

Configurational Statistics of Macromolecules in Solution from Correlations of Liquid Molecules

Stefano A. Mezzasalma*

Department of Biophysics, Biochemistry and Macromolecular Chemistry, University of Trieste, Via Giorgieri 1, 34127 Trieste, Italy

Received: June 7, 2006; In Final Form: August 21, 2006

We address the relevant quest for a simple formalism describing the microstructure of liquid solutions of polymer chains. On the basis of a recent relativistic-type picture of self-diffusion in (simple) liquids named Brownian relativity (BWR), a covariant van Hove's distribution function in a Vineyard-like convolution approximation is proposed to relate the statistical features of liquid and chain molecules forming a dilute polymer solution. It provides an extension of the Gaussian statistics of ideal chains to correlated systems, allowing an analysis of macromolecular configurations in solution by the only statistical properties of the liquid units (and vice versa). However, the mathematical solution to this issue is not straightforward because, when the liquid and polymer van Hove's functions are equated, an inverse problem takes place. It presents some conceptual analogies with a scattering experiment in which the correlation of the liquid molecules acts as the radiation source and the macromolecule as the scatterer. After inverting the equation by a theorem coming from the Tikhonov's approach, it turns out that the probability distribution function of a real polymer can be expressed from a static Ornstein–Uhlenbeck process, modified by correlations. This result is used to show that the probability distribution of a true self-avoiding walk polymer (TSWP) can be modeled as a universal Percus–Yevick hard-sphere solution for the total correlation function of the liquid units. This method suits in particular the configurational analysis of single macromolecules. The analytical study of arbitrary many-polymer systems may require further mathematical investigation.

Introduction

Brownian relativity (BWR) has been lately formulated to study the universal picture exhibited by liquid solutions of linear, neutral, flexible, and homogeneous polymer chains.¹ To fix the ideas, consider a simple liquid and imagine that its diffusion coefficient (D) is playing a similar role to the light speeds in special relativity. If N liquid molecules are merged together to form a macromolecule with contour length N , the consequent mobility decrease ($D \rightarrow D/N$) perturbs locally the starting diffusive medium. This gives rise to spatiotemporal transforms which, in a special theory, rely on the Lorentz group² and, in a general-relativistic description, on the Einstein's field equations.³ Basic polymer quantities such as size, characteristic times, and transport coefficients are thus constrained to scale with the repeat unit number (N) and, in the limit of large enough molecular weights, a new framework for scaling phenomena is afforded.^{4,5} Apart from universality in the repeat unit number, it turned out a further universal mechanism, which was termed geometrical scaling.^{6,7} Instead of counting over the monomer number only, polymer configurations can be conceived as shapes, carrying a statistical information that scales geometrically from the characteristic length of its monomeric unit. In short, what is geometrical at small (molecular) scales would get statistical at larger (polymer) scales.

In this work, the distribution function of a true self-avoiding walk polymer is rebuilt by the total correlation of liquid molecules. Once time and space form a joint diffusional continuum, all distribution functions defined therein are evidently constrained to each other. In other words, as in special

relativity, time and space are no longer absolute and independent; in BWR, any statistical feature should be equally found somewhat in each subsystem sharing the diffusive spacetime. The phenomenology displayed by macromolecules in solution would so enclose the statistical properties of the fluid where they embed. Vice versa, simple liquids would stand for arenas from which extracting the characteristics of any molecular configuration fluctuating and diffusing across it. Whenever statistics are less complicated or more accessible at some characteristic scale, one could thus exploit the information carried by the other spacetime scale.

This is just the line followed in this work, where the configurational distribution function of a given class of macromolecules is derived from the statistical knowledge of the smaller spacetime scale of the single liquid molecules. Formally, the equation to start from is a covariant van Hove distribution function in a Vineyard-like convolution approximation,^{8,9} which was previously inferred from BWR to relate the statistics ruling liquid and chain molecules, forming a dilute polymer solution.¹⁰ For any formal or conceptual detail, the reader may check directly the several references on this subject.^{1,4,5,10} Here, a brief account of the previous work has been outlined in the following paragraph.

Brownian Relativity (BWR) and the Covariant Vineyard's Approximation

In the starting BWR formulation,¹ a diffusive spacetime interval, defined as:

$$d\sigma^2 = D dt - dr^2 \quad (1)$$

* E-mail: mezzasalma@bbcm.units.it.

is preserved upon changing diffusive reference frame, (\bar{r}^2, t) f (r'^2, t') :

$$d\sigma^2 = d\sigma'^2 \quad (2)$$

Here, D specifies the diffusion coefficient of the liquid molecule, t is time, and \bar{r}^2 is the mean-square end-to-end distance, averaged over all path configurations. Equation 1 points out a Lorentz-type invariance at long wavelengths (or times) that may either refer to a marked liquid molecule or a polymer chain. It forms the basis by which different scaling properties of polymer solutions were determined, with and without long-range correlations.

