Different statistical mechanical ensembles for a stretched polymer

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Imposing to a single polymer chain of N monomers either a fixed pair of forces $\pm\mathbf{f}$ acting at the chain ends (stress ensemble) or a fixed end-to-end vector $\mathbf{R}$ (strain ensemble) does correspond to the use of different statistical mechanical ensembles. In particular, the two elasticity laws, $R_f=g(f)$ and $f_R=h(R)$, where R_f is the length of the average end-to-end vector $\langle\mathbf{R}\rangle_f$ in the stress ensemble and f_R is the intensity of the average internal force $\langle\mathbf{f}\rangle_R$ in the strain ensemble, are not equivalent. For these conjugated ensembles, the quantity $\Delta_f=f-h(g(f))$ and more generally $\Delta_O=\langle O\rangle_f-\langle O\rangle_R$ where O is an arbitrary observable, is studied systematically in this paper for a wide class of polymer models corresponding to chains at temperatures equal or above the theta point. The leading term $\Delta_O^{(2)}$ of an expansion of Δ_O in terms of the successive moments of the end-to-end vector fluctuations in the stress ensemble can be used to analyze the scaling properties of Δ_f. For the Gaussian and the freely jointed chain models, $\Delta_O\propto 1/N$ for large N with the particularity that, for the elasticity law, Δ_f strictly vanishes for the Gaussian chain at any finite N. For chains in good solvent, the usual result $\Delta_f\propto 1/N$ at fixed f is only valid in the highly stretched chain regime (Pincus regime). N independent large ensemble differences of the order of 20% on Δ_f are noticed when the chain is stretched over a distance of the order of the unstretched chain average end-to-end distance R_0. These effects decrease to the 1% level for $R_f>3R_0$. Monte Carlo calculations for a chain model containing both excluded volume and finite extensibility features illustrate the distinction between the elasticity laws in the two ensembles over all stretching regimes. Our study suggests that the nature of the constraints used in single chain micromanipulations could be relevant to the interpretation of experimental elasticity law data. [S1063-651X(99)15411-4]

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I. INTRODUCTION

The study of the elastic behavior of a single linear polymer is a standard application of statistical mechanical concepts [1–5]. In this field of renewed interest [6], it is sometimes noticed (see [1,4,5,7]) that ensembles corresponding to a fixed end-to-end vector $\mathbf{R}$ or to fixed stretching forces $\pm\mathbf{f}$ acting at the chain ends can lead to distinct elasticity laws. Long ago, Flory pointed out [1] that these two conjugated single chain ensembles can be seen as polymer counterparts of, respectively, the constant volume and constant pressure ensembles of N-particle systems. In the latter case, away from phase transitions, there are correction terms of $O(N^{-1})$ for finite size effects on intensive properties like the energy per particle, the density or the pressure. To our knowledge, the nature of the equivalent correction terms for single stretched chain ensembles has never been discussed systematically (for general models). Elasticity laws relative to different single chain ensembles have been compared long ago for ideal chain models. The same linear elasticity law follows independently of the ensemble chosen for Gaussian chains. For the freely jointed chain model (FJC), made of N segments of length b, the Langevin function relates the (imposed) force on chain ends to the average extension of the polymer while the inverse Langevin function gives the average internal force for a fixed end-to-end vector $\mathbf{R}$ up to correction terms which vanish as N^{-1} in the limit of infinitely long chains (see page 321 in [1] and chapter 6 in [4]).

To which extent the elastic behavior of a single polymer chain with excluded volume (EV) interactions and finite extensibility (FE) is dependent upon the nature of the external constraint imposed at the chain ends is the central question on which we focus. Although the general approach we take in the present paper could be exploited in other applications, we prefer to leave for future work elasticity features of particular biological molecules [6] or universal properties of stretched polyelectrolytes [8]. The chain elasticity in the globular state (below the theta point) [9] will not be considered here as our analysis is restricted to single phase systems far from phase transition boundaries.

The correct statistical mechanical ensemble to associate with an experimental measurement probing single chain properties is an issue of great interest given the actual breakthrough of experimental setups probing directly single chain mechanical or thermodynamic properties like for instance elasticity, finite extensibility or adsorption/desorption of a chain on/from a surface. In all these experiments, the ends of a single chain are controlled externally, either directly or indirectly.

In the original experiment of Bustamante's group [10], one end of the DNA chain is chemisorbed to a glass support while the other end is chemically bounded to a micron-sized bead to which well calibrated external forces can be imposed while the average position of the bead is being recorded by fluorescence microscopy. Along the same lines, the brownian motion of a hairy polystyrene bead temporarily tethered to a glass surface by a single chain under bead-surface repulsive

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force conditions was analyzed and the polymer ''spring constant'' determined [11].

Viovy and coworkers devised another setup [12] where the chain is rigidly maintained by a mobile piezomicromanipulator at one end and, at the other end, by a flexible tube through which light is deviated in a way which has been previously calibrated against known forces within the piconewton range. The light deflection angle is then a measure of the average internal contractile force for an imposed end-to-end vector. Atomic force microscopy (AFM) has been recently developed towards single chain force measurements probing the vertical stretching of a chain grafted on a surface [13] or detaching a single polyelectrolyte chain adsorbed on a charged surface [14,15].

In order to focus on the single chain elasticity law of a N-segment linear polymer within an ensemble characterized either by a pair of fixed stretching forces applied at the chain ends or by a fixed end-to-end vector, we need to introduce some specific notations. Let us first consider that the polymer ends are subjected to a pair of external forces $-\mathbf{f}$ and $+\mathbf{f}$ acting, respectively, on the beads indexed 0 and N. The resulting average end-to-end vector $\mathbf{R}_f \equiv \langle \mathbf{r}_N - \mathbf{r}_0 \rangle_f$, where $\mathbf{r}_i$ stands for the position vector of bead i and $\langle \cdots \rangle_f$ represents a fixed-f ensemble average, can be written as $\mathbf{R}_f = R_f \hat{\mathbf{f}} \equiv g(f)\hat{\mathbf{f}}$ where $\hat{\mathbf{f}} \equiv \mathbf{f}/|\mathbf{f}|$ is a unit vector pointing in the direction of $\mathbf{f}$. The relationship $R_f = g(f)$ gives the elasticity law in the f ensemble for f intensities defined, in principle, over the range $[0,\infty]$. When the same polymer is subjected to a fixed end-to-end vector $\mathbf{r}_N - \mathbf{r}_0 = \mathbf{R} \equiv R\hat{\mathbf{R}}$ where we introduced the unit vector $\hat{\mathbf{R}}$, an average internal force $\mathbf{f}_R = f_R \hat{\mathbf{R}} \equiv h(R)\hat{\mathbf{R}}$ develops within the polymer. These forces, namely $+\mathbf{f}_R$ and $-\mathbf{f}_R$, which act respectively on beads 0 and N, tend usually to contract the chain $[h(R) > 0]$ but they sometimes act in the opposite direction, as when EV forces between end beads give rise to a repulsion at short distance $[h(R) < 0]$. The relationship $f_R = h(R)$ is the elasticity law in the fixed-R ensemble which, in principle, covers values of R in the range $[0,\infty]$. We will consider the difference $\Delta_f = f - h(g(f))$ between these force intensities as a measure of the non equivalence of the elasticity laws in both ensembles.

The fact that we focus on this particular manifestation of the distinction between both conjugated ensembles does not imply that it is the only one. Other single chain properties of a stretched polymer like its gyration tensor, the NMR residual dipolar interaction or the chain structure factor in scattering experiments should also depend upon the nature of the applied constraint. Even if these applications are not discussed in the present paper, we give the theoretical basis to establish the connection between the averages of any observable calculated in the stress or in the strain ensembles.

The nature of the difference between the fixed-f and fixed-R single polymer conformational ensembles is formally similar for any particular R (or f) value but, as well qualitatively and quantitatively, the effect turns out to be radically different for the small and the large extension regimes defined, respectively, by $R/R_0 \ll 1$ and $R/R_0 \gg 1$, where R_0 is the average (in the mean square sense) of the unstretched chain end-to-end vector.

In the low-f regime of the fixed-f ensemble, the EV chains are usual (weakly perturbed) three-dimensional (3D) self-avoiding walks while in the low-R limit of the fixed-R ensemble, all conformations are close to a cyclic structure and EV chain ends are mutually repelling due to forces which are largely of entropic origin: the members of the two ensembles are thus forming two quite different families of conformations. It must be realized here that our attitude is quite formal as the relevance of the stress or strain ensembles considered in this paper (and in standard textbooks [1,5]) is of little experimental relevance in the $R/R_0 \ll 1$ regime. Real single chain elasticity experiments involving micromanipulations on chain ends use needles, beads, or microtubes on which chain ends are grafted: a more realistic study of the effects of the constraints on the single chain elasticity in the weak stretching regime should then include additional confinement effects.

