{T}_s)^2 \; ,$$

with $\mathbf{T}_s = (\mathbf{R}_{s+1} - \mathbf{R}_s)/|\mathbf{R}_{s+1} - \mathbf{R}_s| \approx (\mathbf{R}_{s+1} - \mathbf{R}_s)/l_0$, and κ a positive bending constant. For *any* positive κ, the molecular configuration minimizing (1) (classical ground state) is a straight line of length $L = N l_0$: $\mathbf{R}_s = \mathbf{R}_0 + \hat{\mathbf{t}} l_0 s$, where $\hat{\mathbf{t}}$ is an arbitrary unit vector. So, the ground state is characterized by a nonzero *orientational* order parameter $(\partial \mathbf{R})/(\partial s) = l_0 \hat{\mathbf{t}}$. A tensile force f applied to chain ends along $\hat{\mathbf{t}}$ contributes the term $-f\hat{\mathbf{t}}(\mathbf{R}_N - \mathbf{R}_0)$ to the potential energy . A *weak* f stretches the ground state in a Hookean manner; the strain is

$$\Delta L / L = \Delta \left| \frac{\partial \mathbf{R}}{\partial s} \right| \Big/ l_0 = f / Y \; ,$$

where $Y = 4 l_0^3 V''(l_0^2)$ is a Young modulus. In a continuum notation, (1) can be rewritten as

$$U = \int_0^N ds \left[V \left[\left| \frac{\partial \mathbf{R}}{\partial s} \right|^2 \right] + \kappa \left[\frac{\partial^2 \mathbf{R}}{\partial s^2} \right]^2 \right] , \tag{2}$$

with V, for $|\partial_s \mathbf{R}| \approx l_0$, of the form

$$V \left[\left| \frac{\partial \mathbf{R}}{\partial s} \right|^2 \right] = V(l_0^2) + \frac{V''(l_0^2)}{2} \left[\left[\frac{\partial \mathbf{R}}{\partial s} \right]^2 - l_0^2 \right]^2$$
$$= \text{const} + \frac{r}{2} \left[\frac{\partial \mathbf{R}}{\partial s} \right]^2 + \frac{u}{4} \left[\left[\frac{\partial \mathbf{R}}{\partial s} \right]^2 \right]^2 . \tag{2$'$}$$

This form is reminiscent of a Ginzburg-Landau model with $\mathbf{M} = (\partial \mathbf{R})/(\partial s)$ as an orientational order parameter: For $r < 0$, the energy is minimized by a nonzero $\mathbf{M}$ of *arbitrary* orientation [11].

To discuss quantum effects, we consider the full *quantum* chain Hamiltonian

$$\hat{H} = -\sum_{s=0}^{N} \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{R}_s^2} + U(\mathbf{R}_0, \mathbf{R}_1, \ldots, \mathbf{R}_N) - f\hat{\mathbf{t}}(\mathbf{R}_N - \mathbf{R}_0). \tag{3}$$

The first term in (3) is kinetic energy of monomers with mass m. To study (3), we apply the quantum-statistical ("imaginary time") Feynman path integral method [12]. At a temperature T, quantum chain partition function has the form $\prod_s \int D\mathbf{R}_s(\tau) \exp(-H_{\text{eff}})$, with

$$H_{\text{eff}} = \frac{1}{\hbar} \int_0^{\hbar / k_B T} d\tau \left[\sum_{s=0}^{N} \frac{m}{2} \left[\frac{\partial \mathbf{R}_s}{\partial \tau} \right]^2 + U[\mathbf{R}_0(\tau), \mathbf{R}_1(\tau), \ldots, \mathbf{R}_N(\tau)] - f\hat{\mathbf{t}}[\mathbf{R}_N(\tau) - \mathbf{R}_0(\tau)] \right] . \tag{4}$$

Here, τ is the imaginary time and $\mathbf{R}_s(\tau=0)=\mathbf{R}_s(\tau=\hbar/k_BT)$ [12]. In the continuum notation

$$H_{\text{eff}}=\frac{1}{\hbar}\int_0^{\hbar/k_BT}d\tau\int_0^N ds\left[\frac{m}{2}\left[\frac{\partial\mathbf{R}}{\partial\tau}\right]^2+V\left[\left|\frac{\partial\mathbf{R}}{\partial s}\right|^2\right]+\kappa\left[\frac{\partial^2\mathbf{R}}{\partial s^2}\right]^2-f\hat{\mathbf{t}}\frac{\partial\mathbf{R}(s,\tau)}{\partial s}\right] . \tag{5}$$

Applying the path integral method, we mapped our quantum problem into a two-dimensional classical statistical-mechanics problem (5) for a d-component field $\mathbf{R}(s,\tau)$ living in the region $0<\tau<\hbar/k_BT$, $0<s<N$. This region extends to the entire (τ,s) plane in the long-chain limit $(N\to\infty)$ and in the ground state $(T\to 0)$. This feature makes the *quantum* chain ground-state problem similar to *classical* statistical physics of membranes [2]. However, these two problems are still qualitatively different in detail, as discussed in the following sections.