The previous constraint can be generalized to any length scale, and the following summarizes the procedure adopted in a late study.¹⁰ It suffices, starting from the Fourier transform of the functional displacement associated with the heat-diffusion equation, setting:

$$\int \left(\frac{\partial G_{S,N}}{\partial t} - D \nabla^2 G_{S,N} \right) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} = \text{invar} \quad (3)$$

where ∇^2 is the Laplacian, \mathbf{r} is the position vector, and \mathbf{q} is the wave vector. The function $G_{S,N} = G_{S,N}(\mathbf{r}, t)$ denotes the time-displaced distribution for a particle pair in a system of N units, tending to a pointwise Dirac function at initial times, $G_{S,N}(\mathbf{r}, t \rightarrow 0) = \delta(\mathbf{r})$. It can be shown that the former invariance turns out being equivalent to:¹⁰

$$\frac{F_N(q, t)}{F_{\text{eq}}(q, t)} = \text{invar} \quad (4)$$

where:

$$F_N(q, t) = \overline{\exp(i\mathbf{q} \cdot \mathbf{r})} \quad (5)$$

is the moment-generating function for the implied probability distribution ($G_{S,N}$) and the Gaussian profile:

$$F_{\text{eq}}(q, t) = \exp(-Dq^2 t) \quad (6)$$

describes, as usual, the equilibrium state. We may use at this point the spacetime symmetry implied by BWR for both liquid and chain molecules. From any couple of molecular sites (n, m), eq 1 implies:

$$D(\Delta_{nm}t' - \Delta_{nm}t) = \Delta_{nm}\bar{r'^2} - \Delta_{nm}\bar{r^2} \quad (7)$$

where the symbols $\Delta_{nm}(\dots) = (\dots)_n - (\dots)_m$ denote the spatiotemporal displacements to be calculated in both molecular and macromolecular systems. Explicitly stating the spatial statistics by a Wiener-like process¹¹ of molecular step size l , $\Delta_{ks}\bar{r^2} = (k-s)l^2$, returns in the end the following relationship:

$$\overline{\exp\{i\mathbf{q} \cdot (\mathbf{r}_n - \mathbf{r}_m)\}} F_N(q, t_n - t_m) = \text{invar} \quad (8)$$

to be summed over all molecules forming each subsystem.

In a dilute polymer solution, the couple of terms on the left generate separated contributions that, getting back to the spacetime domain, are:

$$G_{S,N}(\mathbf{r}, t) + \bar{\rho}_N h_N(\mathbf{r}) \otimes G_{S,N}(\mathbf{r}, t) = \text{invar} \quad (9)$$

$\bar{\rho}_N$ being the average density at equilibrium and \otimes denoting the

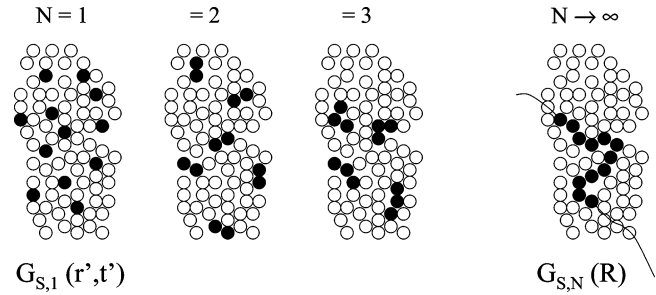


Figure 1. Scheme of the covariant Vineyard's convolution approximation for Brownian reference frames with increasing unit numbers, from $N = 1$ (liquid molecules) to $N \rightarrow \infty$ (macromolecule).

spatial convolution. The first term describes the wandering of a particle away from an arbitrary initial spacetime point, and the second the probability to find a (chemically alike) particle that is distinct from and correlated to the one initially located at the origin. In compact form, eq 9 may be rewritten as a Vineyard's convolution approximation that, owing to BWR, preserves its form both in liquid (subindex 1) and chain (N) reference systems:

$$G_N(\mathbf{r}, t) = G_{D,N}(\mathbf{r}) \otimes G_{S,N}(\mathbf{r}, t) = G_1(\mathbf{r}', t') \quad (10)$$

In this representation, G_N is a total van Hove function, $G_{S,N}$ is the self-correlation, and:

$$\bar{\rho}_N G_{D,N}(\mathbf{r}) = \bar{\rho}_N \delta(\mathbf{r}) + \bar{\rho}_N^2 h_N(\mathbf{r}) \quad (11)$$

is a probability distribution function for density fluctuations, taking the self-correlation and the affinity between homogeneous fluid constituents into account.

As will be seen in the next two sections, eq 10 can be exploited to get the configurational statistics of (long) polymer chains from the correlation behavior in the liquid system. On approaching very large unit numbers ($N \rightarrow \infty$), the expression in eq 9 reduces in fact to a static relationship, which not only describes polymer universality in the hydrodynamic regime,¹ but at any wavelength scale (see also Figure 1).

Analysis of the Inverse Problem

Tikhonov's Approach. To invert the previous relation and get the configurational distribution of a real chain, one can make use of a theorem relying on Tikhonov's regularization method, frequently adopted to work out a wide class of ill-posed equations.¹²

Let $X, Y \in H$ be two Hilbert spaces and $K: X \rightarrow Y$ specifying a linear and bounded operator, such that the equation $Kx = y$ defines an inverse problem for some $x \in X$ and a fixed $y \in Y$. Hilbert spaces (H) generalize the Euclidean space definition, i.e., a linear space endowed with some scalar (or inner) product. They obey a completeness property with respect to the natural metric (or norm) induced by the scalar product, and ensuring the existence of limits, when expected. Moreover, H are said to possess infinite dimension, in the sense that $\forall m \in N$, it is always possible, finding m linearly independent elements (or vectors). All finite-dimensional inner product spaces, as our diffusive Minkowski's spacetime, are clearly Hilbert's. Thus, the equation $Kx = y$ will be identified with the covariant Vineyard's approximation, where x, y and X, Y describe respectively the statistical states and domains of a chain long N and a molecular ensemble of N liquid units.