Considering now the strong stretching regime of the fixed-f ensemble, it turns out that the end-to-end vector fluctuates only slightly around the mean so that the two ensembles give almost the same averages for any single chain structural property. A systematic study of the ensemble influence on the elasticity law will however allow us to investigate the interesting crossover regime $R/R_0 \approx 1$ which should be experimentally relevant as, in this regime, confinement effects are probably negligible with respect to the ensemble effects discussed in this paper. The difference Δ_f in the elasticity laws will be discussed theoretically and then applied to different standard chain models in continuous space. We will consider Gaussian chains, freely jointed chains, and EV chains according to the end-to-end distribution obtained from renormalization group theory (RGT). A last model containing both EV and FE characteristics will also be discussed on the basis of extensive Monte-Carlo simulations. The adopted hard sphere necklace model is a semiflexible chain with hard sphere repulsion terms between monomers. Both fixed-f and fixed-R elasticity laws can be extracted from such simulations which in addition, are useful to test the domain of validity of RGT and the nature of the crossover behavior between the scaling regime and the FE region, the latter region being actually the main focus of the new experiments on single molecule stretching. The technique we used in our simulations, namely the configurational biased Monte Carlo method adapted to stretched chains, has also been implemented to study the elongation of a realistic chain model of polyethylene but this topic will be discussed elsewhere [16].

It should be recalled at this point that Monte Carlo calculations have been successfully applied within the context of a single stretched EV chain, starting with the work of Webman, Lebowitz, and Kalos [17] which demonstrated the existence of a Pincus blob regime in the intermediate regime of the elasticity law. The behavior $R_f \propto f^{(1/\nu)-1}$, where $\nu \approx 0.6$ is the Flory scaling exponent for good solvent conditions, remains today a property which was originally predicted theoretically [18], subsequently checked by simulations [17], but not yet directly verified experimentally. Much later, Wittkop *et al.* [19] performed a more extensive Monte Carlo study of the same single EV chain elasticity law, showing that RGT correctly predicts the cross-over between the linear stretching regime (at weak forces) and the Pincus blob regime. In 1995, Cifra and Bleha [20] studied the effect of varying the solvent quality on the elasticity law, in particular the separa-

tion between enthalpic and entropic contributions to the stretching force. Recently, two of us [21] reported Monte Carlo results on the scattering function of a stretched chain showing the signature of Pincus blobs on the structure factor. It is interesting to note that, with the exception of Cifra and Bleha's work which follows a fixed-R statistical mechanical formulation, all MC works mentioned above are formulated in the fixed-f ensemble. A different stretched chain ensemble where only one component of the end-to-end vector is constrained has been used in a recent series of MC studies [22,23] aimed at studying the coil-globule phase transition under stretching. As transverse end-to-end vector fluctuations are sampled while they are frozen in the fixed R-ensemble we consider (where the vector $\mathbf{R}$ is fully constrained), the elasticity law in this unusual ensemble should be intermediate between the two cases discussed in the present paper.

Our paper is organized as follows. In the next section, we start by defining quite generally the different single chain stretching domains to which we will refer throughout the paper. In Sec. III, we remind the statistical mechanical formalism required to derive the elasticity law in both the fixed-f and the fixed-R ensembles which enables us to properly define the central quantity Δ_f mentioned earlier. We then evaluate exactly this quantity for various standard chain models relative to chains at the theta point or in good solvent. We cover here ideal chains (the Gaussian and the FJC cases) and EV chains using the RGT end-to-end vector distribution of unstretched chains. In Sec. IV, we establish two formal expansions of the average of an arbitrary observable $\langle O\rangle_f$ around $\langle O\rangle_R$ computed in a fixed-R conjugated ensemble. We discuss various convergence aspects of these expansions for the different chain models. For the particular case of Δ_f where O is simply chosen to be the internal force acting on the chain ends, we find a leading term in the expansion, namely the second order expression $\Delta_f^{(2)}$, which turns out to be a good approximation of Δ_f in the $R/R_0>1$ stretching domain. In that case, scaling properties of Δ_f can be estimated from those of $\Delta_f^{(2)}$. In the last part of this section, Monte Carlo calculations relative to the hard-sphere necklace model (which combines FE and EV characteristics) are presented. Conclusions and perspectives are gathered in the final Sec. V.

II. SINGLE CHAIN STRETCHING DOMAINS

Consider a linear polymer of N Kuhn segments (we suppose $N\gg 1$) each of size b undergoing Brownian motion in a solution at temperature T. The average end to end distance of the chain is $R_0\approx bN^{\nu}$ where ν is the scaling exponent equal to $\nu=0.5$ or $\nu\approx 0.6$ for θ and good solvent conditions, respectively. When this polymer is subjected to stretching forces $\pm\mathbf{f}$ at its ends, the average end-to-end distance shows three distinct regimes which can be predicted by scaling arguments [18,24,17].

A. Linear regime

At small forces $[f<f^*\equiv(k_BT/R_0)]$, the relative extension increases linearly with the global reduced force $\eta_g=(fR_0/k_BT)$

$$\frac{R_f}{R_0}=\frac{1}{3}\eta_g. \tag{1}$$

The effective spring constant k, which relates the extension R_f to the stretching force f, $f=kR_f$, is thus $k=3k_BT/R_0^2$.

B. Pincus blob regime

For forces in the range $f^*<f<f^{**}\equiv(k_BT/b)$, i.e., when f lies in the domain where $\eta_g>1$ and the local reduced force $\eta_l\equiv(fb/k_BT)<1$, the universal scaling corresponds to the so-called Pincus blob behavior [18,24]

$$\frac{R_f}{R_0}=A\,\eta_g^{(1/\nu-1)}, \tag{2}$$

where A is a constant. When excluded volume forces are absent, one has $\nu=0.5$ and $A=1/3$ so that Eq. (2) extends the validity of the small force linear law of Eq. (1) up to f^{**}. For EV chains, $A\approx 0.46$ [17,21].

C. Finite extensibility regime

Finally, when the force is such that $f\geqslant f^{**}$, the finite extensibility (FE) regime is entered and a model specific behavior follows. This is the region which is most studied experimentally [6,13].

D. About the N dependence of R_f at fixed f

For later purposes, it is useful to discuss at this stage the N dependence of the average end-to-end vector at fixed f in the different domains. In the linear regime, the N dependence is related to the spring constant varying as $N^{-2\nu}$. For both the Pincus blob regime and the finite extensibility regime (sometimes collectively denoted as the strong stretching regime in the following), the average extension scales like N at fixed f, a behavior expected when the extension of the stretched polymer overcomes the size of the unstretched chain [24].

E. Typical force crossover values in experimental setups

Crossover values f^* and f^{**} for some micromanipulations on stretched macromolecules at 300 K reported in the introduction are easily estimated on the basis of published values of the contour length L_c of individual chains and of the Kuhn segment length b which combine to give $R_0^2=L_cb$. For a DNA chain of length $L_c\approx 30$ μm in physiological conditions for which $b=0.1$ μm [10], one finds $f^*\approx 0.003$ pN and $f^{**}\approx 0.05$ pN and we note that, in Ref. [10], data points are reported for $f\geqslant f^{**}$. The AFM study of individual dextran filaments leads to $f^*=0.2$ pN and $f^{**}=7$ pN using $b=0.6$ nm and $L_c\approx 1$ μm [13]. Exploring the power law regime would be rather difficult as f should be of the order of a few pN while natural fluctuations seem to be of the order of 20 pN. Improved precision could however be obtained by averaging over many successive stress or strain cycles over the range of end-to-end vector lengths of interest [13].

III. FIXED-f AND FIXED-R ENSEMBLES FOR A SINGLE POLYMER CHAIN

A. A reminder of textbook statistical mechanics

We now establish the theoretical context more explicitly by starting from the equilibrium distribution function of the chain end-to-end vector $\mathbf{R}=\mathbf{r}_N-\mathbf{r}_0$ which in the absence of external forces is defined as

$$W_0(\mathbf{R},N)=\frac{\int d\mathbf{r}^N\delta(\mathbf{r}_N-\mathbf{r}_0-\mathbf{R})\exp[-\beta U(\mathbf{r}^N)]}{\int d\mathbf{r}^N\exp[-\beta U(\mathbf{r}^N)]}\equiv\frac{Z_R}{Z}, \tag{3}$$

where $\beta=(1/k_BT)$ is the reciprocal temperature, $\mathbf{r_i}$ is the ith bead position, $U(\mathbf{r}^N)$ is the effective potential energy with $(\mathbf{r}^N)$ representing the set of coordinates of the chain, and δ is the Dirac δ function. The potential energy consists of a sum of bond length constraining potential terms (insuring the connectivity) and possibly EV pair interactions. The numerator Z_R and denominator Z in the above equation are single chain partition functions for a constrained and unconstrained end-to-end vector, respectively. As usual, we associate to Z_R the Helmholtz free energy

$$A(\mathbf{R},N)=-\beta^{-1}\ln Z_R=-\beta^{-1}\ln W_0(\mathbf{R},N)+C(N), \tag{4}$$

where we have indicated the N and $\mathbf{R}$ dependencies. Note also that for any Cartesian component $\alpha=x,y,z$, the first moment of R_α with respect to W_0 vanishes due to space isotropy while the second moment gives $\frac{1}{3}R_0^2$.