III. QUANTUM FLUCTUATIONS AROUND THE STRAIGHT GROUND STATE

We first discuss quantum fluctuations around the classical, straight ground state by writing $\mathbf{R}(s,\tau)=\hat{\mathbf{t}}[l_0s+u(s,\tau)]+\mathbf{h}(s,\tau)$. Here, $u(s,\tau)$ are longitudinal fluctuations, phonons, whereas $\mathbf{h}(s,\tau)$ are transversal $(\hat{\mathbf{t}}\cdot\mathbf{h}=0)$ fluctuations, undulations, perpendicular to the classical ground state. Equation (5) then yields

$$H_{\text{eff}}=\frac{1}{\hbar}\int d\tau\int ds\left[\frac{B}{2}\left[\partial_s u+\frac{1}{2l_0}(\partial_s\mathbf{h})^2\right]^2+\frac{\kappa}{2}(\partial_s^2\mathbf{h})^2+\frac{m}{2}(\partial_\tau\mathbf{h})^2+\frac{m}{2}(\partial_\tau u)^2-f\partial_s u+\cdots\right] , \tag{6}$$

with $B=Y/l_0=4l_0^2V''(l_0^2)$. The ellipses in Eq. (6) indicate various terms irrelevant for the long length-scale properties of the straight ground state. By ignoring the anharmonic terms $\partial_s u(\partial_s\mathbf{h})^2$ and $[(\partial_s\mathbf{h})^2]^2$, Eq. (6) becomes easily tractable. This harmonic approximation to (6) yields the standard Hookean strain response $\langle\partial_s u\rangle\sim f$. Less trivial prediction of the harmonic approximation is a rough character of the quantum ground state: For $f=0$, the transverse chain fluctuations behave, in the ground state, as

$$\langle[\mathbf{h}(s_1)-\mathbf{h}(s_2)]^2\rangle^{1/2}\sim|s_1-s_2|^{1/2} ,$$

indicating that the fluctuating chain, although asymptotically straight, is actually very rough, with its transverse size growing as $\langle(\mathbf{h})^2\rangle^{1/2}\sim\sqrt{N}$.

The anharmonic terms of Eq. (6), $\partial_s u(\partial_s\mathbf{h})^2$ and $[(\partial_s\mathbf{h})^2]^2$, produce some even more striking effects on the ground state. By treating them with a brute force perturbation theory, one can show that they produce fluctuation corrections to the renormalized elastic constant B which, for zero tensile force f, diverge with size of the chain, N (see the Appendix). As discussed in the following (and, in a different way, also in the Appendix), a consequence of this divergent behavior is a nontrivial *softening* of the renormalized (size-dependent) elastic constant B, i.e., Young modulus Y. This elastic constant softens with increasing chain size N according to

$$B_{\text{ren}}(N)=\frac{Y_{\text{ren}}(N)}{l_0}\sim\frac{1}{N} . \tag{7}$$

Similar phenomena are known to occur in crystalline membranes, due to thermal fluctuations. The present quantum polymer problem in Eq. (6) is somewhat similar to that of membranes with *zero* shear modulus [13]. (Still, these two problems are qualitatively different in detail [14].) As in the membrane problem, in the present quantum chain ground-state problem, anharmonic effects can be handled essentially *exactly* (up to irrelevant terms) as detailed here. As the first step, note that Eq. (6) is harmonic in phonon, u variables. Thus, the phonons can be decoupled from undulations by the change of variables: $(\mathbf{h},u)\to(\mathbf{h},u')$, with

$$u(s,\tau)=u'(s,\tau)+\frac{f}{B}s+\int d\tau_1\int ds_1 G(s-s_1,\tau-\tau_1)u_0(s_1,\tau_1) , \tag{8a}$$

where u_0 is a quadratic local functional of $\mathbf{h}$ defined by

$$\partial_s u_0=-\frac{1}{2l_0}(\partial_s\mathbf{h})^2 , \tag{8b}$$

and

$$G(s,\tau)=\int_\omega\int_q\frac{Bq^2}{Bq^2+m\omega^2}e^{isq+i\omega\tau}\quad(\text{for } T=0) . \tag{8c}$$

Note that this change of variables, from $(\mathbf{h},u)$ to $(\mathbf{h},u')$, is a simple shift (its Jacobian is unity). With this change, H_{eff} transforms into

$$H_{\text{eff}}=H(u')+H_0(\mathbf{h})+H_1(\mathbf{h}) ,$$

where

$$H(u')=\frac{1}{\hbar}\int d\tau\int ds\left[\frac{m}{2}(\partial_\tau u')^2+\frac{B}{2}(\partial_s u')^2\right] , \tag{9a}$$

$$H_0(\mathbf{h})=\frac{1}{\hbar}\int d\tau\int ds\left[\frac{m}{2}(\partial_\tau\mathbf{h})^2+\frac{\kappa}{2}(\partial_s^2\mathbf{h})^2+\frac{f}{2l_0}(\partial_s\mathbf{h})^2\right] , \tag{9b}$$

and

$$H_1(\mathbf{h})=\frac{1}{\hbar}\int_\omega\int_q\frac{1}{2}\frac{mB\omega^2q^2}{Bq^2+m\omega^2}|u_0(q,\omega)|^2\quad(\text{for } T=0) . \tag{9c}$$

Here, $u_0(q,\omega)$ is the Fourier transform of the field $u_0(s,\tau)$ defined in Eq. (8b). Thus, $H_1(\mathbf{h})$ is a quartic interaction of the undulations $\mathbf{h}$. This interaction produces *no* nontrivial long length-scale renormalization of the elastic constants in (9b); see the Appendix. Thus, $H_0(\mathbf{h})$ in (9b) describes qualitatively correctly the behavior of chain undulations at long length scales. In particular, this implies that the above harmonic result for the transverse correlations is not altered by the anharmonic effects. Nonetheless, the anharmonic effects seemingly "eliminated" by the change of variables in Eq. (8), *do* have a nontrivial effect on the elastic response to f. To see this, note that, by (8),

$$\langle \partial_s u \rangle = \frac{f}{B} - \frac{1}{2l_0}\langle (\partial_s \mathbf{h})^2 \rangle \, . \tag{10}$$