In Tikhonov's regularization approach, optimizing the error $\|Kx - y\|$ is enforced by an extra constraint, selecting the

solutions that are stable with respect to small perturbations of the initial data.¹² The functional to be minimized for some norm in Y is $L_\alpha(x) = \|Kx - y\|^2 + \alpha\|x\|^2$, where the chosen (approximation strategy for the) regularization parameter α (>0) controls the convergence and fixes the best approximation to $x_\alpha = x(\alpha) \in X$, such that $L_\alpha(x_\alpha) = \min_x \{L_\alpha(x)\}$.

If one considers integral equations of the form:

$$\int_0^z x(s) ds = y(z) \quad (12)$$

with $z \in [0, 1]$, $y \in H(0, 1)$, and $y(0) = 0$, it can be proved that the solution $x_\alpha \equiv x(z, \alpha)$ fulfills the following differential equation in $z \in (0, 1)$:¹³

$$-\alpha x''(z) + x(z) = y'(z) \quad (13)$$

where primes abbreviate the symbol of z -derivatives, and:

$$\lim_{s \rightarrow 1} x(s) = \lim_{s \rightarrow 0} x'(s) = 0 \quad (14)$$

are the boundary conditions.

Inverting the Covariant Vineyard's Approximation. The former theorem can be applied to invert the covariant van Hove's equation, precisely (eq 10):

$$G_{D,N} \otimes G_{S,N} = G_{D,1} \otimes G_{S,1} \quad (15)$$

where both convolution products, defined for any couple of arbitrary functions f and g as:

$$f \otimes g = \int_0^R f(R-r)g(r) dr = g \otimes f \quad (16)$$

are conceived as a function of a common scale R . We thus take advantage of the previously discussed equivalence, for polymer statics and dynamics of liquid molecules, set by BWR in the limit of very large molecular ensembles^{1,4-6,10} ($N \rightarrow \infty$).

In Tikhonov's language, the functional to be minimized takes the form (eq 10):

$$L_\alpha(G_{S,N}(R)) = \|G_{D,N} \otimes G_{S,N} - G_1\|^2 + \alpha\|G_{S,N}\|^2 \quad (17)$$

where the polymer self-correlation is the function in which eq 15 is solved. To this end, the formal choices to be made are:

$$\begin{cases} x(s) = G_{S,1}(R-s)\tilde{h}_1(s) - G_{S,N}(s)\tilde{h}_N(R-s) + A(s, R) \\ y(s) = \Delta G(s) - \Delta G_0 \end{cases} \quad (18)$$

with $\Delta G(z) = G_{S,N}(z) - G_{S,1}(z)$ denoting the self-correlation change at point z upon varying the molecular unit number ($1 \rightarrow N$), and $\Delta G_0 \equiv \Delta G(0)$. The class of functions $A = A(s, R)$ is introduced in all generality to specify the boundary condition for the self-correlation change at $z = 0$:

$$\int_0^R A(s, R) ds = -\Delta G(0) \quad (19)$$

introduced in $y = y(s)$ to ensure $y(0) = 0$. As will be seen, a part of the approximation strategy is choosing opportune boundary conditions for the molecular and macromolecular self-correlations. Total correlation functions for each subsystem are taken here into account through $\tilde{h}_K(s) = 4\pi s^2 h_K(s)$ ($K = 1, N$). Now, by explicitly stating the second derivative:

$$x''(R) = \lim_{s \rightarrow R} \{\gamma_{1,0}\tilde{h}_1''(s) - 2\gamma_{1,1}\tilde{h}_1'(s) + \gamma_{1,2}\tilde{h}_1(s) - \widehat{h}_N G_{S,N}(s) + A''(s, R)\} \quad (20)$$

and intending all functions to be continuous in $s \in (0, 1)$, eq 13 can be rewritten as

$$(\Delta G)' = \alpha[\widehat{h}_N G_{S,N}(R) - \gamma_{1,0}\tilde{h}_1''(R) + 2\gamma_{1,1}\tilde{h}_1'(R) - \gamma_{1,2}\tilde{h}_1(R)] + \gamma_{1,0}\tilde{h}_1(R) + A_\alpha(R) \quad (21)$$

where the following notations and values are adopted, $\widehat{h}_N \equiv \tilde{h}_N''(0) = -8\pi\bar{\rho}_N$, and

$$\gamma_{K,i} \equiv \left(\frac{d^i G_{S,K}}{ds^i} \right)_{s=0}$$

with $A_\alpha(R) \equiv -\alpha A''(R, R) + A(R, R)$ and $\tilde{h}_K(0) = \tilde{h}_K'(0) = 0$ ($K = 1, N$). The total interchain correlation function (\widehat{h}_N) does not appear, and this is due in part to the inverse problem setting (eq 18) and in part to the boundary conditions involved.