In the fixed-R ensemble, the average of an observable $O(\mathbf{r}^N)$ is given by

$$\langle O\rangle_R=Z_R^{-1}\int d\mathbf{r}^N O(\mathbf{r}^N)\,\delta(\mathbf{r}_N-\mathbf{r}_0-\mathbf{R})\exp[-\beta U(\mathbf{r}^N)]. \tag{5}$$

Under the end-to-end vector constraint, the choice $\mathbf{O}=-(\partial U/\partial\mathbf{r}_0)$ yields the average internal force $\mathbf{f}_R$ acting on the end-bead 0 which lies along $\hat{\mathbf{R}}=(\mathbf{R}/R)$ by symmetry. To see this explicitly, let us substitute O in Eq. (5) and let us use the identity

$$-\frac{\partial U}{\partial\mathbf{r}_0}\exp(-\beta U)=\beta^{-1}\frac{\partial[\exp(-\beta U)]}{\partial\mathbf{r}_0}.$$

Integration by parts transfers the application of the derivative to the δ function. Given the nature of the argument of the δ function appearing in Eq. (5), the gradient operation with respect to $\mathbf{r}_0$ can be substituted with a gradient with respect to $\mathbf{R}$ so that the expression turns out to be finally equivalent to the gradient of $\ln W_0$ with respect to $\mathbf{R}$ [see Eq. (3)]. Keeping consistency with notations used in the Introduction, we thus have

$$\left\langle-\frac{\partial U}{\partial\mathbf{r}_0}\right\rangle_R=\left\langle+\frac{\partial U}{\partial\mathbf{r}_N}\right\rangle_R=-\frac{1}{\beta}\frac{\partial[\ln W_0(\mathbf{R},N)]}{\partial\mathbf{R}}$$

$$=\frac{\partial A(\mathbf{R},N)}{\partial\mathbf{R}}=f_R\hat{\mathbf{R}}\equiv h(R)\hat{\mathbf{R}}. \tag{6}$$

The equation $f_R=h(R)$ defines the elasticity law in the fixed R ensemble.

In the fixed-f ensemble, the end-to-end vector fluctuates around a nonzero vector $\langle\mathbf{R}\rangle_f$ parallel to $\mathbf{f}$. The relevant partition function becomes [1]

$$Z_f(\mathbf{f},N)=\int d\mathbf{R}\,Z_R\exp(\beta\mathbf{f}\cdot\mathbf{R})$$

$$=Z\int d\mathbf{R}\,W_0(\mathbf{R},N)\exp(\beta\mathbf{f}\cdot\mathbf{R}). \tag{7}$$

The f ensemble average of a microscopic variable $O(\mathbf{r}^N)$ will be written as

$$\langle O\rangle_f=Z_f^{-1}\int d\mathbf{r}^N O(\mathbf{r}^N)\exp\{-\beta[U(\mathbf{r}^N)-(\mathbf{r}_N-\mathbf{r}_0)\cdot\mathbf{f}]\}. \tag{8}$$

It follows from the above equations that the average and fluctuations of the end-to-end vector are given as partial derivatives of Z_f according to

$$\langle\mathbf{R}\rangle_f=\frac{1}{\beta}\frac{\partial}{\partial\mathbf{f}}\ln Z_f=R_f\hat{\mathbf{f}}\equiv g(f)\hat{\mathbf{f}}, \tag{9}$$

$$\langle\delta\mathbf{R}\delta\mathbf{R}\rangle_f=\frac{1}{\beta^2}\frac{\partial}{\partial\mathbf{f}}\frac{\partial}{\partial\mathbf{f}}\ln Z_f=\frac{1}{\beta}\left(\frac{\partial g(f)}{\partial f}\hat{\mathbf{f}}\hat{\mathbf{f}}+\frac{g(f)}{f}(\mathbf{1}-\hat{\mathbf{f}}\hat{\mathbf{f}})\right), \tag{10}$$

where $\delta\mathbf{R}=(\mathbf{R}-R_f\hat{\mathbf{f}})$.

The first equation defines the elasticity law, $R_f=g(f)$, in the f ensemble and states that the average elongation in a direction transverse to $\hat{\mathbf{f}}$ vanishes by symmetry. Fluctuations are still given in terms of $g(f)$ and its first derivative. If we denote, respectively, as $\delta R_\parallel$ and $\delta R_\perp$ the longitudinal and transverse components of fluctuations in the fixed-f ensemble, we obtain from Eq. (10)

$$\langle\delta R_\parallel^2\rangle_f=\frac{1}{\beta}\frac{\partial g(f)}{\partial f}, \tag{11}$$

$$\langle\delta R_\perp^2\rangle_f=\frac{1}{\beta}\frac{g(f)}{f}. \tag{12}$$

The nonequivalence between fixed-f and fixed-R ensembles shows up in the fact that the relationships $f_R=h(R)$ [Eq. (6)] and $R_f=g(f)$ [Eq. (9)] are not inverse functions of one another. The function Δ_f introduced earlier to measure this ensemble difference can thus be expressed as $\Delta_f=f-h(g(f))$. Alternatively, the same ensemble dependence of the elasticity law can also be formulated as $\Delta_R=R-g(h(R))$.

B. Elasticity laws in the two stretched chain ensembles for specific models

In this section, we use the above theoretical framework to estimate the importance of the ensemble effects on the single polymer elasticity law for standard chain models. We will treat the universal models for ideal chains and for chains in good solvent and finally look at the freely jointed chain to appreciate the ensemble effects when finite extensibility is incorporated in the model.

1. Long chains at or above the θ point

If we restrict ourselves to θ and good solvent conditions, the equilibrium end-to-end vector distribution $W_0(\mathbf{R},N)$ evolves, as the number of monomers N increases, to an expression $W_0(\mathbf{R},N)\propto(C/R_0^3)\hat{w}(x)$ where $\hat{w}(x)$ is a universal function of the reduced distance $x=(R/R_0)$ and where the explicit N dependence is left into the measure only. We have [26]

$$W_0(\mathbf{R},N)d\mathbf{R} \underset{N\to\infty}{\to} Cx^{\gamma}\exp(-Dx^{\delta})d\mathbf{x}, \tag{13}$$

where C is a normalization constant and $\mathbf{x}$ the reduced end-to-end vector. The RGT parameters for good solvent chains are $D=1.2063$, $\delta=(1-\nu)^{-1}=2.4272$, and $\gamma=0.275$ while, for Gaussian chains, we simply have $D=\frac{3}{2}$, $\delta=2.0$, and $\gamma=0.0$.

For later purposes, it is important to note that the relevance of this distribution for finite chains idealized as N Kuhn segments of length b, is restricted to the range $b\ll R\ll Nb$ [24]. Within the fixed-R ensemble, the force function $f_R=h(R)$ can be obtained by applying Eq. (6) to the particular expression (13). Using reduced quantities, one gets the general result

$$\beta R_0 f_R \equiv \eta_g = -\frac{\gamma}{x}+\frac{D}{(1-\nu)}x^{\nu/(1-\nu)} \tag{14}$$

which reduces to the linear law $\beta R_0 f_R=3x$ in the Gaussian case.

Alternatively, we get the elasticity law and the end-to-end vector fluctuations relative to the fixed-f ensemble by applying to the particular end-to-end distribution function (13) the series of Eqs. (7), (9), and (10). For Gaussian chains, the linear law $R_f=g(f)=R_0(\eta_g/3)$, turns out to be identical to the elasticity law [Eq. (14)] in the fixed-R ensemble. The end-to-end vector fluctuations in the fixed-f ensemble, which can be obtained directly from $g(f)$ on the basis Eqs. (11) and (12), are independent of f and thus identical to the unstretched case.