Then, by calculating the average in Eq. (10) with respect to $H_0(\mathbf{h})$, Eq. (9b),

$$\langle (\partial_s \mathbf{h})^2 \rangle = (d-1)\int_\omega \int_q \frac{\hbar q^2}{m\omega^2 + \kappa q^4 + (f/l_0)q^2} \qquad (\text{for } T=0)\,, \tag{11}$$

one obtains

$$\langle \partial_s u \rangle = -c_1 + \frac{f}{B} + c_2\sqrt{f} \tag{12}$$

for a weak f acting on the ground state of a very long chain ($T=0$, $N=\infty$). Here, $c_1=(d-1)\hbar/4l_0(m\kappa)^{1/2}$, and $c_2=c_1/\pi(l_0\kappa)^{1/2}$. So, a weak f induces the strain

$$e = \frac{\langle \partial_s u \rangle_f - \langle \partial_s u \rangle_{f=0}}{l_0}$$

behaving as

$$e = \frac{f}{Y} + \frac{c_2}{l_0}\sqrt{f} \, . \tag{13}$$

The first term in (13) is the ordinary Hookean response. The second term arises due to a suppressive effect of the tensional force on chain undulations [see Eq. (9b)] yielding a singular contribution to the average $\langle (\partial_s \mathbf{h})^2 \rangle$ in (10) of the form $-\sqrt{f}$. For a sufficiently weak f, the $\sqrt{f}$ term in (13) dominates. Equation (13) can be rewritten as

$$e = \frac{f}{Y}\left[1 + \left[\frac{f_G}{f}\right]^{1/2}\right] , \tag{13'}$$

where f_G is a Ginzburg force scale

$$f_G = \frac{(d-1)^2}{16\pi^2 l_0^5}\frac{\hbar^2 Y^2}{m\kappa^2} \, . \tag{13''}$$

For $f \ll f_G$ one has an *anomalous* elastic response of the form $e \sim \sqrt{f}$ rather than the Hookean one, $e \sim f$. Thus, the linear Hooke law, normally expected to be valid for a weak f, breaks down. Physically, the "$e \sim \sqrt{f}$" law reflects an elastic response to f which is much stronger than the standard, Hookean one arising from stretching of bonds between monomers [the first term in (13)]. In fact, the dominant effect of a weak f is not bond stretching, but a suppression of chain undulations that produces a straightening of the chain. Because of the soft nature of undulations, this straightening produces a contribution to the strain growing much faster with f than in the Hooke law.

Related to this anomalous elastic response is the softening of the renormalized Young modulus anticipated in Eq. (7). To see this, consider the renormalized Young modulus defined by

$$\frac{1}{Y_{\text{ren}}(N)} = \lim_{f\to 0}\frac{\partial e}{\partial f} = \lim_{f\to 0}\frac{1}{l_0}\frac{\partial \langle \partial_s u \rangle}{\partial f} \, , \tag{14}$$

or, by (10),

$$\frac{1}{Y_{\text{ren}}(N)} = \frac{1}{Y} - \frac{1}{2l_0^2}\lim_{f\to 0}\frac{\partial \langle (\partial_s \mathbf{h})^2 \rangle}{\partial f} \, . \tag{15}$$

As $e \sim f^{1/2}$ for infinite chains ($N=\infty$), one has, by (14), Y_{ren} $(N=\infty)=0$. For a finite chain, $N<\infty$, we obtain from (15) by using (11) with the lower momentum cutoff $q_N=\pi/N$,

$$\frac{1}{Y_{\text{ren}}(N)} = \frac{1}{Y} + \frac{1}{q_N}\frac{d-1}{8\pi l_0^3}\frac{\hbar}{m^{1/2}\kappa^{3/2}} \, . \tag{16}$$

Thus,

$$Y_{\text{ren}}(N) = \frac{Y}{1+(q_G/q_N)} = \frac{Y}{1+N/N_G} \, , \tag{17}$$

where N_G and q_G are, respectively, the Ginzburg chain size and the corresponding Ginzburg wave vector,

$$q_G = \frac{\pi}{N_G} = \frac{d-1}{8\pi l_0^3}\frac{Y\hbar}{m^{1/2}\kappa^{3/2}} \, , \tag{18}$$

or, by (13''),

$$N_G = \frac{2\pi}{\left[\dfrac{f_G}{\kappa l_0}\right]^{1/2}} \, . \tag{18'}$$

For long chains with $N \gg N_G$, by (17) one has the softening of the Young modulus we anticipated before in Eq. (7). For these chains we find

$$e = \frac{f}{Y_{\text{ren}}(N)} = \frac{N}{N_G}\frac{f}{Y} \tag{19}$$

for $f \ll f_N$, with

$$f_N = l_0\kappa\left[\frac{2\pi}{N}\right]^2 = f_G\left[\frac{N_G}{N}\right]^2 \sim \frac{1}{N^2} \, . \tag{20}$$

Thus, in a range of weak forces that vanishes as $N \to \infty$, the elastic response is linear, however, with a softened Young modulus. On the other hand, for tensile forces in the range $f_N < f < f_G$, one has previously described anomalous elastic response with $e \sim f^{1/2}$, whereas for $f > f_G$ the response is nonanomalous, $e = f/Y$. In the Appendix, we present an alternative derivation of Eqs. (16) and (17) and of the anomalous elastic response discussed in this section.

