Response of single polymers to localized step strains

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(Received 22 September 2008; published 16 January 2009)

In this paper, the response of single three-dimensional phantom and self-avoiding polymers to localized step strains are studied for two cases in the absence of hydrodynamic interactions: (i) Polymers tethered at one end with the strain created at the point of tether, and (ii) free polymers with the strain created in the middle of the polymer. The polymers are assumed to be in their equilibrium state before the step strain is created. It is shown that the strain relaxes as a power law in time t as $t^{-\eta}$. While the strain relaxes as $1/t$ for the phantom polymer in both cases; the self-avoiding polymer relaxes its strain differently in case (i) than in case (ii): As $t^{-(1+\nu)/(1+2\nu)}$ and as $t^{-2/(1+2\nu)}$, respectively. Here ν is the Flory exponent for the polymer, with value ≈ 0.588 in three dimensions. Using the mode expansion method, exact derivations are provided for the $1/t$ strain relaxation behavior for the phantom polymer. However, since the mode expansion method for self-avoiding polymers is nonlinear, similar theoretical derivations for the self-avoiding polymer proves difficult to provide. Only simulation data are therefore presented in support of the $t^{-(1+\nu)/(1+2\nu)}$ and the $t^{-2/(1+2\nu)}$ behavior. The relevance of these exponents for the anomalous dynamics of polymers is also discussed.

I. INTRODUCTION

If a polymer is subjected to local step strain, i.e., a small part of a polymer is made to undergo a relatively fast conformational change, during subsequent evolution the polymer will readjust itself in an attempt to relieve its strain. The local conformational change will alter the polymer's local chain tension; and the new chain tension will be unable to maintain the polymer in equilibrium. In response to that, monomers will be pulled from (or pushed away to) the adjacent part of the polymer, thereby spreading the effect of the local strain. In time, the effect of the local strain will spread through the entire polymer along its backbone, before equilibrium conditions can be finally restored.

Studies on strain relaxation in collective polymeric systems are abundant in traditional polymer physics, such as for (dilute and/or semidilute) polymer solutions and for polymer melts [1]. From this perspective, how a single polymer relieves its local step strain may seem to be a purely theoretically motivated problem. However, experimentalists' ability to manipulate polymeric systems at single polymer level—especially in the context of biological polymers, or biopolymers—have rapidly grown in the last few years; e.g., DNA separation in nanochannels [2], dynamics of RNA polymerase [3], biopolymer translocation [4–9], packaging and ejection of bacteriophage DNA during infection [10,11], surface desorption of polymers using a pulling force [12]. Such single polymer experiments have been continuously challenging polymer theorists; one can almost claim that polymer physics at a single polymer level is being reborn through these recent developments. Indeed, our motivation to study the response of single polymers to localized step strains, stem from the fact that there are systems whose dynamics are determined by the polymers' local strain relaxation mechanism. Take, for example, polymer translocation, where the polymer passes through a narrow pore in a membrane [4–9]. A translocating polymer is composed of two polymer strands (labeled A and B, respectively), one on each

side of the membrane. The only way the two strands interact with each other is through the pore: As the monomers translocate, they leave one strand to join the other. Monomers leaving strand A locally increases the chain tension of strand A at the pore, and as they join strand B across the membrane, they reduce the chain tension of strand B, also locally at the pore. How the segments relieve these local strains determines the dynamics of translocation [13–16]. Similarly, in the case of polymer adsorption on a rigid surface, when a monomer gets adsorbed, it creates a local (at the adsorbing surface) step strain in the polymer, and the adsorption kinetics is governed by how the polymer relieves this strain [17].

The fact that local step-strain relaxations of a polymer is governed by a power law in time can be argued on general theoretical grounds. Let us consider the application of the step strain of magnitude ϵ_0 at a given location (say the n^*th monomer) of a polymer of length N at $t=0$. This strain will excite all fluctuation modes of the polymer. The amplitude a_q of the qth mode ψ_q can be obtained from the equation $\epsilon_0 = \Sigma_q a_q^{(0)} \psi_q$, $q=1,2,\ldots,N$. Typically, in polymer physics, the qth fluctuation mode of a polymer has an associated relaxation time $\tau_q \sim (N/q)^\beta$ for some β, where $\tau_N \sim N^\beta$ is the longest relaxation time of the polymer, corresponding to the slowest mode $q=1$ of the polymer ($\beta=1+2\nu$ for a Rouse polymer, and $\beta=3\nu$ for a Zimm polymer). The subsequent evolution of this strain will then be given by $\epsilon(t) = \Sigma_q a_q^{(0)} \psi_q \exp(-t/\tau_q)$. The local contribution of these summed over a large number of exponentials at n^* will yield a power law, implying that $\epsilon_{n*}(t) \sim t^{-\eta}$ for some η, multiplied by the overall terminal exponential decay $\sim \exp(-t/\tau_N)$. Such power laws are often referred to as "memory effects." The quantity η, the exponent for the power law, characterizes the response of single polymers to local step strains. For the two physical systems discussed above, namely polymer translocation and adsorption of polymers on rigid surfaces, it is the exponent η that dictates the dynamics [13–17].

The purpose of this paper is to report the exponent η for phantom and self-avoiding polymers in three dimensions in

the absence of hydrodynamic interactions. The specific way we create the local strain in the polymers is as follows. At a given location (say the n*th monomer) of an equilibrated polymer of length N, we inject $p(\ll N)$ crumpled monomers at $t=0$, bringing its length to $N+p$. Following the monomer injection at $t=0$, apart from the newly injected monomers, the polymer follows random walk (or self-avoiding walk) statistics, i.e., the strain in the polymer is localized at monomer number n*. In the subsequent evolution of the polymer, we then keep track of how these p crumpled monomers unfold themselves, which yields us the exponent η. Note that the specific way we choose to create the local strain in the polymers is indeed motivated by the actual microscopic dynamics of polymer translocation or polymer adsorption on a rigid surface: As remarked above, for polymer translocation it is the addition or disappearance of monomers to the polymer segments on either side of the membrane that creates the local strain (and similarly for the case of polymer adsorption on a rigid surface).