For EV chains, the end-to-end vector moments in the f ensemble, namely R_f, $\langle\delta R_{\parallel}^2\rangle_f$, and $\langle\delta R_{\perp}^2\rangle_f$, can be estimated numerically on the basis of Eqs. (9), (11), and (12) (see also Ref. [19]). For completeness, we give the expressions to be evaluated numerically in terms of the global reduced force η_g,

$$\frac{R_f}{R_0}\equiv x=\frac{1}{\eta_g}\left[\left(\frac{\eta_g c_2}{s_1}\right)-1\right], \tag{15}$$

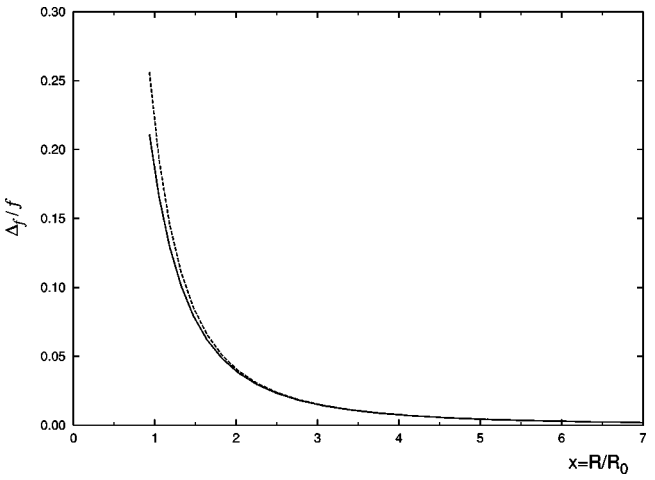

FIG. 1. Δ_f/f is shown as a universal function of the reduced extension $x=R/R_0$ for the RGT model. The lines (—) represent the direct differences while the dashed lines (– – –) show the predictions of $\Delta_f^{(2)}$ according to Eq. (43).

$$\frac{\langle\delta R_{\parallel}^2\rangle_f}{R_0^2}=\frac{s_3}{s_1}-\left(\frac{c_2}{s_1}\right)^2+\frac{1}{\eta_g^2}, \tag{16}$$

$$\frac{\langle\delta R_{\perp}^2\rangle_f}{R_0^2}=\frac{1}{\eta_g^2}\left[\left(\frac{\eta_g c_2}{s_1}\right)-1\right], \tag{17}$$

where we have defined

$$s_i(\eta_g)=\int_0^{\infty}dy\,\sinh(\eta_g y)y^{i+\gamma}\exp[-Dy^{1/1-\nu}], \tag{18}$$

$$c_i(\eta_g)=\int_0^{\infty}dy\,\cosh(\eta_g y)y^{i+\gamma}\exp[-Dy^{1/1-\nu}]. \tag{19}$$

For chains in good solvent satisfying the universal distribution function Eq. (13), the elasticity laws in fixed-f and fixed-R ensembles, i.e., Eqs. (15) and (14), respectively, are found to be quite different. This is shown in Fig. 1 where the universal behavior of Δ_f/f is plotted against the reduced distance x. The difference is small (below 2%) for chains stretched over distances at least three times their typical unstretched chain value ($R>3R_0$), it amounts to about 20% for $R\approx R_0$ and it diverges as the distance decreases to zero. The elastic behavior of chains in good solvent thus presents quantitative differences depending upon the nature of the stretching constraint. These effects culminate at short end-to-end distances ($R<R_0$) where both distributions of conformations are intrinsically different as we mentioned in the Introduction. This is however a regime of little experimental relevance as confinement effects should be taken into account. The effects observed for EV chains in the R regime $R_0<R<3R_0$, which corresponds to the crossover regime between the linear and the Pincus regime discussed in Sec. II, should be observed for finite chains as long as finite extensibility does not interfere, a feature which is ensured as soon as $3R_0\ll Nb$, i.e., when $N\gg 3^{5/2}$. Finite extensibility effects will be specifically considered in the next section for the FJC model.

Let us finally remark that the ideal chain result $\Delta_f = 0$, which is valid for arbitrary N, is somewhat surprising when one considers that, at least at short end-to-end distances, the distribution of conformations is very different in the two ensembles. We will see the origin of this absence of constraint effects on the elasticity properties of Gaussian chains in the next section.

2. The FJC model: Finite extensibility effects

The FJC model is the prototype of an ideal chain with limited extensibility. This model of N freely jointed rigid bonds of length b evolves towards the Gaussian model as N gets large, as long as the end-to-end distance R remains much smaller than the contour length of the chain $L_c = Nb$ [1,4].

To analyze the FJC elasticity law in the fixed-R ensemble, we exploit the known expression of $W_0(\mathbf{R},N)$, namely an integral over reciprocal space to be evaluated numerically [1]. The average force intensity $h(R)$ estimated using Eq. (6), requires an additional integral over reciprocal space to be calculated. We have

$$W_0(\mathbf{R},N) = \frac{1}{2\pi^2 R} s_1', \tag{20}$$

$$h(R) = \frac{1}{R} - \frac{c_2'}{s_1'}, \tag{21}$$

where we have introduced more general compact notations (which will be useful for later purposes)

$$s_i' = \int_0^\infty dq\, q^i \sin(qR) \left[\frac{\sin(qb)}{qb}\right]^N, \tag{22}$$

$$c_i' = \int_0^\infty dq\, q^i \cos(qR) \left[\frac{\sin(qb)}{qb}\right]^N. \tag{23}$$

Alternatively, the partition function for the FJC at fixed f can be evaluated analytically by straightforward calculations [4]. The average end-to-end vector and its fluctuations at fixed-f [see Eqs. (11) and (12)] are easily obtained. One finds the classical result $(R_f/L_c) \equiv y = \mathcal{L}(\eta_l)$ where $\eta_l = (bf/k_BT)$ is the local reduced force, y is the relative extension, and $\mathcal{L}(u) \equiv \coth(u) - 1/u$ is the well-known Langevin function. Use of Eqs. (11) and (12) leads to fluctuation expressions $\langle \delta R_\parallel^2 \rangle_f = Nb^2[1 - 2\mathcal{L}(\eta_l)/\eta_l - \mathcal{L}^2(\eta_l)]$ and $\langle \delta R_\perp^2 \rangle_f = Nb^2 \mathcal{L}(\eta_l)/\eta_l$.

In Fig. 2, we show the behavior of Δ_f/f for various lengths according to the FJC model ($N=16$, $N=32$, $N=64$, and $N=128$) in terms of the relative extension y covering a force range $\eta_l \leqslant 4.0$. The results clearly show that, as predicted by Flory [1], the ensemble effects on the FJC elasticity law are dominated by a $1/N$ term. We note that Δ_f/f decreases below the 1% level for chains with $N > 100$ but amounts 10% for the $N=16$ case at $y=0.75$. The Gaussian chain limit for the elasticity law ensemble difference (namely $\Delta_f/f = 0$) is indeed recovered from the FJC result, for $y \ll 1$, when N goes to infinity.

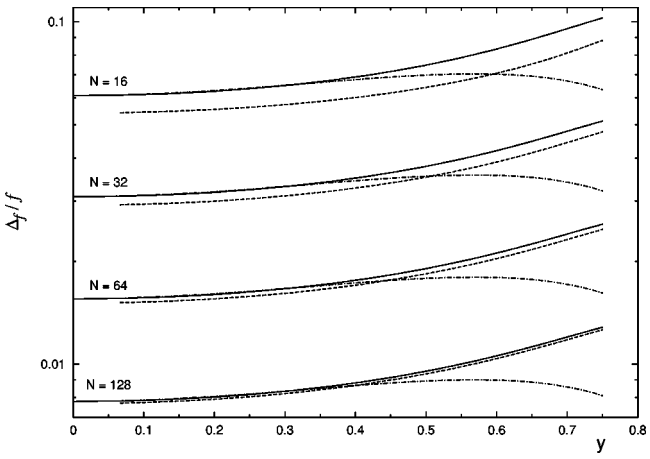

FIG. 2. Δ_f/f is shown as a function of the reduced extension $y = R/L_c$ for the FJC model with $N=16$, 32, 64, and 128. The lines (—) represent the exact differences while the dashed lines (– – –) show the predictions of $\Delta_f^{(2)}$ according to Eq. (43). The dotted-dashed lines are polynomial fits (see text).

IV. THE CONNECTION FORMULAS BETWEEN FIXED-f AND FIXED-R ENSEMBLES

In the previous section, we have shown that single chain elasticity laws are in general different in conjugated stretched chain ensembles. While the effect is accidentally zero for Gaussian chains, the relative difference Δ_f/f is below the percent level only when EV chains, independently of their length, are stretched over a distance which is larger than three times their equilibrium end-to-end distance. Finally, for FJC chains, $\Delta_f/f \approx 1/N$ over a wide range of local reduced forces $\eta_l < 4$, provided N is larger than ≈ 15.