Finally, let us discuss the chain's longitudinal, phonon fluctuations. Within harmonic approximation to Eq. (6) one obtains

$$\langle [u(s)-u(s')]^2 \rangle^{1/2} \sim [\ln|s-s'|]^{1/2} \, , \tag{21}$$

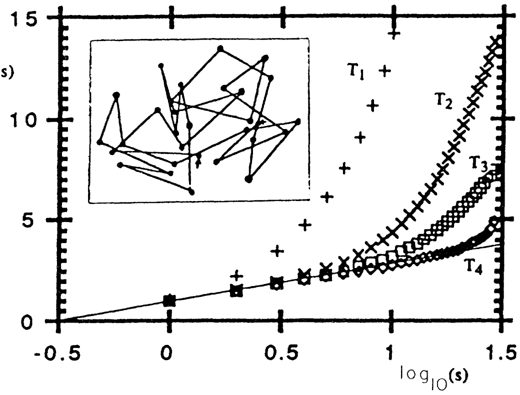

FIG. 1. Inset: Non-self-avoiding (self-intersecting) polymer in its crumpled ground state. Positional correlation function $\phi(s)$ vs $\log_{10}(s)$, for various temperatures $(T_1 > T_2 > T_3 > T_4)$. As T decreases, all curves collapse to $\phi(s) \sim \log_{10}(s)$.

as for any one-dimensional crystal in its quantum ground state. However, anharmonic interactions between phonons and undulations in Eq. (6) substantially modify this harmonic result for $|s-s'| \gg N_G$. We find, by (8a)–(8c) and (9b),

$$\langle [u(s)-u(s')]^2 \rangle^{1/2} \sim |s-s'|^{1/4} \tag{22}$$

for $|s-s'| \gg N_G$.

IV. CRUMPLED GROUND STATE

Quantum undulations have a disordering effect on the chain orientational order. For example, by (12), for $f=0$,

$$\langle \partial_s \mathbf{R} \rangle = \hat{\mathbf{t}} \left[l_0 - \frac{1}{2l_0} \langle (\partial_s \mathbf{h})^2 \rangle \right] = \hat{\mathbf{t}} l_0 [1 - \tfrac{1}{2}(\kappa_c/\kappa)^{1/2}] ,$$

with $\kappa_c = (d-1)^2 \hbar^2 / 4 l_0^4 m$. So, the chain projection onto the direction of the orientational ordering $\hat{\mathbf{t}}$ is shorter than that in the absence of undulations. This suggests that the straight ground state may become unstable for chains with a small value of bending rigidity constant, $\kappa < \kappa_c$. In other words, chains with sufficiently small bending rigidity may exhibit a *crumpled ground state.*

We proceed by discussing first non-self-avoiding flexible chains at $T=0$. Classically, these chains are straight for any positive value of bending rigidity κ. To examine how this is altered by the presence of quantum fluctuations, we solved our model (5) exactly in the large-d limit, in a standard fashion [14]. For $f=0$, we find a *zero-temperature* second order phase transition occurring for $\kappa = \kappa_c = d^2 \hbar^2 / 4 l_0^4 m$. For $\kappa > \kappa_c$, the ground state is asymptotically straight with a nonzero $\langle \partial_s \mathbf{R} \rangle = \hat{\mathbf{t}} l_0 [1 - (\kappa_c/\kappa)^{1/2}]^{1/2}$ vanishing, as $(\kappa - \kappa_c)^{1/2}$, at the critical point. On the other side, for $\kappa < \kappa_c$, we find an *orientationally disordered ground state,* $\langle \partial_s \mathbf{R} \rangle = 0$, which has a highly crumpled appearance. For positional correlations, $\phi(s_1 - s_2) = \langle [\mathbf{R}(s_1) - \mathbf{R}(s_2)]^2 \rangle$, we find

$$\phi(s_1 - s_2) \sim \ln|s_1 - s_2| . \tag{23}$$

Thus, the chain's external size (radius of gyration) grows very slowly with N as $R_g \sim [\ln(N)]^{1/2}$. Equation (23) is valid beyond the large-d limit, as we verified by quantum Monte Carlo simulations of non-self-avoiding chains in $d=2$ and 3. Simulations were carried out, in a standard way [15], by discretizing the imaginary time τ in $N_\tau = (\hbar / k_B T)/\Delta\tau$ time intervals. This reduces our microscopic model (4) to a classical statistical-mechanics problem of $N_\tau N$ interacting particles. For chains with a small κ, our simulations indicate a highly crumpled ground state (see Fig. 1), with positional correlations as in (23), for any d. Analytic explanation for this superuniversality of (23) is that in the crumpled phase, at long length scales, the effective *renormalized* Hamiltonian has a form as in (5) with $V \to V_{\text{ren}} = r(\partial_s \mathbf{R})^2$ with a *positive r,* i.e.,

$$H_{\text{ren}} = \frac{1}{\hbar} \int_0^{\hbar/k_B T} d\tau \int_0^N ds \left[\frac{m}{2} (\partial_\tau \mathbf{R})^2 + \frac{r}{2} (\partial_s \mathbf{R})^2 \right] . \tag{24}$$