We calculate η for two different cases each for three-dimensional phantom and self-avoiding polymers: (i) Polymers tethered at one end with the strain created at the point of tether, and (ii) free polymers with the strain created in the middle of the polymer. We derive that $\eta=1$ in both cases; however, for the self-avoiding polymer we show that $\eta=(1+\nu)/(1+2\nu)$ for case (i), and $\eta=2/(1+2\nu)$ for case (ii). Here ν is the Flory exponent for the polymer, with value ≈ 0.588 in three dimensions. We provide exact derivations for the $1/t$ strain relaxation behavior for the phantom polymer using the mode expansion method. The mode expansion method for a self-avoiding polymer is nonlinear, and hence similar theoretical derivation for η for the self-avoiding polymer proves difficult to provide. Only high-precision simulation data are therefore presented in support of the $t^{-(1+\nu)/(1+2\nu)}$ and the $t^{-2/(1+2\nu)}$ step-strain-relaxation behaviors of the self-avoiding polymer.

Although the problem of local step-strain-relaxation behavior in the polymers is motivated in this paper in view of polymer translocation and polymer adsorption, note that both physical processes correspond to the case (i) while the tether point lies on a rigid surface. The presence of the surface, in principle, can influence the strain-relaxation mechanism, and alter the value of η from its value in the absence of the surface. However, since in Refs. [13–15] it was shown—using a model that allowed direct observation of the local strain relaxation—that $\eta=(1+\nu)/(1+2\nu)$ for a self-avoiding polymer for the case of (i) in the presence of a rigid surface as well, the result of this paper therefore implies that the local strain release mechanism for self-avoiding tethered polymers is unaffected by the presence of a surface at the tether point. Note that recently, albeit indirectly, a different polymer model has confirmed that $\eta=(1+\nu)/(1+2\nu)$ for a self-avoiding polymer for the case of (i) in the presence of a rigid surface [18,19], in support of Refs. [13–15].

This paper is organized as follows. In Sec. II A we use the mode expansion technique for a phantom polymer for the case of (i) and derive that $\eta=1$. In Sec. II B, we then consider case (ii) for a phantom polymer to again derive that $\eta=1$. In Sec. III we report the corresponding results for self-avoiding polymers, and discuss the reasons why the self-

avoiding behaves differently in case (i) than in case (ii). The paper is then concluded in Sec. IV with a discussion on the relevance of these exponents for the anomalous dynamics of polymers.

II. RESPONSE OF PHANTOM POLYMERS TO LOCAL STEP STRAIN

With $\vec{r}(n,t)$ as the physical location of the nth monomer of the polymer at time t, we start with the Rouse equation for a phantom polymer and add thermal noise $\vec{f}(n,t)$ to it,

$$\frac{\partial \vec{r}}{\partial t} = \frac{\partial^2 \vec{r}}{\partial n^2} + \vec{f}(n,t). \tag{1}$$

In Eq. (1) the thermal noise $\vec{f}(n,t)$ satisfies the property that $\langle \vec{f}(n,t) \rangle = 0$ and $\langle f_\alpha(n,t) f_\beta(n',t') \rangle = 2\delta_{\alpha\beta}\delta(n-n')\delta(t-t')$; $\alpha,\beta=x,y,z$. For case (i), the polymer with its zeroth monomer tethered at the origin we define the qth mode for a polymer of length $(N+p)$, tethered to a fixed point at the origin as [1]

$$\vec{X}_q(t) = \frac{1}{N+p} \int_0^{N+p} dn \, \sin(k_q n)\vec{r}(n,t), \tag{2}$$

with $k_q = \frac{\pi(2q+1)}{2(N+p)}$, and $q=1,2,3,\ldots$, and similarly $\vec{f}_q$, the qth mode for the thermal noise. The sine-expansion in Eq. (2) satisfies the boundary condition that $\vec{r}(0,t)=0 \ \forall t$, and also that at the free end $\frac{\partial \vec{r}(n,t)}{\partial n}|_N=0$. For case (ii) we define the qth mode for a polymer of length $(N+p)$, moving freely in space as [1]

$$\vec{X}_q(t) = \frac{1}{N+p} \int_0^{N+p} dn \, \cos(k_q n)\vec{r}(n,t), \tag{3}$$

with $k_q = \frac{\pi q}{(N+p)}$, and $q=0,1,2,3,\ldots$, and similarly $\vec{f}_q$, the qth mode for the thermal noise. In this case the cosine-expansion satisfies the boundary condition that at the free ends of the polymer $\frac{\partial \vec{r}(n,t)}{\partial n}|_0 = \frac{\partial \vec{r}(n,t)}{\partial n}|_N = 0$.

In terms of the transforms (2) and (3) the Rouse equation (1) reduces to the Langevin form

$$\frac{\partial \vec{X}_q}{\partial t} = -k_q^2 \vec{X}_q + \vec{f}_q, \tag{4}$$

where $\vec{f}_q$ is defined similar to Eq. (2) [respectively Eq. (3)]. This reduction to the Langevin form also yields

$$\langle f_{p\alpha}(t) \rangle = 0, \quad \langle f_{p\alpha}(t) f_{q\beta}(t') \rangle = \frac{1}{N+p}\delta_{pq}\delta_{\alpha\beta}\delta(t-t'). \tag{5}$$

In terms of $\vec{X}_q(t)$ the monomer locations in physical space are then given by

$$\vec{r}(n,t) = 2\sum_q \sin(k_q n)\vec{X}_q(t)$$

and

$$\vec{r}(n,t) = 2\sum_q \cos(k_q n)\vec{X}_q(t). \tag{6}$$

for the end-tethered and free polymers, respectively.