We should bring now into the model a couple of main physical features, the polymer self-avoidance at the origin and liquid molecules at the long wavelength limit. To do so, observe that a real, self-avoiding polymer is characterized by nonnegligible excluded volume effects, reflected in its distribution functions by a sharp decrease at small R . In other words, it is highly improbable that its configuration returns arbitrarily close to its starting point,¹⁴ whence $G_{S,N}(0) = 0$ ($\equiv \gamma_{N,0}$). Furthermore, at the long wavelength regime, a Gaussian distribution function may be generally set to¹⁵ $G_{S,1}(s) = (2\pi\sigma^2)^{-3/2} \exp(-s^2/2\sigma^2)$, where the root-mean-square (σ) behaves here as a spatial scale, at which total and self-correlations may be observed. This results in the following coefficients, $\gamma_{1,1} = 0$, $\gamma_{1,0} = (2\pi\sigma^2)^{-3/2}$ and $\gamma_{1,2} = -\gamma_{1,0}/\sigma^2$, where as a consequence of the excluded volume, $\gamma_{1,0} \equiv -\Delta G_0$ and $\gamma_{1,2} \equiv \Delta G_0/\sigma^2$.

Accordingly, a first integration transforms the previous equation into:

$$\Delta G = \int_0^R \{-\alpha_N G_{S,N}(r) + \Gamma_{0\alpha}\tilde{h}_1(r) + \Gamma_{2\alpha}\tilde{h}_1''(r) + A_\alpha(r)\} dr \quad (22)$$

the former coefficients being compacted for convenience into, $\alpha_N \equiv -\alpha\widehat{h}_N = 8\pi\alpha\bar{\rho}_N \geq 0$, $\Gamma_{0\alpha} = \gamma_{1,0} - \alpha\gamma_{1,2} = -\Delta G_0(1 + \alpha/\sigma^2) \geq 0$, $\Gamma_{2\alpha} = \alpha\Delta G_0 \leq 0$, with $\Gamma_{1\alpha} = 2\alpha\gamma_{1,1} = 0$. In short, α_N and $\Gamma_{2\alpha}$ acts as two coupling constants, one for the polymer density and the other for the self-correlation change. $\Gamma_{0\alpha}$ couples instead the self-correlation and length scale (σ) changes. With increasing scale ($\sigma \rightarrow \infty$), both $\Gamma_{0\alpha}$ and $\Gamma_{2\alpha}$ tend to annul their dependence on the regularization parameter (α). Moreover, including the only long-range correlations would have the 2-fold effect of improving the mathematical problem definition and impairing the physical description. To reach a good compromise in between, the last contribution in the integrand function can be neglected, setting $A_\alpha(r) = 0$. This choice, together with eq 19 and the boundary conditions in eq 14, constrain the family of functions $A = A(s, R)$ for this problem. The Appendix shows in particular that these relations would mainly affect the interchain correlation function. In the present application, where a single chain will be examined and \tilde{h}_N is basically neglected, there is no particular restriction to point out. However, for arbitrary chain numbers, one may need additional mathematical work.

With this choice, statistical features of polymer and liquid molecules get related through:

$$G'_{S,N}(R) + \alpha_N G_{S,N}(R) = F(R) \quad (23)$$

with:

$$F(r) = G'_{s,1}(r) + \Gamma_{0\alpha}\tilde{h}_1(r) + \Gamma_{2\alpha}\tilde{h}_1''(r) \quad (24)$$

and admit the following general solution to be considered in $R \in (0, 1)$ when all constant terms are regarded as constant model coefficients:

$$G_{s,N}(R) = \exp(-\alpha_N R) \left\{ \int_0^R F(r) \exp(\alpha_N r) dr + \text{const} \right\} \quad (25)$$

One may thus recognize two separated contributions, one of which (\mathcal{G}) being Gaussian-like and the other (\mathcal{H}) identifying a perturbation that alters the ideal chain statistics:

$$G_{s,N}(R) = \mathcal{G}(R) + \mathcal{H}(R) \quad (26)$$

As to the first, a simple integration by parts leads to:

$$\begin{aligned} \mathcal{G}(R) &= \exp(-\alpha_N R) \left\{ \int_0^R G'_{s,1} \exp(\alpha_N r) dr + \text{const} \right\} \\ &= G_{s,1}(R) + S \exp(-\alpha_N R) \left\{ \Phi\left(\frac{R}{\sqrt{2}\sigma} - \Sigma\right) - c \right\} \end{aligned} \quad (27)$$

Φ being the probability error integral and $S \equiv \sqrt{\pi}\gamma_{1,0} \Sigma \exp \Sigma^2$, where $\Sigma \equiv \alpha_N \sigma / \sqrt{2}$ and $c = \Phi(\Sigma) + (\gamma_{1,0} - \text{const})/S$ is a normalization factor, which is not fully independent but constrained here to $G_{s,N}(0) = 0$. The perturbation term depends instead on the total correlation function of the liquid molecules (h_1) and its first two derivatives, obtaining:

$$\begin{aligned} \mathcal{H}(R) &= \Gamma_{2\alpha} \exp(-\alpha_N R) \int \tilde{h}_1''(r) \exp(\alpha_N r) dr + \\ &\quad \Gamma_{0\alpha} \exp(-\alpha_N R) \int \tilde{h}_1(r) \exp(\alpha_N r) dr \\ &= \Gamma_{2\alpha} [\tilde{h}_1'(R) - \alpha_N \tilde{h}_1(R)] + (\alpha_N^2 \Gamma_{2\alpha} + \\ &\quad \Gamma_{0\alpha}) \exp(-\alpha_N R) \int \tilde{h}_1(r) \exp(\alpha_N r) dr \end{aligned} \quad (28)$$