For $T=0$, this Hamiltonian yields positional correlations as in (23) in any d [16]. In Fig. 1 we give our Monte Carlo results for positional correlations $\phi(s_1 - s_2)$, obtained at various temperatures, illustrating quantum-to-classical crossover. Both the simulations of the microscopic model (4) and analytic calculations done with (24) show that the quantum form (23) is valid for $|s_1 - s_2| < N^* \sim T^{-1}$, whereas for $|s_1 - s_2| > N^*$ one has the classical random walk behavior, $\phi(s_1 - s_2) \sim |s_1 - s_2|$. As in more familiar situations with ordinary crystals [6], this quantum-to-classical crossover produces heat capacity C vanishing as $T \to 0$. By (24), one can show that $C \sim T$ as $T \to 0$ and the crumpled ground state is reached.

On the other hand, for chains with $\kappa > \kappa_c$, the straight ground state is reached as $T \to 0$. Then one has a *different* heat capacity law of the form $C \sim \sqrt{T}$ as can be obtained by a simple calculation with Eq. (9b) (with $f=0$). At any *finite* $T > 0$ and for *any* $\kappa > 0$ (bigger or smaller than κ_c), a chain will have a crumpled shape provided its size N is bigger than persistence size $N_p(T)$ [17]. For $\kappa < \kappa_c$, $N_p(T)$ has a finite zero-T limit, since the crumpled ground state is reached then. For $\kappa > \kappa_c$, the straight ground state is reached as $T \to 0$ and $N_p(T)$ diverges as T^{-1}. For $\kappa > \kappa_c$, the quantum-to-classical crossover size, $N_{q\text{-}c}(T)$ diverges as $T^{-1/2}$. For chains with $N < N_{q\text{-}c}(T)$, one has the quantum behavior found before, with $\langle (\mathbf{h})^2 \rangle^{1/2} \sim N^{1/2}$ (Sec. III), whereas for $N_{q\text{-}c}(T) < N < N_p(T)$, one has a scaling behavior with $\langle (\mathbf{h})^2 \rangle^{1/2} \sim N^{3/2}$ induced by thermally excited undulations.

Thus far, we considered non-self-avoiding chains. Inclusion of self-avoiding interactions in the form of short-range repulsion between all monomer pairs may, however, strongly affect the crumpled ground state (whereas it should not have any qualitatively new effects on the straight ground state). For example, in the case of crystalline membranes, self-avoiding interactions are believed to suppress the crumpled phase at any T [10]. On the other hand, long self-avoiding polymers are well known to be crumpled at any finite T. Then, the interesting question is whether self-avoiding polymers can remain crumpled at $T=0$, i.e., in the ground state. In other words, is the crumpled ground state we found before for non-self-avoiding flexible chains suppressed by inclusion of self-avoiding interactions? To investigate this, we simulated chains with a hard-core repulsion with the hard-core size chosen to ensure that chains do not self-intersect. Figure 2(a) depicts the typical ground-state configuration of a 2D chain with *zero* bare bending constant κ. In spite of this, the chain is apparently straight, as confirmed also from the calculation of positional correlations: $\phi(s_1-s_2)\sim|s_1-s_2|^{2\nu}$, with $\nu=0.96\pm0.3\approx1$ for $d=2$. For $d=3$, we find a similar situation with $\nu=0.85\approx1$, within the size limits of our simulation [Fig. 2(b)]. Thus, most likely, non-self-intersecting chains in $d=2$ and $d=3$ cannot have a crumpled ground state. This suppression of the crumpled ground state is somewhat similar to the suppression of the crumpled phase in self-avoiding crystalline membranes, where such a phase might be, in principle, induced by thermal fluctuations [10]. Since the ground-state problem of the quantum chain is, in the path integral representation, similar to a classical statistical physics of a membranelike object (Sec. II), one may attempt to relate our results for the chain ground state to previous results on membranes [10]. However, there is no direct relationship between these two problems. In the case of chains, self-avoiding interactions contribute to the action of the quantum-statistical Feynman path integral the term of the form

$$\int d\tau \int ds_1 \int ds_2 \delta^d(\mathbf{R}(s_1,\tau)-\mathbf{R}(s_2,\tau)) \ . \tag{25}$$

Note that this self-avoiding interaction is *local* in one, the τ coordinate. On the other hand, the contribution of self-avoiding interactions to the classical Hamiltonian of a crystalline membrane described by molecular positions $\mathbf{R}(\tau,s)$, is of the form

$$\int d\tau_1 \int d\tau_2 \int ds_1 \int ds_2 \delta^d(\mathbf{R}(s_1,\tau_1)-\mathbf{R}(s_2,\tau_2)) \ . \tag{26}$$

This self-avoiding interaction is nonlocal in both the τ and s coordinates. In other words, in the membrane case, Eq. (26), a molecule interacts with any other molecule, whereas in the quantum chain case, Eq. (25), molecules interact only if they have the same value of the τ coordinate. Thus, there is a significant qualitative difference between these two problems. Self-avoiding interactions appear to be qualitatively much weaker (more local) in the quantum chain case. Nonetheless, our numerical simulations indicate that even with this qualitatively weaker self-avoiding interaction, the crumpled chain ground state appears to be suppressed. Note, however, that this suppression appears to be *quantitatively* weak, as demonstrated by the still fairly crumpled appearance of the 3D chain in Fig. 2(b).