In the present section, we express the difference between the ensemble averages in terms of a series expansion with the aim of clarifying to which extend the properties of Δ_f we just summarized, can be understood in terms of second order fluctuations of $\mathbf{R}$ at fixed f. In order to enlarge the potential applications of our theoretical analysis, we will study the single stretched chain ensemble effects on the averages of an arbitrary structural property denoted by an observable $O(\mathbf{r}^N)$. At the end of the section, we will return to the elasticity case on which we focus in this paper.

A. General formalism

We want to compare the averages of an arbitrary observable O in the strain (fixed-$\mathbf{R}$ vector) and in the stress (fixed-$\mathbf{f}$ vector) ensembles. These ensembles imply vector constraints along the same direction (say along the z axis), namely $\mathbf{f} = (0,0,f)$ and $\mathbf{R} = \mathbf{R}_f = (0,0,R_f)$ where $R_f = g(f)$ [Eq. (9)] or $\mathbf{R} = (0,0,R)$ and $\mathbf{f} = \mathbf{f}_\mathbf{R} = (0,0,f_R)$ where $f_R = h(R)$ [Eq. (6)].

On the basis of expressions (3), (4), (5), (7), and (8), we can write the basic relationship between ensembles averages, namely

$$\langle O \rangle_f = Z_f^{-1} \int d\mathbf{R}\, Z_R \langle O \rangle_R \exp(\beta \mathbf{R} \cdot \mathbf{f})$$

$$= Z_f^{-1} \int d\mathbf{R} \langle O \rangle_R \exp\{-\beta[A(\mathbf{R},N) - \mathbf{R} \cdot \mathbf{f}]\}. \tag{24}$$

A systematic and formally exact expansion of this equation can be obtained directly by replacing the observable average $\langle O\rangle_R$ on the r.h.s. of Eq. (24) by its Taylor expansion around $R=R_f$ and by performing all integrations [25]. This expansion that we will denote by $E1$ leads to an infinite series in terms of averages of end-to-end vector fluctuations of all orders in the fixed-f ensemble: note that the first order term is zero but has been kept here to indicate the structure of the infinite series,

$$\langle O\rangle_f=(\langle O\rangle_R)_{\mathbf{R}=R_f\hat{\mathbf{f}}}+\left(\frac{\partial}{\partial\mathbf{R}}\langle O\rangle_R\right)_{\mathbf{R}=R_f\hat{\mathbf{f}}}\langle\delta\mathbf{R}\rangle_f+\frac{1}{2}\left(\frac{\partial}{\partial\mathbf{R}}\frac{\partial}{\partial\mathbf{R}}\langle O\rangle_R\right)_{\mathbf{R}=R_f\hat{\mathbf{f}}}:\langle\delta\mathbf{R}\delta\mathbf{R}\rangle_f+\cdots. \quad (25)$$

The expansion in Eq. (25) is exact and directly compares ensemble averages in the fixed-f and fixed-R conjugated ensembles for force intensity f and end-to-end vector length set to $R=g(f)$, respectively. However, its convergence, is difficult to assess in general.

Another series expansion, called $E2$, can be obtained by applying the steepest descent technique [27]. In order to replace the fixed-f distribution by a multivariate Gaussian distribution, one has to develop, to second order in $\mathbf{R}$, the exponent $\beta[A-\mathbf{R}\cdot\mathbf{f}]$ around its minimum $R_m\hat{f}$. The location of the free energy minimum is the solution of the implicit equation

$$\mathbf{f}=\frac{\partial A(\mathbf{R},N)}{\partial\mathbf{R}}, \quad (26)$$

which, by using Eqs. (4) and (6), yields $R_m=h^{-1}(f)$. The covariance matrix $\mathbf{C}(R_m)$ is given by

$$\mathbf{C}^{-1}(R_m)=\beta[\nabla_{\mathbf{R}}\nabla_{\mathbf{R}}A(\mathbf{R},N)]_{\mathbf{R}=R_m\hat{\mathbf{f}}}=\beta\left[(\mathbf{1}-\hat{\mathbf{R}}\hat{\mathbf{R}})\frac{h(R)}{R}+\hat{\mathbf{R}}\hat{\mathbf{R}}\left(\frac{\partial h}{\partial R}\right)\right]_{\mathbf{R}=R_m\hat{\mathbf{f}}}. \quad (27)$$

Subsequent Taylor expansion of $\langle O\rangle_R$ around $R_m(f)$ up to second order provides the leading term of the series expansion in terms of R_m and $C(R_m)$

$$\langle O\rangle_f=(\langle O\rangle_R)_{\mathbf{R}=R_m\hat{\mathbf{f}}}+\frac{1}{2}\left(\frac{\partial}{\partial\mathbf{R}}\frac{\partial}{\partial\mathbf{R}}\langle O\rangle_R\right)_{\mathbf{R}=R_m\hat{\mathbf{f}}}:\mathbf{C}(R_m)+\cdots. \quad (28)$$

The development $E2$ again relates averages of an observable in conjugated ensembles. However while $E1$ [Eq. (25)] relates ensembles with identical end-to-end vector and slightly different forces, the steepest descent expansion $E2$ treats ensembles with the same force f but different R values, namely R_f for the fixed-f ensemble and R_m for the fixed-R ensemble.

Expansion $E2$ is *a priori* more transparent when discussing the convergence of the series. For that purpose, Eq. (24) can be rewritten in terms of a new intensive variable $\mathbf{r}=\mathbf{R}/N$,

$$\langle O\rangle_f=\frac{N}{Z_f}\int d\mathbf{r}\langle O\rangle_{Nr}\exp(-N[\beta a(\mathbf{r},N)-\beta\mathbf{r}\cdot\mathbf{f}]), \quad (29)$$

where $a(\mathbf{r},N)$ is the free energy per segment for a chain at fixed end-to-end vector $\mathbf{R}=N\mathbf{r}$. This expression resembles the fixed volume/fixed pressure ensemble transformation relation for a N-particle system on the basis of which finite size effects are derived in statistical mechanics [25]. Equation (29) suggests that the N dependency of the series based on the steepest descent expansion should be examined while keeping $\langle\mathbf{r}\rangle$ constant. The underlying motivation is that one expects that the differences between ensembles should vanish for N infinite.

While series expansions $E1$ [Eq. (25)] is formally exact, getting more than a leading term in $E2$ [Eq. (28)] is not a trivial case. These difficulties arise when considering third order correction terms in the free energy expansion required by the steepest descent technique or when finite chain size corrections in $a(\mathbf{r},N)$ need to be taken into account. Fortunately, in usual cases where N is sufficiently large for the single bond free energy $a(\mathbf{r},N)$ to become intensive (at fixed $\langle r\rangle$), and as long as the average $\langle O\rangle_R$ is at least quadratic in R, the leading term of order $1/N$ given by Eq. (29) will fairly well represent the ensemble difference. However, if we choose to study the ensemble effects on the elasticity law with the choice $\mathbf{O}=\mathbf{r}_N-\mathbf{r}_0$ on the basis of Eq. (28), the leading term vanishes for that particular (linear) observable and the next term in the expansion will require the consideration of higher order terms. We have not attempted to follow this route any further in the present work.

Because of the above difficulties when dealing with expansion $E2$, we will exploit mainly expansion $E1$ when dealing with the difference between fixed-f and fixed-R averages of an arbitrary observable relative to the stretched chain system. We will analyze the structure of the single bond free energy for each of these models. More particularly, we will investigate the convergence of the expansion $E1$ [Eq. (25)] when N and possibly f are varied.

B. Link between ensembles for specific chain models

Let us start by adopting for W_0 and its associated free energy expression the universal model function for theta point and good solvent polymers defined by the distribution (13). We have

$$\beta A(\mathbf{R},N)=D\left(\frac{R}{bN^{\nu}}\right)^{1/(1-\nu)}-\gamma\ln\left(\frac{R}{bN^{\nu}}\right)+K, \quad (30)$$

where K is a constant. Note that by adopting this description we neglect finite extensibility effects, i.e., we are limited to $R\ll Nb$.

The free energy per bond derived form Eq. (30) is

$$\beta a(r,N)=D\left(\frac{r}{b}\right)^{1/(1-\nu)}-\frac{\gamma}{N}\ln\left(\frac{r}{b}\right)+\frac{K}{N} \quad (31)$$

which becomes intensive when $N\to\infty$.