A. Local strain relaxation for case (i): End-tethered phantom polymers

As we crumple the extra $p(\ll N)$ monomers at the tether point to an equilibrated polymer of length N at time $t=0$, the length of the polymer instantaneously becomes $N+p$. The ensuing time evolution of the polymer is then described by

$$\vec{X}_q(t) = e^{-k_q^2 t}\vec{X}_q(0) + \int_0^t dt'\, e^{-k_q^2(t-t')}\vec{f}_q(t'), \tag{7}$$

i.e.,

$$\vec{r}(n,t) = 2\sum_q \sin(k_q n)\left(e^{-k_q^2 t}\vec{X}_q(0) + \int_0^t dt'\, e^{-k_q^2(t-t')}\vec{f}_q(t')\right). \tag{8}$$

After the injection of p monomers at $t=0$, to follow the deviation from random-walk statistics along the polymer's backbone at a given location of the polymer, say at monomer number n_0, we consider another nearby monomer n_1, define $n=|n_1-n_0|$ and $r^2(n,t)=[\vec{r}(n_1,t)-\vec{r}(n_0,t)][\vec{r}(n_1,t)-\vec{r}(n_0,t)]$,

$$r^2(n,t) = 4\sum_{q,q'}\Bigg[\underbrace{[\sin(k_q n_1)-\sin(k_q n_0)]}_{A_q(n_1,n_0)}\left(e^{-k_q^2 t}\vec{X}_q(0)\right.$$
$$\left. + \int_0^t dt'\, e^{-k_q^2(t-t')}\vec{f}_q(t')\right)\Bigg]$$
$$\times\Bigg[\underbrace{[\sin(k_{q'} n_1)-\sin(k_{q'} n_0)]}_{A_{q'}(n_1,n_0)}\left(e^{-k_{q'}^2 t}\vec{X}_{q'}(0)\right.$$
$$\left. + \int_0^t dt''\, e^{-k_{q'}^2(t-t'')}\vec{f}_{q'}(t'')\right)\Bigg]. \tag{9}$$

With the aid of Eq. (5), for a given polymer realization at $t=0$, the average over the evolution histories (i.e., noise realizations) for $t>0$, denoted by the angular brackets $\langle\cdots\rangle$, for this polymer, yields

$$\langle r^2(n,t)\rangle = 4\sum_{q,q'}\{A_q(n_1,n_0)A_{q'}(n_1,n_0)e^{-(k_q^2+k_{q'}^2)t}[\vec{X}_q(0)\vec{X}_{q'}(0)]\}$$
$$+ \frac{6}{(N+p)}\sum_q \frac{A_q^2(n_1,n_0)}{k_q^2}(1-e^{-2k_q^2 t}). \tag{10}$$

At $t\to\infty$, the t-dependent terms drop out, leaving us with

$$\langle r^2(n,t\to\infty)\rangle = \frac{6}{(N+p)}\sum_q \frac{[\sin(k_q n_1)-\sin(k_q n_0)]^2}{k_q^2}$$
$$\approx \frac{6}{\pi}\int_0^\infty dx\, \frac{[\sin(n_1 x)-\sin(n_0 x)]^2}{x^2} = 3n, \tag{11}$$

which confirms that the polymer returns to equilibrium as $t\to\infty$, as it should.

Since the strain at $t=0$ is created at the tether point, i.e., at monomer number zero of the polymer (of length $N+p$), to quantify its relaxation we track $\langle\|r^2(n,t)\|\rangle$ by choosing $n_0=n^*=0$ and $n_1=n$, with $n\sim O(p)$. Here $\|\cdots\|$ denotes a second average over equilibrated configurations of the polymer at $t=0$. From Eqs. (9) and (5), we can then write

$$\langle\|r^2(n,t)\|\rangle = 3n$$
$$+ 4\sum_{q,q'}[\sin(k_q n)\sin(k_{q'} n)e^{-(k_q^2+k_{q'}^2)t}\|\vec{X}_q(0)\vec{X}_{q'}(0)\|]$$
$$- \frac{6}{(N+p)}\sum_q \frac{\sin^2(k_q n)}{k_q^2}e^{-2k_q^2 t}. \tag{12}$$

Notice that if the polymer of length $(N+p)$ were already at equilibrium at $t=0$ (i.e., no step strain were created anywhere in the polymer), then it would have remained in equilibrium $\forall t>0$; i.e., $\langle\|r^2(n,t)\|\rangle \equiv \langle\|r^2(n,t)\|^{(eq)}\rangle = 3n \ \forall t$. In that case, Eq. (12) would reduce to

$$4\sum_{q,q'}[\sin(k_q n)\sin(k_{q'} n)e^{-(k_q^2+k_{q'}^2)t}\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\|]$$
$$= \frac{6}{(N+p)}\sum_q \frac{\sin^2(k_q n)}{k_q^2}e^{-2k_q^2 t}, \tag{13}$$

where $\vec{X}_q^{(eq)}(0)$ is obtained from Eq. (2) for the polymer at equilibrium at $t=0$. An explicit calculation of Eq. (13) has also been provided in Appendix A [Eqs. (A1)–(A5)].

Based on Eq. (13) we can now replace the last term on the right-hand side (rhs) of Eq. (12) by the left-hand side (lhs) of Eq. (13) to write

$$\langle\|r^2(n,t)\|\rangle - 3n = 4\sum_{q,q'}\sin(k_q n)\sin(k_{q'} n)e^{-(k_q^2+k_{q'}^2)t}g_{q,q'}, \tag{14}$$

with $g_{q,q'} = \underbrace{\|\vec{X}_q(0)\vec{X}_{q'}(0)\|}_{g_{q,q'}^{(1)}} - \underbrace{\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\|}_{g_{q,q'}^{(2)}}$. The quantity $g_{q,q'}^{(2)}$ has already been simplified in Eq. (13) as $\tag{9}$

$$g_{q,q'}^{(2)} = \frac{3}{(N+p)}\frac{1}{2k_q k_{q'}}\delta_{k_q,k_{q'}}, \tag{15}$$

while the quantity $g_{q,q'}^{(1)}$ is explicitly evaluated in Appendix B [Eqs. (B1)–(B4)]. Having combined these two quantities, in the limit of $p \to 0$ we find that

$$g_{q,q'} \approx -\frac{3p}{(N+p)^2 k_q k_{q'}}, \tag{16}$$

which, when used in conjunction with Eqs. (12) and (14), we obtain

$$\langle \| r^2(n,t) \| \rangle = 3n - \frac{12p}{(N+p)^2} \sum_{q,q'} \frac{\sin(k_q n)\sin(k_{q'} n)e^{-(k_q^2+k_{q'}^2)t}}{k_q k_{q'}}$$
$$= 3n - \frac{12p}{\pi^2} \left(\int_0^\infty dx \frac{\sin(nx)e^{-x^2 t}}{x} \right)^2 \approx 3n - \frac{3np}{\pi t} \tag{17}$$

at long times. In other words, the local strain at the tether point relaxes as $1/t$; i.e., the local step strain relaxation exponent $\eta = 1$.