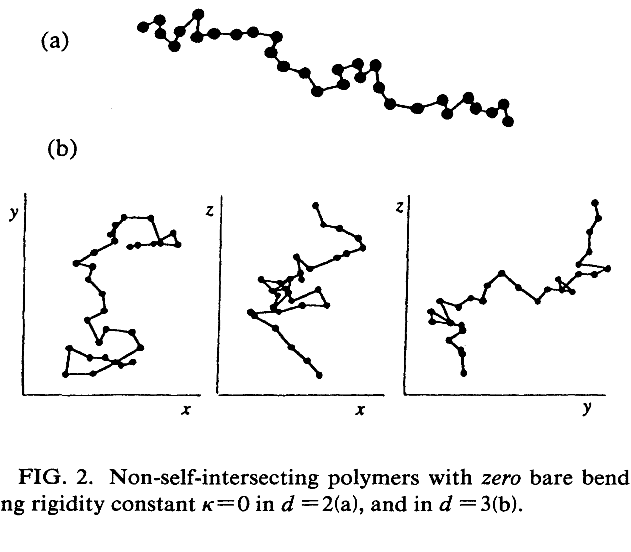

FIG. 2. Non-self-intersecting polymers with *zero* bare bending rigidity constant $\kappa=0$ in $d=2$(a), and in $d=3$(b).

V. DISCUSSION

The discussions of Secs. III and IV suggest that for practical purposes, the most interesting prediction of this paper is the anomalous elastic response of long chains in their straight ground state, of the form $e\sim\sqrt{f}$. In Sec. III we found that such a response exists in chains whose size N is bigger than the Ginzburg size N_G, Eqs. (18) and (18′), for forces smaller than the Ginzburg force f_G, Eq. (13″).

Here, we discuss the experimental observability of this anomalous elastic behavior in systems of potential interest for molecular nanotechnology. As a rather general example, we will discuss the common hydrocarbon polyethylene chain, $(\text{—CH}_2\text{—})_M$ [18]. In the absence of quantum fluctuations, its ground state is the well known zigzagged configuration in Fig. 3. Here [18],

$$r_0=1.52\times10^{-10}\ \text{m} \tag{27}$$

and

$$\theta_0=109.47^\circ \ , \tag{28}$$

$[\cos\theta_0\approx-\frac{1}{3}]$. It is convenient to consider $(\text{CH}_2)_2$ groups as unit elements (cells) of the chain, as indicated in Fig. 3. Thus, the mass entering into the equations of Sec. III is

$$m=2m_{\text{C}}+4m_{\text{H}} \ , \tag{29}$$

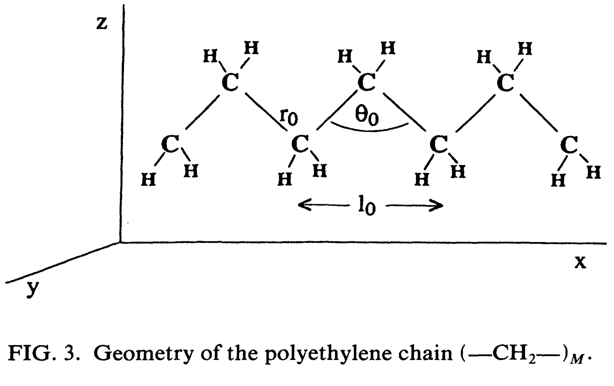

FIG. 3. Geometry of the polyethylene chain $(\text{—CH}_2\text{—})_M$.

whereas the cell size is

$$l_0=2r_0\sin\frac{\theta_0}{2}\ . \tag{30}$$

Now, N entering into the equations of Sec. III is the number of $(CH_2)_2$ groups, i.e., $M=2N$ is the number of carbon atoms in the chain. In contrast to the model of Sec. III, the polyethylene ground state in Fig. 3 breaks the invariance for rotations in the y-z plane. In effect, the bending energy term of Eq. (6), $\kappa(\partial_s^2\mathbf{h})^2$, is here replaced by

$$\kappa_y(\partial_s^2 h_y)^2+\kappa_z(\partial_s^2 h_z)^2\ , \tag{31}$$

with, in general, $\kappa_y\neq\kappa_z$.

To proceed, we need to estimate the bare elastic constants Y, κ_y, and κ_z. This can be done by considering energy costs of small fluctuations around the regular configuration in Fig. 3. To accomplish this, we used potential energy estimates frequently used in nanotechnology calculations [18]. We find [19]

$$Y=\frac{8k_\theta\tan^2(\theta_0/2)}{l_0}\ , \tag{32}$$

$$\kappa_z=\frac{k_\theta}{l_0^2}\ , \tag{33}$$

and

$$\kappa_y=\frac{V}{6l_0^2\cos^2(\theta_0/2)}\ . \tag{34}$$

Here [18],

$$k_\theta=0.45\times10^{-18}\ \mathrm{J} \tag{35}$$

and [19]

$$V=0.14\times10^{-18}\ \mathrm{J}\ . \tag{36}$$

By (32)–(36),

$$\frac{\kappa_y}{\kappa_z}\approx0.15\ .$$

So, κ_y is an order of magnitude smaller than κ_z. Thus, we can simplify our estimates by ignoring undulations along the z direction (in this way we will slightly *underestimate* the anharmonic effects of Sec. III). In effect, we can use formulas of Sec. III with $d-1=1$ and $\kappa=\kappa_y$ as in (34), m as in (29), l_0 as in (30), and Y as in (32). With these estimates, we obtain, by Eqs. (13″) and (18) [or (18′)],