The Ornstein–Uhlenbeck Spatial Process. It may be noteworthy to remark that eq 23 is formally similar to the initial value problem arising from the Langevin equation:

$$dV(t) = -\beta V(t) dt + dW(t) \quad (29)$$

where $V(t)$ is the stochastic velocity in continuous time of a Brownian motion, β is a characteristic constant frequency, and $W(t)$ denotes a Wiener process. In fact, when $V(0) = 0$, the solution turns out to be an adapted modification of the Ito integral:

$$V(t) = \exp(-\beta t) \int_0^t \exp(\beta s) dW(s) \quad (30)$$

defining the so-called Ornstein–Uhlenbeck stochastic process.¹¹ This representation is equivalent to ours (eq 25) upon mapping $t \rightarrow R$, $\beta \rightarrow \alpha_N$, and $dW(s) \rightarrow F(s) ds$. From developing the function F , one concludes that the stochastic process ruling the real polymer distribution function results from a linear superposition (L) of the Wiener's, with three other statistical contributions coming from the liquid phase:

$$W(s) \rightarrow L(W(s), \overline{\delta(\Delta N)^2}, \delta P, h_1(s)) \quad (31)$$

A first, in the molecular unit number (N), is related to the fluctuation's equation of state, and connects the integral of the total correlation function:¹⁶

$$\bar{\rho}_1 \int \tilde{h}_1(r) dr = \frac{(\overline{\Delta N})^2}{N} - 1 \equiv \frac{\delta(\overline{\Delta N})^2}{N} \quad (32)$$

Those further originate from $\tilde{h}_1'(s)$. One is the total correlation of the liquid molecules ($h_1(s)$), the second ($sh_1'(s)$) can be understood better by writing the virial's equation of state for a dilute system as:¹⁷

$$P = \bar{\rho}_1 k_B T \left(1 - \frac{\bar{\rho}_1}{6} \int r h_1'(r) dr \right) \equiv P_{\text{ideal}} + \delta P \quad (33)$$

where $P_{\text{ideal}} = \bar{\rho}_1 k_B T$ and $h_1'(r) \simeq (-g_1(r)/k_B T)(du_1/dr)$. Here, P is pressure, k_B is the Boltzmann's constant, T is the absolute temperature, $g_1(r) (= 1 + h_1(r))$ is the pair correlation function, and $u_1(r) (\simeq -k_B T \ln g_1(r))$ is the pairwise molecular potential.

The above remarks still suggest that correlations are dealt by BWR within a generalized Gaussian statistics. When they vanish, the relative unit number fluctuation, the total correlation function, and pressure are retrieved to their ideal gas values. We are left again with the unperturbed Wiener's and Ornstein–Uhlenbeck processes, of which Einstein's theory is known to be a good approximation for a free Brownian particle.¹⁸

The Scaling Hypotheses and the Percus–Yevick Correlation Function. In a numerical investigation, one should first be able to access the specific correlation functions, involved case by case, and then rebuild numerically the configurational statistics according to the implied equations. The inversion of the covariant van Hove's function would benefit itself from using numerical techniques. In anticipating this opportunity, one may seek some scaling hypothesis, making the model less complicated and letting physics better emerge. There are two points that can be reasonably adopted, (i) a small regularization parameter ($\alpha \ll 1$) and a polymer length scale defined through $\alpha_N R \rightarrow \rho$; (ii) a functional form for the total correlation function of the liquid molecules built on the Percus–Yevick solution.

Point (i) renders the general form of the polymer self-correlation independent of the numerical values taken by the macroscopic densities in the host medium. As a consequence, the Gaussian-like contribution becomes:

$$G_0(\rho) = G_{s,1}\left(\frac{\rho}{\alpha_N}\right) + \gamma_{0,0} \exp(-\rho) \quad (34)$$

and its perturbation simplifies into:

$$\mathcal{H}(\rho) = \gamma_{1,0} \exp(-\rho) \int \tilde{h}_1(\rho) \exp(\rho) d\rho \quad (35)$$

α_N , $\gamma_{0,0}$, and $\gamma_{1,0}$ playing the role of three heuristic coefficients, and $\rho = \alpha_N R$ being the aforesaid length scale change. The exponential term in eq 34 modifies the ideal Gaussian statistics and may be used to require the polymer self-avoidance at the origin, $G_0(\rho \rightarrow 0) = 0$ ($\gamma_{0,0} = -\gamma_{1,0}$). On displacing it, the second contribution (\mathcal{H}) is expected to become more important and bring the correlations of the liquid molecules at the polymer scale.

Concerning point (ii), Percus and Yevick's (PY) is the simplest and best known integral equation for the pair correlation function (or radial distribution function) of classical fluids. They gave an exact solution for the direct interparticle correlation function, earlier introduced by Ornstein and Zernike, of a simple liquid of hard spheres with particle diameter d and packing parameter $\eta (= (\pi/6)\bar{\rho}_1 d^3)$. Their innermost expression behaves as a cubic polynomial with quadratic term absent ($r < d$) and is equal to zero elsewhere ($r \geq d$). Accordingly, the radial distribution function $g(r) = h(r) + 1$ turned out to be:¹⁹

$$rg(r) = \begin{cases} 0 & (0 \leq \frac{r}{d} < 1) \\ G_M(r) & (M \leq \frac{r}{d} < M+1) \end{cases} \quad (36)$$

where the correlation inside the M th shell can be expressed by polynomials $P_{KM} = P_{KM}(r/d)$ of order $M-1$ and the complex roots of a third-order equation ($\tau_K \in \mathbb{C}$):