B. Local strain relaxation for case (ii): Free phantom polymers

For the local strain relaxation following the injection p crumpled monomers at $n^* = N/2$ into freely moving phantom polymer at $t=0$ we follow the same route as in Sec. II A; however, one needs to replace the sine expansion by the cosine expansion. While Eqs. (7)–(12) are trivially reproduced with this replacement, for the rest of the calculation we need two small modifications. The first one of them is to choose $n_1 = (N+p-n)/2$ and $n_0 = (N+p+n)/2$ such that $\langle \| r^2(n,t) \| \rangle$, as defined above Eq. (9), can once again quantify the local strain relaxation of the polymer. The second one is that $A_q(n_1,n_0)$ is now defined as $A_q(n_1,n_0) = [\cos(k_q n_1) - \cos(k_q n_0)]$. These lead us to the equivalent forms of Eqs. (12) and (13) as

$$\langle \| r^2(n,t) \| \rangle = 3n + 4 \sum_{q,q'} A_q(n_1,n_0)A_{q'}(n_1,n_0)$$
$$\times [e^{-(k_q^2+k_{q'}^2)t} \| \vec{X}_q(0)\vec{X}_{q'}(0) \|]$$
$$- \frac{6}{(N+p)} \sum_q \frac{A_q^2(n_1,n_0)}{k_q^2} e^{-2k_q^2 t} \tag{18}$$

and [as explicitly evaluated in Eqs. (A6)–(A11) in Appendix A]

$$4 \sum_{q,q'} A_q(n_1,n_0)A_{q'}(n_1,n_0)[e^{-(k_q^2+k_{q'}^2)t} \| \vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0) \|]$$
$$= \frac{6}{(N+p)} \sum_q \frac{A_q^2(n_1,n_0)}{k_q^2} e^{-2k_q^2 t}. \tag{19}$$
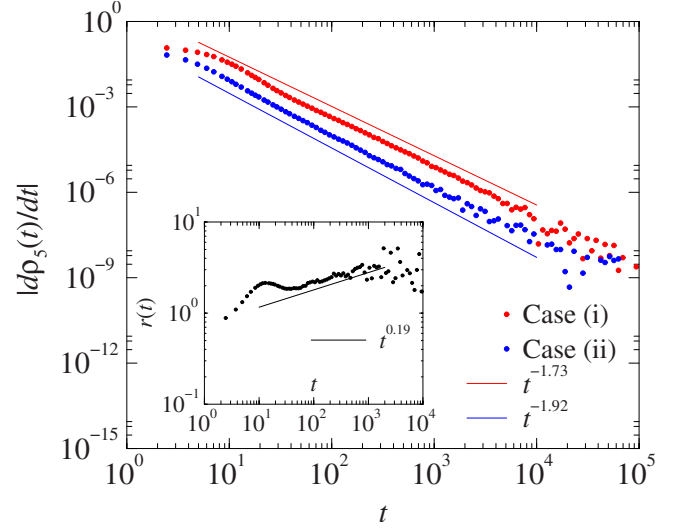

FIG. 1. (Color online) Numerically differentiated data for $|d\rho_5(t)/dt|$ for cases (i) (top set of points, in red) and (ii) (bottom set of points, in blue), for $N=200$ and $p=5$ (10 000 000 realizations each), showing the respective $t^{-(1+\nu)/(1+2\nu)}$ (top straight line, in red) and $t^{-2/(1+2\nu)}$ (bottom straight line, in blue) power-law decay for $\rho_5(t)$. Note that $(1+\nu)/(1+2\nu) \approx 0.73$ and $2/(1+2\nu) \approx 0.92$. We use numerical differentiation in order to remove the $t \to \infty$ offsets of $\rho_5(t)$. The data for case (i) is displaced upwards by a factor of 2 in the y direction. Inset: Ratio $r(t)$ of the $|d\rho_5(t)/dt|$ values for cases (i) and (ii), showing that $r(t)$ follows the power law $t^{(1-\nu)/(1+2\nu)}$; where the value of $(1-\nu)/(1+2\nu)$, the difference in the values of η for cases (i) and (ii), is ≈ 0.19.

Similarly, analogous to Eq. (14) we have

$$\langle \| r^2(n,t) \| \rangle - 3n = 4 \sum_{q,q'} A_q(n_1,n_0)A_{q'}(n_1,n_0)e^{-(k_q^2+k_{q'}^2)t}g_{q,q'}, \tag{20}$$

where $g_{q,q'} = \underbrace{\| \vec{X}_q(0)\vec{X}_{q'}(0) \|}_{g_{q,q'}^{(1)}} - \underbrace{\| \vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0) \|}_{g_{q,q'\,rime}^{(2)}}$, with

$$g_{q,q'}^{(2)} = \frac{3}{(N+p)} \frac{1}{2k_q k_{q'}} \delta_{k_q,k_{q'}} \tag{21}$$

from Eq. (19). The explicit evaluation of $g_{q,q'}^{(1)}$, is carried out in Appendix B [Eqs. (B5)–(B7)]. Having combined $g_{q,q'}^{(1)}$ and $g_{q,q'}^{(2)}$, below we present the final result for $g_{q,q'}$ in the limit of $p \to 0$,

$$g_{q,q'} \approx -\frac{3p}{(N+p)^2} \left(\frac{\sin[k_q(N+p)/2]\sin[k_{q'}(N+p)/2]}{k_q k_{q'}} \right), \tag{22}$$

which, when used in conjunction with Eq. (20), we obtain

$$\langle\|r^2(n,t)\|\rangle = 3n - \frac{12p}{(N+p)^2}\sum_{q,q'}\frac{A_q(n_1,n_0)A_{q'}(n_1,n_0)\sin[k_q(N+p)/2]\sin[k_{q'}(N+p)/2]e^{-(k_q^2+k_{q'}^2)t}}{k_q k_{q'}}. \tag{23}$$