1. Gaussian chain universal model

In this case, $\gamma=0$, $D=\frac{3}{2}$, and $\nu=\frac{1}{2}$. From Eq. (31) we observe that the free energy per bond is strictly intensive and is quadratic in r. The probability distribution in Eq. (29) is Gaussian so that the steepest descent technique can be performed easily to yield expansion $E2$ as an explicit infinite series expansion. It is easy to show that expansions $E1$ and $E2$ are identical in this particular case where the unique elasticity law in both ensembles guarantees $R_f=R_m$. Following expansion $E1$, one has

$$\langle O\rangle_f=\langle O\rangle_{R_f}+\frac{1}{2}\left(\frac{\partial}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{r}}\langle O\rangle_R\right)_{\mathbf{R}=N\mathbf{r}}:\langle\delta\mathbf{r}\,\delta\mathbf{r}\rangle_f+\cdots \tag{32}$$

$$=\langle O\rangle_{R_f}+\frac{1}{N}\frac{b^2}{6}\left[\left(\frac{\partial}{\partial\mathbf{r}}\cdot\frac{\partial}{\partial\mathbf{r}}\langle O\rangle_R\right)_{\mathbf{R}=N\mathbf{r}}\right]+\cdots, \tag{33}$$

where $\langle\delta\mathbf{r}\,\delta\mathbf{r}\rangle_f$ and higher order terms are moments of a three-dimensional Gaussian distribution giving terms in ascending integer powers of N^{-1}.

For regular $\langle O\rangle_R$ functions and for moderately large N, the above series should always converge to a finite value. Note that in the particular case where $\langle O\rangle_R$ is linear in $\mathbf{r}$, like it is precisely the case for the internal force $h(R)$ [see Eq. (14)], $\langle O\rangle_f$ is strictly equal to $\langle O\rangle_{R_f}$ for any finite N and arbitrary f because all terms of the series vanish. This is consistent with the equivalence between elasticity laws relative to both ensembles which was noticed for Gaussian chains with finite number of beads in the previous section.

2. EV chain universal model

For EV chains, the single bond free energy [Eq. (31)] leads to a minimum of $(\beta a(\mathbf{r},N)-\beta\mathbf{r}\cdot\mathbf{f})$, as required in the $E2$ expansion, which is given by

$$\beta rf-\frac{D}{(1-\nu)}\left(\frac{r}{b}\right)^{1/(1-\nu)}=-\frac{\gamma}{N} \tag{34}$$

whose solution r_m is N dependent. When the r.h.s. of Eq. (34) can be neglected, i.e., when $\beta fr\gg(0.275/N)$, one finds

$$r_m=\left(\frac{(1-\nu)}{D}\right)^{(1-\nu)/\nu}(\beta f)^{(1-\nu)/\nu}b^{1/\nu}$$

which gives an extension R_m following the Pincus scaling expression $R_m\approx g(f)$ given by Eq. (2). Accordingly, the above condition can be interpreted in terms of the concept of tensile blobs as $R\gg0.275r_{blob}$ which indicates that, for a fixed f value and thus for a fixed Pincus (tensile) blob size $r_{blob}=(\beta f)^{-1}$, the number of monomers should be large enough for the polymer extension to be several times the blob size [24]. Physically, this means that the chain must be in the strong stretching regime ($\eta_g\gg1$).

The central role played by η_g in the stretched chain in good solvent calls for some additional remarks. The Helmholtz free energy $A(\mathbf{R},N)$ of unstretched EV chains, namely Eq. (30) which follows from Eqs. (3) and (13), can be expressed as a function of a single variable $\mathbf{x}=\mathbf{R}/R_0$

$$\beta A(\mathbf{x})=Dx^{1/(1-\nu)}-\gamma\ln(x)+K, \tag{35}$$

where the N dependence is no longer explicit.

In terms of stretched chain ensembles, the variable conjugated to the reduced end-to-end vector $\mathbf{x}$ is $\overline{\eta}_g$ as $\beta\mathbf{f}\cdot\mathbf{R}=\overline{\eta}_g\cdot\mathbf{x}$. In these variables the ensemble tranformation relation become

$$\langle O\rangle_{\eta_g}=\frac{1}{Z_{\eta_g}}\int d\mathbf{x}\langle O\rangle_x\exp(-[\beta A(\mathbf{x})-\overline{\eta}_g\cdot\mathbf{x}]) \tag{36}$$

and $Z_{\eta_g}=Z_f$.

Equation (36) strictly deals with infinite chains but, as already noticed, this universal behavior applies to finite chains in the R domain where FE effects are not probed. We thus stress here that the conjugated ensembles for EV chains are never equivalent at finite η_g. It must be emphasized that, while ensemble effects tend to disappear as N grows at fixed force f (i.e., increasing η_g), the same effects are unaffected in the combined limit $N\to\infty, f\to0, \eta_g\propto fN^\nu$ constant. The second order expansions of $\langle O\rangle_{\eta_g}$ similar to Eqs. (25) and (28) to transform ensemble averages between conjugated ensembles remain relevant, but the convergence of the expansions is clearly controlled by η_g. For large η_g, which corresponds to a highly stretched state which can result from a large polymer size N at moderate f, a large force f at moderate polymer size N or both large f and N, the series should quickly converge. When values of η_g decrease to a value close to unity, the convergence must be controlled empirically and more terms in the expansions may be necessary to get Δ_O with accuracy. We will illustrate this point with the elasticity law in the next section.

3. Some comments about the FJC model

The link between stretched chain ensemble averages $\langle O\rangle_f$ and $\langle O\rangle_R$ for the FJC model furnishes additional insights about the FE effects. We first note that the stretched chain free energy $A(\mathbf{R},N)$, its first derivative respect to R which is the force $h(R)$, and, if required, its higher derivatives can be calculated numerically using Eq. (21) and its derivatives easily expressed in terms of higher order coefficients s' and c' defined in Eq. (23). Using the above quantities calculated for N up to 128 over the range $0\leqslant\eta_l\leqslant4.00$ corresponding to $r\leqslant0.75$, one expects that the r dependent part of the free energy per monomer presents a size dependence term dominated by a $1/N$ and then a $1/N^2$ term. Moreover, as for the FJC model ([1,4]), $\Delta_f=f-h(g(f))$ at arbitrary f vanishes in the infinite N limit, one should have

$$\beta a=\frac{1}{2}\left(3+\frac{a'}{N}+\frac{a''}{N^2}\right)\left(\frac{r}{b}\right)^2+\frac{1}{4}\left(\frac{9}{5}+\frac{b'}{N}+\frac{b''}{N^2}\right)\left(\frac{r}{b}\right)^4+\cdots \tag{37}$$

$$\beta h(R)b=\left(3+\frac{a'}{N}+\frac{a''}{N^2}\right)\frac{r}{b}+\left(\frac{9}{5}+\frac{b'}{N}+\frac{b''}{N^2}\right)\left(\frac{r}{b}\right)^3+\cdots, \tag{38}$$

where a', a'', b', and b'' are numerical coefficients. We exploited our data on βa and its derivatives for various N to determine empirically these coefficients by polynomial fits and we found $a'=-3.00$, $b'=-4.50$, $a''=1.2684$, b''

$=1.68$. In Fig. 2, we see that expression (37) reproduces indeed the N and r dependence of Δ_f for $r \leqslant 0.4$. The link between ensemble averages for an arbitrary observable $\langle O \rangle$ relative to the FJC model is given by Eqs. (29) where the free energy term is obtained from Eq. (37). The maximum of probability is given by the solution of Eq. (38) which, at low N, gives a N-dependent r_m value. As N increases, Eq. (38) must evolve towards $\beta f b = \mathcal{L}^{-1}(r/b)$. The connection between conjugated ensembles averages will again be dominated by a $1/N$ term.