$$f_G=0.104\times10^{-2}\ \mathrm{nN}\sim10^{-3}\ \mathrm{nN}\ , \tag{37}$$

whereas

$$N_G\approx105\sim10^2\ , \tag{38}$$

corresponding to chains with $M_G=2N_G\approx200$ carbon atoms. Thus, to clearly enough observe the anomalous elastic response $e\sim\sqrt{f}$, one needs polyethylene chains with $N>10N_G$, i.e., with at least 2000 carbon atoms. Moreover, one has to apply tensile forces smaller than $f_G\sim10^{-3}$ nN. On the other hand, the typical scale of the forces proposed to perform manipulations of atoms in building molecular nanotechnology devices is of the order $f\sim1$ nN [20]. Typical forces that might be applied during regular functioning of such devices could be smaller, say, $f\sim10^{-2}-10^{-1}$ nN. Thus, unless these devices are to be used for performing accurate measurements, the anomalous elastic response $e\sim\sqrt{f}$ may not be of practical concern. In order to observe this zero-T response, one has to expel the thermal fluctuations by going to temperatures smaller than a characteristic temperature scale T_G that can be estimated from

$$k_BT_G=\hbar\omega(q_G)\ ,$$

where $q_G=\pi/N_G$, and $\omega(q)$ is the frequency of undulations with wave vector q, $\omega(q)=(\kappa q^4/m)^{1/2}$. With previous estimates, we obtain $T_G\approx35$ mK. If, say, $T=10^{-2}T_G=0.35$ mK, then there exists one decade of length scales (between N_G and $10N_G$) needed for the anomalous response $e\sim\sqrt{f}$ to develop. Thus, to summarize, to directly observe this zero-temperature anomalous elastic response $e\sim\sqrt{f}$, (i) one needs a polyethylene chain with at least 2000 carbon atoms (ten times bigger than the Ginzburg size), (ii) one must apply tensile forces f of the order 10^{-3} nN, and (iii) one must go to temperatures of the order $T\sim10^{-1}$ mK. These force and temperature scales are below those of practical interest for many of the future nanotechnological devices.

The prospects for observing our zero-temperature anharmonic effects, however in a weaker form, are much better by studying the softening of the Young modulus in polyethylene chains shorter than the Ginzburg size, i.e., with less than 200 carbon atoms. These chains behave practically as if at zero temperature if their temperature is $\sim T_G\sim10$ mK. Equation (17) predicts a size-dependent softening of the Young modulus from its bare value Y, for chains with few carbon atoms, down to $Y_{\mathrm{ren}}=\frac{1}{2}Y$, for chains with about 200 carbon atoms. This anharmonic effect of *zero-temperature* quantum fluctuations of polymers is remarkably *quantitatively* strong. For comparison, we note that in order to observe a similar 50% change of three-dimensional smectic-A elastic constants due to anharmonic effects of long length-scale *thermal* fluctuations [21], one needs astronomically large samples with some 10^{25} smectic layers or so.

ACKNOWLEDGMENT

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APPENDIX

Here, we present an alternative discussion of the anomalous elastic response (Sec. III). We start by discussing zero-temperature fluctuation corrections to coupling constants of the elastic Hamiltonian in Eq. (6). To one-loop order, for the fluctuation correction to the elastic constant B we obtain, for zero tensile force,

$$\delta B=-\frac{2(d-1)B^2}{4l_0^2}\int_q\int_\omega\frac{\hbar q^4}{(m\omega^2+\kappa q^4)^2}\ . \tag{A1}$$

This correction diverges with decreasing lower momentum cutoff q_N, i.e., increasing chain size $N=\pi/q_N$, as

$$\delta B \sim -\frac{1}{q_N} \sim -N \ . \tag{A2}$$

In a broader scope, one can consider the present polymer problem as the $D=1$ case of D-dimensional crystalline membranes with *zero shear modulus.* Here, D is the internal dimension of the membrane; $D=2$ for membranes, $D=1$ for polymers. For the quantum ground state of such a membrane with N^D molecules, one obtains

$$\delta B \sim -\frac{1}{q_N^{2-D}} \sim -N^{2-D} \tag{A3}$$

for D less than a critical dimension $D_c=2$ [22]. On the other hand, for membranes with zero shear modulus, there are *no* fluctuation corrections to the bending constant κ and the monomer mass m that diverge as N^{2-D} as in (A3) [23]. Thus, the elastic constant B, i.e., the Young modulus $Y=B/l_0$, is the only coupling in (6) that undergoes a substantial renormalization at long length scales. To find the form of this renormalization, we apply a renormalization group (RG) transformation of the Wilson type to Eq. (6). In a standard fashion, we coarsegrain fluctuations within the shell $\Lambda(b)=\Lambda(0)e^{-b}<|q|<\Lambda(0)$, $-\infty<\omega<+\infty$. To one-loop order, from (A1) we obtain, for $D=1$,

$$\frac{dB}{db}=-w(b)B(b) \ , \tag{A4}$$

where w is a dimensionless coupling constant

$$w(b)=\frac{d-1}{8\pi l_0^2}\frac{\hbar B(b)}{[\kappa(b)]^{3/2}[m(b)]^{1/2}\Lambda(b)} \ . \tag{A5}$$