Finally, with $A_q(n_1,n_0)=2\sin[k_q(N+p)/2]\sin(k_q n/2)$, and $\sin[k_q(N+p)/2]=\sin(\pi q/2)$ for $q=1,2,3,\ldots$, Eq. (18) reduces to

$$\langle\|r^2(n,t)\|\rangle$$

$$= 3n - \frac{48p}{(N+p)^2}\left(\sum_q\frac{\sin(k_q n)\sin^2[k_q(N+p)/2]e^{-k_q^2 t}}{k_q}\right)^2$$

$$= 3n - \frac{48p}{(N+p)^2}\left(\sum_{q\in\text{odd}}\frac{\sin(k_q n)e^{-k_q^2 t}}{k_q}\right)^2$$

$$= 3n - \frac{24p}{\pi^2}\left(\int_0^\infty dx\frac{\sin(nx)e^{-x^2 t}}{x}\right)^2$$

$$\approx 3n - \frac{6np}{\pi t}, \tag{24}$$

which, just like Eq. (17), approaches its asymptotic value $3n$ as $1/t$; i.e., once again the local step-strain-relaxation exponent $\eta=1$.

III. RESPONSE OF SELF-AVOIDING POLYMERS TO LOCAL STEP STRAIN

We use a Monte Carlo based lattice polymer model to study the local step-strain relaxation for self-avoiding polymers. In this model, the polymer consists of a sequential chain of monomers, living on a FCC lattice. Monomers adjacent in the string are located either in the same, or in neighboring lattice sites. Multiple occupation of lattice sites is not permitted, except for a set of adjacent monomers. The polymer moves through a sequence of random single-monomer hops to neighboring lattice sites. These hops can be along the contour of the polymer, thus explicitly providing reptation dynamics. They can also change the contour "sideways," providing Rouse dynamics. The reptation as well as the sideways moves are attempted with rate unity, which provides us with a definition of time in this model. This model has been used before to simulate the diffusion and exchange of polymers in an equilibrated layer of adsorbed polymers [20], polymer translocation under a variety of circumstances [13–16,21], and polymer adsorption to rigid surfaces [17]. Multiple occupation of the same site by adjacent monomers of the polymer, in this model, gives rise to "stored lengths" (see Fig. 2 of Ref. [22] for an illustration). Upon injection of p extra monomers into the polymer at the lattice site where the n^*th monomer [$n^*=0$ and $N/2$ for cases (i) and (ii), respectively] is located at $t=0$ the local stored length density is immediately increased by p. To measure the local strain relaxation of the polymer we therefore track the density of stored lengths per monomer in these new p monomers, $\rho_p(t)$

as a function of time. Of course $\rho_p(t)$ would approach some "offset" value ρ_0 as $t\to\infty$.

We have already argued in the introduction that the strain relaxation behaves as $t^{-\eta}\exp(-t/\tau_N)$. The terminal exponential decay $\exp(t/\tau_N)$ with $\tau_N\sim N^{1+2\nu}$ is expected from the Rouse relaxation dynamics of the entire polymer. To understand the physics behind the exponent η, we use the well-established result for the relaxation time t_n for n self-avoiding Rouse monomers scaling as $t_n\sim n^{1+2\nu}$. On the basis of the expression of t_n, we anticipate that following the injection of p monomers at $t=0$, by time t the extra monomers will be well equilibrated across the inner part of the polymer up to $n_t\sim t^{1/(1+2\nu)}$ monomers around n^*, but not significantly further. This internally equilibrated section of (n_t+p) monomers extends only to $r(n_t)\sim n_t^\nu$, less than its equilibrated value $(n_t+p)^\nu$, because the larger scale conformation has yet to adjust to the local strain. As a result, internally equilibrated section of (n_t+p) monomers remains at a state of excess free energy $\delta F\sim k_B T[\delta_r(n_t)/r(n_t)]^2$. The excess p monomers need to find their own physical space by pushing the other monomers away for both cases (i) and (ii), but for case (i) as the zeroth monomer remains tethered, we expect them to feel a force of magnitude f derived from the excess free energy as $f=\partial F/\partial r(n_t)\sim k_B T\delta r(n_t)/r^2(n_t)\sim t^{-(1+\nu)/(1+2\nu)}$, which dictates the relaxation of the step strain; i.e., $\eta=(1+\nu)/(1+2\nu)$. In case (ii) however, the force derived from the excess free energy does not yield η, as the internally equilibrated section will simply move under the effect of the force. Instead, in case (ii) we expect these p monomers to feel a chemical potential of magnitude μ derived from the excess free energy as $\mu=\partial F/\partial n_t=[\partial F/\partial r(n_t)][\partial r(n_t)/\partial n_t]\sim t^{-2/(1+2\nu)}$. The step-strain relaxation is then dictated by the chemical potential μ; i.e., $\eta=2/(1+2\nu)$. In Fig. 1, by tracking $\rho_5(t)$ for $N=195$ and $p=5$, we provide confirmation of this physics. Note that the result for η for case (i) is consistent with the corresponding two-dimensional case in Ref. [15], as it should be.

IV. DISCUSSION

In this paper, response of single polymers to localized step strains is studied for two cases in the absence of hydrodynamic interactions: (i) Polymers tethered at one end with the strain created at the point of tether, and (ii) free polymers with the strain created in the middle of the polymer. The polymers are assumed to be in their equilibrium state before the step strain is created. Using mode expansion technique for Rouse equation it is shown that for phantom polymers in both cases the strain relaxes in time as $1/t$. However, for self-avoiding polymers for the two cases the strain relaxes as $t^{-(1+\nu)/(1+2\nu)}$ and as $t^{-2/(1+2\nu)}$, respectively, The strain relaxation behavior $t^{-(1+\nu)/(1+2\nu)}$ for a self-avoiding polymer for

case (i) is consistent with an earlier reported result in two dimensions [15]. Based on the results reported here, and combined with those of Refs. [13,16,17] we can conclude that the result for case (i) is independent of the presence of a surface at the tether point.