C. Second order approximation applied to the elasticity case

The series expansion Eq. (25) defines a second order term which should dominate Δ_O provided that we are in the convergence regime of the particular chain model considered. We will again focus on the elasticity law and thus select the variable $O \equiv -(\partial U/\partial z_0)$ where z_0 is the z component of the end bead position $\mathbf{r}_0$. In the fixed-f ensemble, mechanical equilibrium imposes $\langle -(\partial U/\partial z_0) \rangle_f = f$ while, in the fixed-R ensemble, Eq. (6) gives

$$\left\langle -\frac{\partial U}{\partial z_0} \right\rangle_R = h(R)\frac{R_z}{R}$$

where R_z is the z component of the end-to-end vector. The quantity Δ_f introduced earlier in this paper as a measure of the distinction between the elasticity laws in both ensembles, can indeed be expressed as

$$\Delta_f \equiv \left\langle -\frac{\partial U}{\partial z_0} \right\rangle_f - \left\langle -\frac{\partial U}{\partial z_0} \right\rangle_R$$

$$= f - \left(h(R)\frac{R_z}{R} \right)_{\mathbf{R}=\mathbf{R}_f}$$

$$= f - h(R_f). \tag{39}$$

Adapting Eq. (25) to our case provides us with the following second order approximation for Δ_f,

$$\Delta_f^{(2)} = \tfrac{1}{2}\langle \delta\mathbf{R}\,\delta\mathbf{R} \rangle_f : \left[\frac{\partial}{\partial \mathbf{R}} \frac{\partial}{\partial \mathbf{R}} \left(h(R)\frac{R_z}{R} \right) \right]_{\mathbf{R}=\mathbf{R}_f}$$

$$\equiv \frac{1}{2}\langle \delta\mathbf{R}\,\delta\mathbf{R} \rangle_f : \mathbf{T}, \tag{40}$$

where the tensor $\mathbf{T}$ is introduced for convenience. Using diagonal properties of the fluctuation tensor and according to Eqs. (10), (11), and (12), Eq. (40) can be transformed, using Eq. (9), as

$$\Delta_f^{(2)} = \tfrac{1}{2}[\langle \delta R_\parallel^2 \rangle_f T_{zz} + \langle \delta R_\perp^2 \rangle_f (T_{xx} + T_{yy})] \tag{41}$$

$$= \frac{1}{2\beta}\left[\frac{\partial g}{\partial f}\left(\frac{\partial^2 h}{\partial R^2} \right)_{R=g(f)} + \frac{g(f)}{f}\left[\frac{2}{R}\left(\frac{\partial h}{\partial R} - \frac{h}{R} \right) \right]_{R=g(f)} \right] \tag{42}$$

$$= \frac{1}{2\beta}\left[\frac{\partial g}{\partial f}\left(\frac{\partial^2 h}{\partial R^2} \right)_{R=g(f)} + \frac{2}{f}\left(\frac{\partial h}{\partial R} - \frac{h}{R} \right)_{R=g(f)} \right]. \tag{43}$$

Using Eqs. (6), (7), and (9), the expressions Δ_f and $\Delta_f^{(2)}$ can be evaluated for any model for which $W_0(\mathbf{R},N)$ is known. In Figs. 1 and 2, we show, respectively, $\Delta_f^{(2)}$ for the universal EV case and for the FJC model. For the EV model, the approximation is quite good for the range $R \geqslant R_0$ but for $R < R_0$, higher order terms in the expansion should be taken into account. For the FJC case, the second order estimate improves quickly as N gets larger.

Quite generally, at fixed f in the highly stretched chain regime, we know that both $A(\mathbf{R},N)$ and R_f become linear in the chain length N [24]. In that regime, Δ_f can then be shown to vanish like $1/N$ for large N chains, independently of the chain model. This can be proved using the approximation $\Delta_f^{(2)} \approx \Delta_f$ valid in that regime. One takes $R_f = Nz(f)$ and $f_R = h(R) = w(R/N)$ where $z(f)$ and $w(r)$ (with $r = R/N$) are close to being inverse functions of one another. Substituting these formal expressions in $\Delta_f^{(2)}$ [Eq. (43)] gives

$$\Delta_f^{(2)} = \frac{1}{N}\left[\frac{\partial z}{\partial f}\left(\frac{\partial^2 w}{\partial r^2} \right)_{r=z(f)} + \frac{2}{f}\left(\frac{\partial w}{\partial r} - \frac{w}{r} \right)_{r=z(f)} \right], \tag{44}$$

thus indicating a $1/N$ dependence at fixed-f (and thus at fixed $r = R/N$) in any strongly stretched regime such as the Pincus blob regime for EV chains or such as any type of FE regime.

D. Monte Carlo calculations for the stretched hard-sphere necklace model

The semirigid necklace model we now consider consists in $N+1$ hard spheres linearly connected by N rigid bonds of length b. This 3D continuous space model is convenient as it combines most aspects of real polymers in good solvent conditions, namely EV and FE effects. We report in the following a Monte Carlo study of a stretched polymer based on this model with a hard sphere diameter $\sigma = 0.65b$ which garantees that EV interactions are operative at all length scales in the absence of external forces. The particular case $N = 400$ with unperturbed size $R_0 = 36.81b$ [21] was selected for our purposes as such a chain size is sufficiently long to display all stretching regimes of the elasticity law.

The adopted MC method combines configurational bias sampling and reptation moves [28]. A stretched state of the polymer [i.e., under fixed external force $\pm\mathbf{f} = (0,0,\pm f)$] is studied by adding to the potential energy term, a stretching work

$$T = -\mathbf{f}\cdot\mathbf{R}, \tag{45}$$

which is a function of the instantaneous value of the end-to-end vector $\mathbf{R}$. Running the program for various f values gives

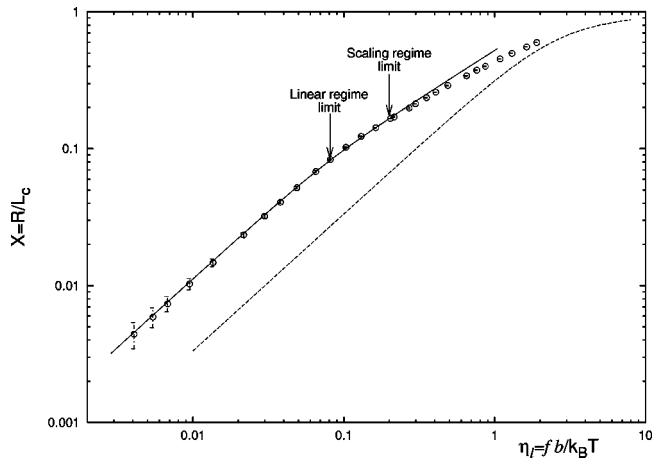

FIG. 3. Elasticity law in the constant stress ensemble for the FJC model (– – –), the RGT prediction (—), and our fixed-f MC results (○○○○), with $N=400$.

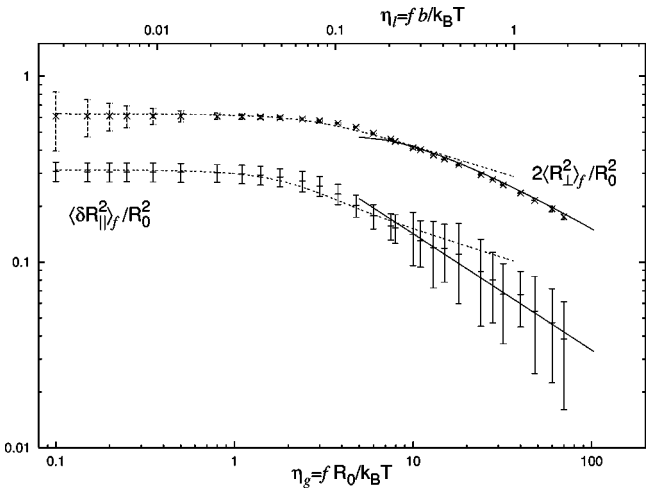

FIG. 4. Fluctuations of the end-to-end vector components both parallel (lower) and perpendicular (upper) to the stretching force of a 400 segment EV chain. The dashed lines (– – –) give the RGT prediction. The continuous line (—) results from exploiting the link between the fixed-f end-to-end fluctuations and the $g(f)$ behavior for the range $\eta_l > 0.2$, which is shown in Fig. 3 (see also text).

the evolution of the average end-to-end vector $\mathbf{R}_f$, i.e., the $g(f)$ data shown in Fig. 3, and its fluctuations shown in Fig. 4.

In Fig. 3, the simulation points are compared to the RGT model prediction [Eq. (15)] for a polymer with unstretched size R_0 adjusted to the actual value of the 400 bonds polymer treated by MC, and also to the 400 bonds FJC prediction, a model to which our MC necklace model reduces when the hard-sphere interactions are suppressed. We observe that the MC results are quite well represented by the RGT curve at low forces [19]. Beyond $\eta_l \approx 0.3$, the data exhibit a smooth crossover to a FJC behavior.

Figure 4 shows the fluctuations of the end-to-end vector components of the same 400 segments EV chain treated by MC and the corresponding RGT predictions for longitudinal and transversal fluctuations. In terms of reduced quantities, the theoretical expressions given by Eqs. (16) and (17), are seen to match the MC data up to $\eta_l \approx 0.3$. At higher forces, FE effects lead to a more rapid decrease of the fluctuations, a behavior fully coherent with the corresponding $g(f)$ evolution given in Fig. 3. This is actually shown by plotting in Fig. 4 the (high stretching) expected behavior of the fluctuations as obtained by Eqs. (11) and (12) obtained by numerical differentiation of the $g(f)$ data in the $\eta_l > 0.3$ regime (see Fig. 3).