$$G_M(r) = \sum_{K=0}^2 P_{KM}(r) \exp(\tau_K r) \quad (37)$$

Thus, if P_M denotes a polynomial of order $M-1$, the simplest behavior to make use of it is:

$$G_M(\rho) = P_M(\rho) \exp(-\rho) [1 + \cos(q_M \rho)] \quad (38)$$

After recalling that $\widetilde{h}_M(\rho) = 4\pi\rho^2 h_M(\rho)$, the simplest form suggested by the PY equation for the M th molecular shell is:

$$\widetilde{h}_M(\rho) \sim p_M(\rho) \exp(-\rho) [1 + \cos(q_M \rho)] \quad (39)$$

q_M being a heuristic wavenumber and $(1/4\pi)p_M(\rho) = a_M\rho^M + \dots + a_1\rho$ denoting a polynomial of order $M \geq 1$ with constant coefficient absent.

Results and Discussion

The point from which this discussion is started is the equivalence in BWR between static and dynamical viewpoints. It generalizes another equivalence, for time and monomer number, met in polymer problems. The Einstein formulas, $r^2(N) = Nl^2$ and $r^2(t) = 6Dt$, mean in fact that a particle diffusing in time and a repeat unit belonging to an ideal chain stand for statistically equivalent systems²⁰ (Figure 2a). In our case, BWR is not only setting space and time together but, because of the molecular mobility scaling, $D \rightarrow D_N \sim DN^{-\mu}$ ($\mu > 0$), the chain unit number as well^{1,4} (Figure 2b). It suffices to write the Lorentz-type transforms for the reference frames linked to the liquid and chain molecules, $d\sigma^2(\text{liquid}, D) = d\sigma'^2(\text{chain}, D_N)$, and applying the mobility scaling for some physically meaningful value of its universal exponent (μ). In this line, the universal scaling laws for the ideal chain size and the Rouse's time were derived from the rules of length contraction and time dilation implied by the Brownian Lorentz transforms.¹

Concerning statistics, when correlations are absent (ideal chains and perfect gases, for which $h_N(r) \rightarrow 0$), it turned out that the Gaussian distribution function is preserved, $G_N(r^2/2r^2) = \text{invar.}$ When $h_N(r) \neq 0$, the covariant van Hove's function extends instead the ordinary Gaussian statistics to correlated media. If so, it is possible that defining a length scale (R) where the statistical behaviors of the two systems finds a unified description. In formula, one obtains the two specular inverse problems addressed in the first paragraphs:

$$G_{D,N} \otimes G_{S,N} = G_{D,1} \otimes G_{S,1} \quad (40)$$

This equation generalizes the invariance of second-order statistical moments, relevant to universality, to any wavelength scale. As a consequence, some extra information can be unavoidably introduced, giving rise to an inverse problem. In physical terms, as soon as the spacetime scale is reduced from the hydrodynamic limit of the Einstein's equation, the presence of extra correlations may produce nonphysical contributions in

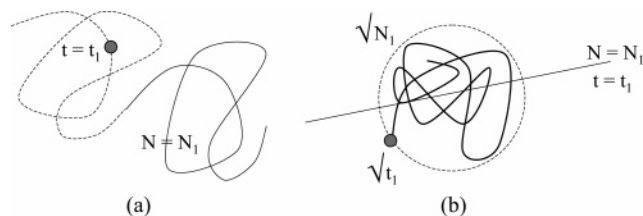


Figure 2. Scheme of (a) the equivalence for repeat unit number and time and (b) its unified extension in BWR. Any static length contraction or time dilation amounts here to an equivalent diffusivity decrease, characterizing the transition from N liquid molecules to an ideal chain of N repeat units.

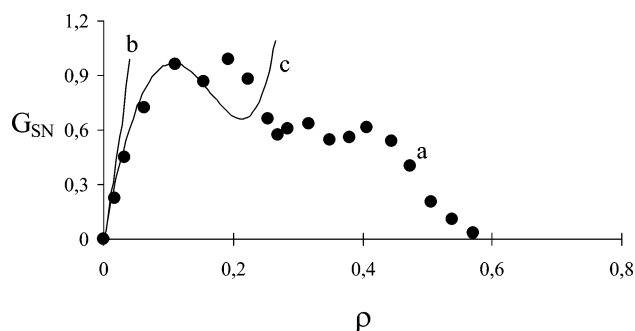


Figure 3. Numerical data (a) and theoretical models (b–c) for self-correlation functions ($G_{S,N}$) in true self-avoiding-walk polymers (TSWP). Numerical experiments are taken from a previous reference.²³ Curves (b) and (c) denote the small-scale behaviors coming respectively from the Gaussian statistics and PY hard-sphere repulsions. In both cases, the two best-fit coefficients were constrained to take the same value and turned out to be $\gamma_{1,0} = 18.90$ and $\alpha_N = 0.35$. A length scale change, set to $\rho \equiv 0.64 \text{ } r/l$, rescaled the original data set in molecular size unit (l).

the probability distribution functions. They will result in statistical instabilities for the inverse problem, to be discriminated and get rid off properly.

A close situation occurs in the so-called scattering inverse problem, where the scattered radiation is used to characterize the scatterers (and the radiation before scattering). Because different types of scattering centers can produce identical scattered radiation patterns, one can have again a not unique solution.²¹ In some techniques, often employed to determine soft matter microstructures (i.e., X-rays), the scattered intensity only reflects the scatterer's pair correlation function. As different microstructures are well described by equal pair correlation functions,²² involving additional physical information becomes mandatory to select among the multiplicity of mathematically possible (but physically unlikely) structure models. Such considerations are useful to understand the analogy of our problem to a scattering experiment, where the simple liquid provides itself the radiation source in the form of "correlation waves", which are scattered by the chain.