Although in both cases (i) and (ii) the local step strain puts the polymer in a state of excess free energy, the difference between the results for the self-avoiding polymers for these two cases stems from the fact that the tether point provides a point of reference for the polymer in case (i), but not in case (ii). As a result, for case (i) we need to consider the force, while for case (ii) we need to consider the chemical potential, derived from the excess free energy. For phantom polymers however, since different parts of the polymer do not interact with each other, there is no need for the strained monomers to physically push away the other monomers of the polymer in order to be able to relieve their strain, and hence for case (i), the force derived from the excess free energy plays no role in the localized strain relaxation for the phantom polymer. In fact, precisely because of the same reason, we expect to see $1/t$ strain relaxation for phantom polymers also in the presence of a surface at the tether point. With $t^{-1} = t^{-2/(1+2\nu)}$ for phantom polymers ($\nu = 0.5$), the relevance of this paper is that one cannot trivially extend the local strain-relaxation behavior for tethered phantom polymers to self-avoiding polymers by replacing $\nu = 0.5$ by $\nu \approx 0.588$ in three dimensions.

In earlier papers [13–16,22], a "voltage-current" relationship $\phi(t) = \int_0^t dt' \, \mu(t-t') \dot{s}(t')$ between $\dot{s}(t)$, the instantaneous rate of translocation, and the polymer's chain tension imbalance $\phi(t)$ across the pore was established, where $\mu(t)$ is the memory effect derived from the polymer's local strain (alternatively, the chain tension) relaxation behavior at the pore. Here $s(t)$ is the number of the monomer located in the pore at time t. Using $\mu(t) \sim t^{-(1+\nu)/(1+2\nu)}$ for unbiased polymer translocation [13,15,22] as in case (i) for self-avoiding polymers in this paper, the anomalous dynamics, characterized by $\langle \Delta s^2(t) \rangle$, where $\Delta s(t)$ is the total number of monomers translocated through the pore in time t, was then derived by using the fluctuation-dissipation theorem, where the angular brackets denote an ensemble average. It was found that for a translocating polymer of length N, $\langle \Delta s^2(t) \rangle \sim t^{(1+\nu)/(1+2\nu)}$ up to the Rouse time $\tau_N \sim N^{1+2\nu}$, and since no memory can survive in the polymer beyond the Rouse time, $\langle \Delta s^2(t) \rangle \sim t$ for $t > \tau_N$, i.e., the pore-blockade time scaling as $N^{2+\nu}$. This result for the scaling of the pore-blockade time is in good numerical agreement with that of Refs. [23,24], obtained using completely different polymer models. Furthermore, having exploited the same "current-voltage" relationship between $\dot{s}(t)$ and the chain tension difference $\phi(t)$ across the pore and that $\mu(t) \sim t^{-(1+\nu)/(1+2\nu)}$ for field-driven translocation as well, the exponent $N^{(1+2\nu)/(1+\nu)}$ scaling was later found for the pore-blockade time for field-driven translocation of a polymer of length N [16] (this result has recently been confirmed [18,19] using other polymer models). Similarly, for the nonequilibrium dynamics of single polymer adsorption to solid surfaces, the adsorption time for a polymer of length N at weak adsorption energies was also found to scale as $N^{(1+2\nu)/(1+\nu)}$ [17]. These results, put together with the discussions in the above paragraph [namely that the value of η for case (i) is independent of the presence of a surface at the tether point], lead us to expect that the pore-blockade time for unbiased translocation should scale as $N^{2+\nu}$ for self-avoiding polymers, and as N^2 for phantom ones, irrespective of whether translocation proceeds through a narrow pore in a membrane or whether it proceeds through a narrow ring (i.e., a pore without a membrane).

It is imperative to ask, based on the local strain relaxation result for case (ii), whether it would be possible to derive an expression for the mean-square-displacement $\langle \Delta r^2(n,t) \rangle$ of the nth monomer in physical space in time t, by tracking the physical location $\vec{r}(n,t)$ for the nth monomer of the polymer at time t. In order to answer this question, let us reconsider the "voltage-current" relationship between the chain tension imbalance across the pore and $\dot{s}(t)$, and note that for translocation $s(t)$ is a scalar variable, while $\vec{r}(n,t)$ is a vector, and as a result, deriving $\langle \Delta r^2(n,t) \rangle$ in a similar manner is more complicated. To illustrate this difficulty, let us return to the deterministic part of Eq. (1): By first expressing $\vec{r}$ as a function of the polymer's contour l, and then expressing the l as a function of n, Eq. (1) reads as

$$\frac{\partial \vec{r}(n,t)}{\partial t} = \frac{\partial^2 \vec{r}}{\partial l^2} \left(\frac{\partial l}{\partial n} \right)^2 + \frac{\partial \vec{r}}{\partial l} \frac{\partial^2 l}{\partial n^2}. \qquad (25)$$

The first term on the rhs of Eq. (25) is a force that acts on the nth monomer perpendicular to the contour of the polymer at the location of the nth monomer at time t, while the second term is a force on the nth monomer that acts along the contour. Note also that the term $\frac{\partial^2 l}{\partial n^2}$ is precisely the imbalance in the chain tension $\frac{\partial l}{\partial n}$ at the nth monomer. In the case of translocation, the fact that the motion of the monomer perpendicular to the polymer's contour in the pore is completely blocked means that the motion of the monomer in the pore is determined entirely by the chain tension imbalance across the pore. For a free polymer however, the first term on the rhs of Eq. (25) does contribute to the motion of the nth monomer, but what is its precise contribution to $\langle \Delta r^2(n,t) \rangle$ is not entirely clear. Nevertheless, if we consider the second term alone, then it does allow us to write a voltage-current relationship (exactly the same as that of Refs. [13–16,22]) between the chain tension imbalance at the nth monomer and the along-the-contour velocity component of the nth monomer, but this time, following the polymer's local strain-relaxation behavior for case (ii), with $\mu(t) \sim t^{-2/(1+2\nu)}$. The application of the fluctuation-dissipation theorem would then imply that $\langle \Delta r^2(n,t) \rangle$ should increase as $t^{2/(1+2\nu)}$ along the polymer's contour, i.e., in physical space $\langle \Delta r^2(n,t) \rangle \sim t^{2\nu/(1+2\nu)}$, untill the Rouse time $\tau_N \sim N^{1+2\nu}$; this is a well-known result in polymer physics.

APPENDIX A: DERIVATION OF $\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\|$ FOR PHANTOM POLYMERS

Here we provide a derivation of Eq. (13) for case (i) and an analogous form of it for case (ii).