On the other hand, the unperturbed end-to-end vector distribution of the chain is needed to estimate the internal force at fixed end-to-end distance according to Eq. (6). It is useful to note that the distribution function of $\mathbf{R}$ in the presence of stretching forces, namely

$$W_f(\mathbf{R},N) = \frac{\int d\mathbf{r}^N \, \delta(\mathbf{r}_N - \mathbf{r}_0 - \mathbf{R}) \exp[-\beta(U(\mathbf{r}^N) - (\mathbf{r}_N - \mathbf{r}_0)\cdot\mathbf{f})]}{\int d\mathbf{r}^N \exp\{-\beta[U(\mathbf{r}^N) - (\mathbf{r}_N - \mathbf{r}_0)\cdot\mathbf{f}]\}} \tag{46}$$

can also be used to get the distribution in the absence of force, i.e., $W_0(\mathbf{R},N)$ of Eq. (3), by exploiting the identity

$$W_0(\mathbf{R},N) = \frac{Z_f}{Z} \exp(-\beta \mathbf{R}\cdot\mathbf{f}) W_f(\mathbf{R},N), \tag{47}$$

where the Z and Z_f partition functions are defined by Eqs. (3) and (7), respectively. By superimposing the distributions W_0 obtained by Eq. (47) within our set of simulations at various fixed forces, the profile of W_0 was retrieved over a large range of R values as shown in Fig. 5. This combination of biased samplings leads to a precise estimate of the distribution up to end-to-end distances of $R \approx 4.5 R_0$, i.e., up to extensions of the order of 40% of the chain contour length where the probability density is reduced to 10^{-9} of its maximum value. As expected, the RGT curve shown in Fig. 5 matches very well our data as long as FE effects are not showing up. The crossover to the FE regime seems to occur somewhere between $R = 2R_0$ and $R = 3R_0$ where we observe that $W_0(\mathbf{R},N)$ starts decreasing more rapidly towards zero than expected from RGT. In order to reproduce this new behavior by a smooth analytic function (to ease further derivation), we used for $R > 2R_0$ the same RGT expression [Eq. (13)] but with the exponent δ and the coefficient D considered as free fitting parameters. The inset of Fig. 5 shows the resulting best fitting curve describing the data above $R = 2R_0$.

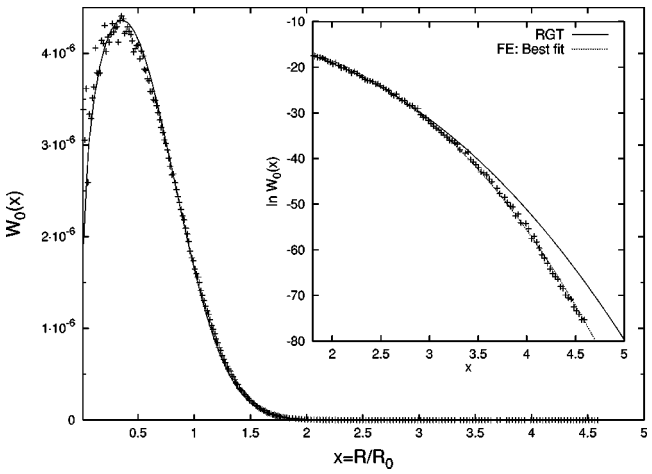

FIG. 5. The equilibrium end-to-end vector distribution for a 400-segment excluded volume chain. The line shows the RGT model prediction for small and intermediate extensions. In the inset, we show the same function for extension values corresponding to rarely occurring highly stretched configurations so that FE deviations from the RGT prediction can be detected in our MC data.

The fixed-R force $h(R)$ of the necklace chain can now be obtained according to Eq. (6) by combining two curves obtained by derivation of $\ln W_0$ functions, the first one on the basis the RGT function and the second one using the ad hoc fitting curve of $\ln W_0$ in the FE regime. The resulting function $h(R)$ is described by two portions valid in different R domains, as shown in Fig. 6. The change of sign at $x \approx 0.35$ shows the specific distance where entropic forces equilibrate.

V. CONCLUSIONS

The distinction between fixed force and fixed end-to-end vector single chain ensembles was pointed out in this paper

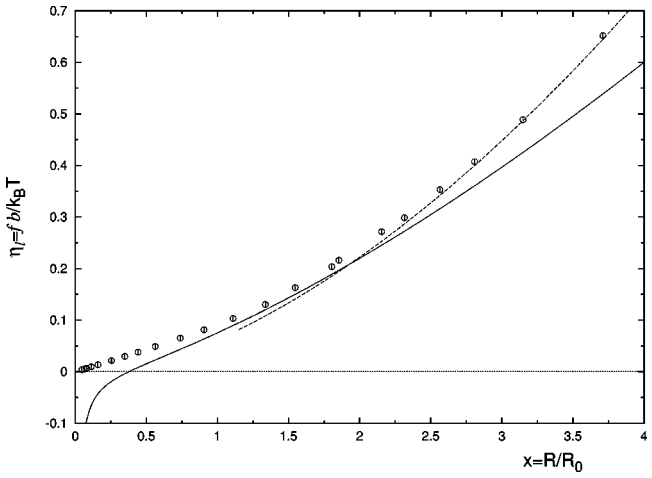

FIG. 6. Force-extension relationships for the necklace EV model in the fixed **f** and the fixed **R** ensembles. The MC results for $g^{-1}(R)$ illustrate the elasticity law in the f ensemble ($\bigcirc\bigcirc\bigcirc\bigcirc$). For $h(R)$, the internal force in the fixed-R ensemble, the RGT prediction is represented (—) over the whole range of $x=R/R_0$ while the finite extensibility prediction using the fitting curve used in Fig. 5 (see text) is shown in the domain of $x>1$ (– – –): the actual evolution of $h(R)$ in the simulation follows a smooth crossover from the RGT curve to the second one.

in connection with the single polymer elasticity law at or above the theta temperature. Actually, our approach has been more general: we have given some general tools to appreciate, for a generic observable O, the distinction between averages computed in the two stretched chain conjugated ensembles. We found that the correction term Δ_O can take the form of an infinite series, the nth term being the product of an average nth order fluctuation term in the fixed f ensemble and a nth order gradient respect to the end-to-end vector components which is computed at the average end-to-end vector value $\langle \mathbf{R} \rangle_f$. This series always converges for Gaussian chains (because of the fluctuation term only) while, for chains in good solvent represented by the RGT theory, it converges only in the high stretching regime ($R > R_0$).

The elasticity law in the stress ensemble $R_f = g(f)$ plays a central role in this paper. When convergence in the Δ_f expansion is sufficiently fast, this ensemble difference in the force can be estimated using the leading term $\Delta_f^{(2)}$ given by Eq. (43). In this expression, fluctuations terms can be evaluated from $R_f = g(f)$ using Eqs. (11) and (12) while the gradient terms requiring the fixed-R elasticity law $f_R = h(R)$ can be approximated by $f = g^{-1}(R)$. In this way, we could establish the following main results. Quite generally, ideal chains lead to similar linear elasticity laws up to the FE regime where marginal differences of $O(1/N)$, already discussed by Flory [1], are detected.

Much stronger effects are noticed for chains in good solvent, with the largest deviations between ensembles when the (average) end-to-end distance lies below R_0, the unstretched average value. This situation is however of little experimental relevance because confinement effects should be added to the description. For polymers in good solvent in the stretching regime $R \geqslant R_0$, one finds a relative difference in the force between ensembles which decreases from 20% down to 2% as the distance grows from R_0 to $3R_0$.

Stress-strain single chain laws are actually being probed by new experimental set-ups allowing micro-manipulations which either control the end-to-end vector or the stretching force. The experimental situation differs in various aspects from the idealized ensemble description of textbooks which is adopted in the present paper. To mention a few, consider that elasticity measurements are often done dynamically at finite velocity, that corrections must take into account the finite compliance of the microlever handling the polymer end when measuring the force or that confinement effects may play a role. However, our analysis remains largely relevant and could further be modified to take some of the above effects into account.

A direct experimental test of the single EV chain elasticity law in the Pincus blob regime remains to be done. What the present work suggests is that experimentalists might probe in this stretching regime different variants of the elasticity law depending upon the constraints introduced by specific set-ups ranging from fixed-f to fixed-R conditions. About the much studied biological macromolecules where specific intramolecular forces resist to the stretching forces applied at chain ends, ensemble effects depending on the nature of the applied constraint should be considered in the molecular interpretation of elasticity data.

We note finally that the existence of specific EV single chain elasticity laws for different single stretched chain en-

sembles may have interesting implications for the elastic behavior of swollen networks where the nature of the junction constraints is at the heart of network elasticity theories.

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