By (A4) and (A5), and taking into account the absence of a substantial renormalization of κ and m $[(d\kappa/db)=0$, $(dm/db)=0]$, we obtain, for $D=1$,

$$\frac{dw}{db}=w-w^2 \ . \tag{A6}$$

The RG equation (A6) has a stable anharmonic fixed point with $w^*=1$. Integration of (A6) yields

$$w(b)=\frac{w(0)e^b}{1-w(0)+w(0)e^b} \ . \tag{A7}$$

By (A4),

$$B(b)=B(0)\exp\left[-\int_0^b db'w(b')\right] \ . \tag{A8}$$

Eqs. (A8) and (A7) imply

$$B(b)=\frac{B(0)}{1-w(0)+w(0)e^b} \ , \tag{A9}$$

or, in terms of the momentum cutoff $\Lambda=e^{-b}\Lambda(0)$,

$$B_{\text{ren}}(\Lambda)=\frac{B}{1-w(0)+[\Lambda(0)w(0)]/\Lambda} \ , \tag{A10}$$

with

$$w(0)=\frac{d-1}{8\pi l_0^2}\frac{\hbar B}{\kappa^{3/2}m^{1/2}\Lambda(0)} \ . \tag{A11}$$

By introducing the Ginzburg wave vector $q_G=\pi/N_G$, as in Eq. (18), and noting that $q_G=w(0)\Lambda(0)$,

$$B_{\text{ren}}(\Lambda)=\frac{B}{1-w(0)+(q_G/\Lambda)} \ . \tag{A12}$$

With $B_{\text{ren}}=Y_{\text{ren}}/l_0$, and $\Lambda=q_N=\pi/N$, Eq. (A12) becomes identical to Eq. (17) of Sec. III. Thus, for $\Lambda\to 0$,

$$Y_{\text{ren}}(\Lambda)\sim\Lambda \tag{A13}$$

for zero tensile force $f=0$. Let us rederive the anomalous elastic response $e\sim\sqrt{f}$ of Sec. III by means of (A13). A nonzero f introduces an effective short wave vector cutoff, Λ_f, to membrane undulations. For $q<\Lambda_f$, the stress contribution to the undulation energy $(f/l_0)q^2$ [see Eqs. (9b) and (11)], dominates the bending energy contribution κq^4. Thus, $(f/l_0)\Lambda_f^2\approx\kappa\Lambda_f^4$, i.e. [24],

$$\Lambda_f\sim\sqrt{f} \ . \tag{A14}$$

The elastic response can be calculated as

$$e=\frac{f}{Y_{\text{ren}}(\Lambda_f)} \ . \tag{A15}$$

By (A13) and (A15), $e\sim f/\Lambda_f$, so that by (A14), $e\sim\sqrt{f}$, in agreement with Sec. III.

The Young modulus scaling (A13), obtained in this Appendix from the perturbative one-loop RG, is actually exact to all orders in perturbation theory, as suggested in the approach pursued in Sec. III based upon a change of variables decoupling phonons from undulations [see Eqs. (8) and (9)]. All the RG results presented in this Appendix we obtained before in Sec. III from the harmonic undulations Hamiltonian (9b). The anharmonic undulation interaction in (9c) is actually irrelevant. By considering it as a perturbation to (9b), one can show that this perturbation expansion is finite in the infrared, i.e., it does not contain divergent behavior like that in (A2) or (A3). Thus, the harmonic undulation Hamiltonian (9b) captures the behavior of undulations at long length scales correctly.

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[14] Note that in (6) the imaginary time, τ direction is "hard" with energy $\sim(\partial_\tau \mathbf{h})^2$. This is in contrast to the similar model for studying thermal fluctuations of two-dimensional crystalline membranes around their flat phase (see Ref. [4]) in which all directions are soft [say, energy $\sim(\partial_\tau^2 \mathbf{h})^2$].

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[16] Eq. (12) becomes formally equivalent to the model for non-self-avoiding tethered membranes in their crumpled phase (see Refs. [2] and [5]), provided one identifies the imaginary time τ with one of the two internal membrane dimensions.

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$$E(\phi)=E_{\rm CC}(\phi)+4E_{\rm CH}(\phi)+4E_{\rm HH}(\phi)\ ,$$

with

$$E_{\rm CC}=\tfrac{1}{2}\{V_1[1-\cos(\phi)]+V_2[1-\cos(2\phi)] + V_3[1-\cos(3\phi)]\}\ ,$$

$$E_{\rm CH}(\phi)=\tfrac{1}{2}V_3^{\rm CH}[1-\cos(3\phi)]\ ,$$

and

$$E_{\rm HH}(\phi)=\tfrac{1}{2}V_3^{\rm HH}[1-\cos(3\phi)]\ .$$

Here, $V_1=1.39\times10^{-21}$ J, $V_2=1.88\times10^{-21}$ J, $V_3=0.65\times10^{-21}$ J, $V_3^{\rm CH}=1.85\times10^{-21}$ J, and $V_3^{\rm HH}=1.65\times10^{-21}$ J [18]. For small ϕ, $E(\phi)\approx\frac{1}{4}V\phi^2$, with

$$V=V_1+4V_2+9(V_3+4V_3^{\rm CH}+4V_3^{\rm HH})=0.14\times10^{-18}\ {\rm J}\ .$$

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[24] Here we use the fact that the tensile force f is not renormalized at long length scales. This can be deduced from a Goldstone-type theorem invoking breaking of the rotational invariance in the presence of a tensile force; see Ref. [13].