For case (i), by definition

$$\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\| = \frac{1}{(N+p)^2}\int_0^{N+p} dn \, \sin(k_q n)\int_0^{N+p} dn' \, \sin(k_{q'}n')\|\vec{r}(n)\vec{r}(n')\|^{(eq)}. \tag{A1}$$

In equilibrium the polymer satisfies random walk statistics along its entire backbone. Hence, with $\Theta(x)$ denoting the Heavyside function of x,

$$\|\vec{r}(n)\vec{r}(n')\|^{(eq)} = 3n\Theta(n'-n) + 3n'\Theta(n-n'), \tag{A2}$$

which reduces Eq. (A1) to

$$\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\| = \frac{3}{(N+p)^2}\left(\int_0^{N+p} dn\, n\, \sin(k_q n)\int_n^{N+p} dn'\, \sin(k_{q'}n') + \int_0^{N+p} dn'\, n'\, \sin(k_{q'}n')\int_{n'}^{N+p} dn\, \sin(k_q n)\right)$$

$$= \frac{3}{(N+p)^2}\left(\int_0^{N+p} dn\, n\, \frac{\sin(k_q n)\cos(k_{q'}n)}{k_{q'}} + \int_0^{N+p} dn'\, n'\, \frac{\sin(k_{q'}n')\cos(k_q n')}{k_q}\right)$$

$$= \frac{3}{(N+p)^2}\left(\frac{\sin[2k_q(N+p)]-2k_q(N+p)\cos[2k_q(N+p)]}{4k_q^3}\delta_{k_q,k_{q'}} + (1-\delta_{k_q,k_{q'}})\right.$$

$$\left.\times \frac{k_q\cos[k_{q'}(N+p)]\sin[k_q(N+p)]-\cos[k_q(N+p)]\{(k_q^2-k_{q'}^2)(N+p)\cos[k_{q'}(N+p)]+k_{q'}\sin[k_{q'}(N+p)]\}}{k_q k_{q'}(k_q^2-k_{q'}^2)}\right). \tag{A3}$$

The second step of Eq. (A3) requires $\cos[k_q(N+p)]=\cos[k_{q'}(N+p)]=0$, while in the last step using $\cos[k_q(N+p)] = \cos[k_{q'}(N+p)]=0$, we first see that $\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\| \propto \delta_{k_q,k_{q'}}$, and moreover, with $\sin[2k_q(N+p)]=0$ and $\cos[2k_q(N+p)]= -1$, we obtain

$$\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\| = \frac{3}{(N+p)}\frac{1}{2k_q^2}\delta_{k_q,k_{q'}}, \tag{A4}$$

i.e.,

$$4\sum_{q,q'}[\sin(k_q n)\sin(k_{q'}n)e^{-(k_q^2+k_{q'}^2)t}\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\|] = \frac{6}{(N+p)}\sum_q \frac{\sin^2(k_q n)}{k_q^2}e^{-2k_q^2 t}. \tag{A5}$$

To derive a similar expression for $\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\|$ for case (ii) we express $\vec{r}(n,0)$, the physical location of the nth monomer at $t=0$, relative to $\vec{r}(0,0)$, the physical location of the first monomer at $t=0$ as $\vec{r}(n,0)=\vec{r}(0,0)+\vec{r}'(n,0)$. Then

$$\vec{X}_q(0) = \frac{1}{(N+p)}\int_0^{N+p} dn\, \cos(k_q n)\vec{r}(n,0) = \frac{1}{(N+p)}\int_0^{N+p} dn\, \cos(k_q n)[\vec{r}(0,0)+\vec{r}'(n,0)], \tag{A6}$$

implying that

$$\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\| = \frac{1}{(N+p)^2}\int_0^{N+p} dn\, \cos(k_q n)\int_0^{N+p} dn'\, \cos(k_{q'}n')[\|r^2(0,0)\| + \|\vec{r}'(n)\vec{r}'(n')\|]^{(eq)}$$

$$= \frac{1}{(N+p)^2}\int_0^{N+p} dn\, \cos(k_q n)\int_0^{N+p} dn'\, \cos(k_{q'}n')\|\vec{r}'(n)\vec{r}'(n')\|^{(eq)}. \tag{A7}$$

To obtain the second step of Eq. (A7) $\|r^2(0,0)\|=0$ has been used by a trivial translation of origin to obtain $\vec{r}(0,0)=0$, without affecting any part of the calculation.

In terms of $\vec{r}'(n,0)$, we can once again use

$$\|\vec{r}(n)\vec{r}(n')\|_{p=0} = 3n\Theta(n'-n) + 3n'\Theta(n-n'), \tag{A8}$$

which reduces the expression for $\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\|$ to

$$\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\| = \frac{3}{(N+p)^2}\left(\int_0^{N+p} dn\, n\cos(k_q n)\int_n^{N+p} dn'\cos(k_{q'}n') + \int_0^{N+p} dn'\, n'\cos(k_{q'}n')\int_{n'}^{N+p} dn\cos(k_q n)\right) =$$

$$-\frac{3}{(N+p)^2}\left(\int_0^{N+p} dn\, n\frac{\cos(k_q n)\sin(k_{q'}n)}{k_{q'}} + \int_0^{N+p} dn'\, n'\frac{\cos(k_{q'}n')\sin(k_q n')}{k_q}\right)$$

$$= \frac{3}{(N+p)^2}\left(\frac{2k_q(N+p)\cos[2k_q(N+p)] - \sin[2k_q(N+p)]}{4k_q^3}\delta_{k_q,k_{q'}} + (1 - \delta_{k_q,k_{q'}})\right.$$

$$\times \left.\frac{k_{q'}\cos[k_{q'}(N+p)]\sin[k_q(N+p)] - \sin[k_{q'}(N+p)]\{(k_q^2 - k_{q'}'^2)(N+p)\sin[k_q(N+p)] + k_q\cos[k_q(N+p)]\}}{k_q k_{q'}(k_q^2 - k_{q'}^2)}\right).$$

(A9)

The second step of Eq. (A9) requires $\sin[k_q(N+p)]$ $=\sin[k_{q'}(N+p)]=0$, while in the last step using $\sin[k_q(N+p)]=\sin[k_{q'}(N+p)]=0$, we first see that $\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\|$ $\propto \delta_{k_q,k_{q'}}$, and moreover, with $\sin[2k_q(N+p)]=0$ and $\cos[2k_q(N+p)]=1$, we obtain

$$\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\| = \frac{3}{(N+p)}\frac{1}{2k_q^2}\delta_{k_q,k_{q'}}. \quad \text{(A10)}$$