The derived equations will be employed here to model a concrete case of a certain difficulty. Solid points in Figure 3a are taken in fact from the self-correlation function of a "true self-avoiding walk polymer" (TSWP) against the end-to-end distance in molecular size unit (r/l) in a computer-grown ensemble of 18,500 monomers. All details may be found in a thorough analysis presented elsewhere,²³ developed on the basis of models currently employed to describe polymer statistics. Gaussian, exponential, and power law models provide in fact best fits that are often satisfactory, from which basic quantities as the radius of gyration and the Hausdorff dimension are

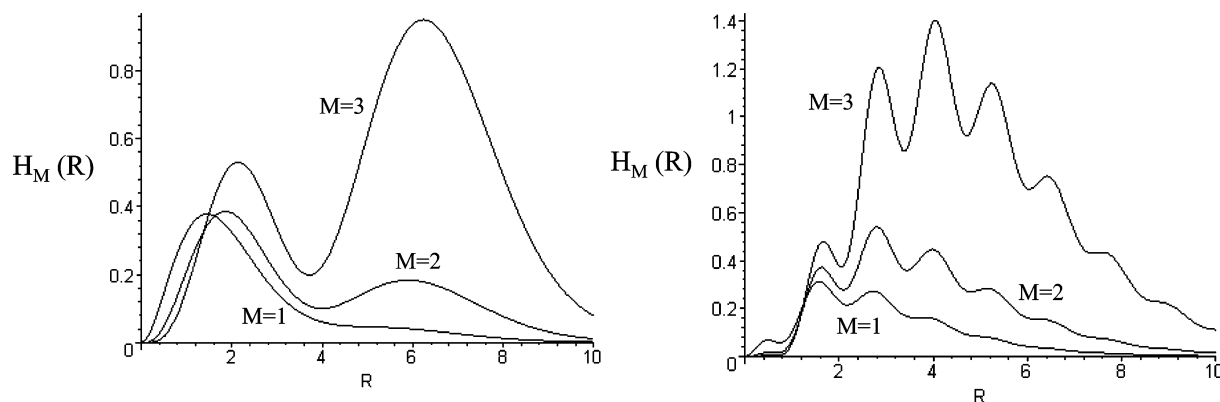


Figure 4. Chain perturbation terms, $\mathcal{H}_M = \mathcal{H}_{1,2,3}(\rho)$ when (a) $q_M = 1$ and (b) $q_M = 5$. Adjustable weighting factors took in all cases the following values, $\gamma_{1,0} = a_M \equiv 1$ and $a_{K < M} \equiv 0$.

extrapolated correctly. In case of a TSWP, nevertheless, none of them is a good candidate to either reproduce the so-called Guinier region (the small wavenumber regime) or the mild oscillations in the structure factor. As suggested by the relative minima in the spatial representation of Figure 3a, they arise from a certain number of chain loops in which the segment's random walk reverses its direction.²³ Their irregularity indicates that monomers in the neighborhood of a given loop will be equally distant from some other belonging to another loop.

It is worth remembering that a TSWP should not be confused with the more popular self-repelling polymer (SRP). While the former describes random trajectories, constrained to avoid sites which were already visited, SRP is representative of the excluded volume problem. Here, the probability of meeting a given monomer comes from the Boltzmann weight which is set from the beginning to account for the total amount of self-intersecting configurations (see, e.g., the popular Flory model).²⁴ A TSWP turns out to be less expanded than a SRP, and their universal exponents are sensibly different. These chain models refer moreover to a couple of distinct situations, both typical of polydispersed solutions. A TSWP behaves as a chain endowed with weight-average molecular weight, whose excluded volume is screened by the surrounding molecules. SRP identifies instead a long Flory-type chain, self-interacting within the overall good solvent that is formed by all the surrounding n -mer units.^{25,26}

In this study, the configurational TSWP statistics are tackled by the correlations of liquid molecules. To do so, one needs to work out the perturbation term (\mathcal{H}_M) for the M th shell of a PY fluid consisting of hard spheres with fixed diameter (d), $h(r) = h_M(r)$ ($Md \leq r < (M+1)d$). Inserting eq 39 into eq 35 yields:

$$\exp(\rho)\mathcal{H}_M(\rho) = P_{M+1}(\rho) + \left(\frac{\sin M\rho}{M}\right) \sum_{k=0}^{[M/2]} \frac{(-1)^k}{M^{2k}} p_M^{(2k)}(\rho) + \left(\frac{\cos M\rho}{M}\right) \sum_{k=1}^{[(M/2)+(1/2)]} \frac{(-1)^{k-1}}{M^{2k-1}} p_M^{(2k-1)}(\rho) \quad (41)$$

where $[k]$ and (k) denote respectively the integer part of k , and the k th ρ -derivative, while $P_{M+1}(\rho) = \int p_M(\rho') d\rho'$. Once evaluated at some appropriate order, the equation (from eqs 26, 34, 35):

$$G_{S,N}(\rho) = \mathcal{G}_0(\rho) + \mathcal{H}_M(\rho) \quad (42)$$

can be applied to interpret the TSWP correlation function in a

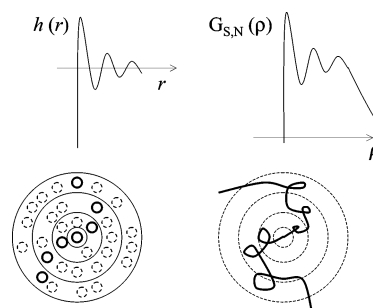


Figure 5. Schemes of rebuilding polymer configurations in solution by fluctuations of liquid molecules.