Equation (10) then yields

$$4\sum_{q,q'} A_q(n_1,n_0)A_{q'}(n_1,n_0)[e^{-(k_q^2+k_{q'}^2)t}\|\vec{X}_q^{(eq)}(0)\vec{X}_{q'}^{(eq)}(0)\|]$$

$$= \frac{6}{(N+p)}\sum_q \frac{A_q^2(n_1,n_0)}{k_q^2}e^{-2k_q^2 t}. \quad \text{(A11)}$$

APPENDIX B: DERIVATION OF $g_{q,q'}^{(1)}$ FOR PHANTOM POLYMERS

To evaluate $g_{q,q'}^{(1)}$ for case (i) we note that $\vec{X}_q(0)$ $=\frac{1}{N+p}\int_0^{N+p} dn\sin(k_q n)\vec{r}(n,0)$, and since $\vec{r}(n,0)\equiv 0$ for $n\leq p$ by construction, $\vec{X}_q(0)=\frac{1}{N+p}\int_0^N dn\sin[k_q(n+p)]\vec{r}(n+p,0)$, and hence

$$g_{q,q'}^{(1)} = \frac{1}{(N+p)^2}\int_0^N dn\int_0^N dn'\sin[k_q(n+p)]\sin[k_{q'}(n'+p)]$$

$$\times\|\vec{r}(n+p)\vec{r}(n'+p)\|. \quad \text{(B1)}$$

Since the polymer was in equilibrium before the p crumpled monomers were injected at the tether point, we can write

$$\|\vec{r}(n+p)\vec{r}(n'+p)\| = 3n\Theta(n'-n) + 3n'\Theta(n-n'). \quad \text{(B2)}$$

Thereafter, using Eq. (B2), and $\cos[k_q(N+p)]=\cos[k_{q'}(N+p)]=\sin[(k_q-k_{q'})(N+p)]=\sin[(k_q+k_{q'})(N+p)]=\sin[2k_q(N+p)]=0$ and $\cos[2k_q(N+p)]=-1$, the expression for $g_{q,q'}^{(1)}$ in Eq. (B1) simplifies as

$$g_{q,q'}^{(1)} = \frac{3}{(N+p)^2}\int_0^N dn\, n\sin[k_q(n+p)]\int_n^N dn'\sin[k_{q'}(n'+p)]$$

$$+ \int_0^N dn'\, n'\sin[k_{q'}(n'+p)]\int_{n'}^N dn\sin[k_q(n+p)]$$

$$= \frac{3N}{2(N+p)^2 k_q^2}\delta_{k_q,k_{q'}} - \frac{3}{(N+p)^2}\frac{\sin[(k_q+k_{q'})p]}{2k_q k_{q'}(k_q+k_{q'})}$$

$$- \frac{3}{(N+p)^2}\frac{\sin[(k_q-k_{q'})p]}{2k_q k_{q'}(k_q-k_{q'})}(1 - \delta_{k_q,k_{q'}}). \quad \text{(B3)}$$

In the limit $p\to 0$ the two terms proportional to $\delta_{k_q,k_{q'}}$ in Eq. (B3) cancel each other, as Eqs. (15) and (B3) then leave us with

$$g_{q,q'} \approx -\frac{3p}{(N+p)^2 k_q k_{q'}}. \quad \text{(B4)}$$

To evaluate $g_{q,q'}^{(1)}$ for case (ii) we express $\vec{r}(n,0)$, the physical location of the nth monomer at $t=0$, relative to $\vec{r}(0,0)$, the physical location of the first monomer at $t=0$ as $\vec{r}(n,0)=\vec{r}(0,0)+\vec{r}(n,0)$, to obtain

$$g_{q,q'}^{(1)} = \frac{1}{(N+p)^2}\int_0^{N+p} dn\int_0^{N+p} dn'\cos(k_q n)\cos(k_{q'}n')$$

$$\times\|\vec{r}'(n,0)\vec{r}'(n',0)\|$$

$$= \frac{1}{(N+p)^2}\left(\int_0^{N+p} dn\int_n^{N+p} dn'\cos(k_q n)\cos(k_{q'}n')f(n)\right.$$

$$+ \left.\int_0^{N+p} dn'\int_{n'}^{N+p} dn\cos(k_q n)\cos(k_{q'}n')f(n')\right), \quad \text{(B5)}$$

where $f(n)=[3n\Theta(N/2-n)+3N/2\Theta(n-N/2)\Theta(N/2+p-n)+3(n-p)\Theta(n-N/2-p)]$. Thereafter, with $\sin[k_q(N+p)]=\sin[k_{q'}(N+p)]=\sin[(k_q-k_{q'})(N+p)]=\sin[(k_q+k_{q'})(N+p)]=0$ and $\cos[2k_q(N+p)]=1$, we find

$$g_{q,q'}^{(1)} = \frac{3}{(N+p)^2} \frac{2k_q N + 2 \sin(k_q p)\cos[k_q(N+p)]}{4k_q^3} \delta_{k_q,k_{q'}} - \frac{3}{(N+p)^2}$$

$$\times \left(\frac{\cos[(k_q - k_{q'})(N+p)/2]\sin[(k_q - k_{q'})p/2]}{k_q k_{q'}(k_q - k_{q'})} - \frac{\cos[(k_q + k_{q'})(N+p)/2]\sin[(k_q + k_{q'})p/2]}{k_q k_{q'}(k_q + k_{q'})} \right)(1 - \delta_{k_q,k_{q'}}). \quad \text{(B6)}$$

In the limit $p \ll N$, Eq. (B6) can be expanded to obtain

$$g_{q,q'}^{(1)} \approx \frac{3}{2(N+p)k_q k_{q'}} \delta_{k_q,k_{q'}} - \frac{3p}{(N+p)^2} \left(\frac{\sin[k_q(N+p)/2]\sin[k_{q'}(N+p)/2]}{k_q k_{q'}} \right). \quad \text{(B7)}$$

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