wide scale range. In fact, the perturbation term corresponding to the M th liquid shell is simply established from eq 41 to:

$$\mathcal{H}_M = \left[I_M(\rho) + \frac{\rho^{M+1}}{M+1} \right] \exp(-\rho) \quad (43)$$

where, for the first three shells ($M = 1, 2, 3$, from top), I_M reads:

$$I_M(\rho) = \int_0^\rho \rho'^M \cos(q_M \rho') d\rho' = \begin{cases} \frac{\cos(q_M \rho)}{q_M^2} + \frac{\rho \sin(q_M \rho)}{q_M} - q_M^{-2} \\ \frac{2\rho \cos(q_M \rho)}{q_M^2} + \frac{\rho^2 \sin(q_M \rho)}{q_M} - \frac{2 \sin(q_M \rho)}{q_M^3} \\ \frac{\rho^3 \sin(q_M \rho)}{q_M} + \frac{3\rho^2 \cos(q_M \rho)}{q_M^2} - \frac{6 \cos(q_M \rho)}{q_M^4} - \frac{6\rho \sin(q_M \rho)}{q_M^3} + 6q_M^{-4} \end{cases} \quad (44)$$

Their characteristic trends have been illustrated in Figure 4 for some values of the heuristic polynomial and wavenumber coefficients.

The innermost behavior clearly implies a zero pair correlation function,¹⁶ $h_0(r) = -1$ ($r < d$), and the corresponding perturbation reads (eq 35):

$$\mathcal{H}_0(\rho) = 8\pi\gamma_{1,0} \left(\exp(-\rho) - 1 + \rho - \frac{\rho^2}{2} \right) \quad (45)$$

To understand the physical significance of the former relation, one may look at the scheme of Figure 5, illustrating how polymer statistics is rebuilt by BWR. Owing to the covariant Vineyard's law, the polymer self-repulsion is described by a statistical convolution, combining large and small wavelength

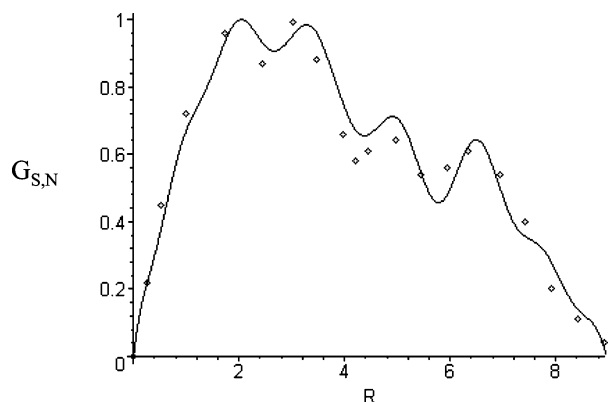


Figure 6. Modeling the data in Figure 5a by means of $G_{S,N} = G_{S,N}(R)$ (eq 42). Experimental coefficients were extrapolated to $\gamma_{1,0} = 1.36$, $\alpha_N = 4.15$, $M = 10$, $a_{2K+1} = \{a_1 = -1.65, a_{K>1} \equiv 0\}$, and $a_{2\leq 2K\leq 10} = \{1.32, -4.9 \times 10^{-3}, -5.69 \times 10^{-3}, 4.06 \times 10^{-4}, -5.1 \times 10^{-6}\}$. The correlation peak number was set to $q_M \equiv 4$, while $R \equiv 10$ r/l .

contributions in the liquid at the larger scale of the polymer chain. Thus, while the innermost correlation profile expresses the small-scale repulsion of liquid molecules, the last eq 44 translates the impossibility for a self-intersecting path to arbitrarily return near its initial point and can be adopted to model the real chain behavior at small length scales ($R \gtrsim 0$). The final result is a smoother repulsion term, depending on the hindrance caused by the chain volume, $\mathcal{H}_0(\rho) = -1/3(2/\pi^3)^{1/2} - (\rho/\sigma)^3 + \mathcal{O}(\rho^4)$. Of course, a similar mechanism is expected to take place for the irregular oscillations shown in Figure 3a. They would reflect the characteristic wiggles often exhibited by radial distribution functions in liquid systems. The higher monomer concentrations in TSWP loops would thus correspond to the statistical behavior of molecular shells (or correlation peaks) in liquids (Figure 4).

Stepping back to Figure 3a, to show the accuracy of eq 42 at different length scales, each main statistical behavior was investigated. While the Gaussian-type regime (eq 34 and Figure 3b) rebuilds fairly well, the real chain behavior near the origin ($\rho \gtrsim 2.5 \times 10^{-2}$), the hard-sphere model (eq 42 and Figure 3c) does suffice to describe the first oscillation ($\rho \gtrsim 1.6 \times 10^{-1}$). The initial measurements were rescaled by $\rho \equiv 0.64$ r/l , and one has two independent coefficients, constrained in both instances (b–c) to take the same value (see the caption to Figure 3). Performing a best fit in the whole wavelength range requires instead applying the previous eq 42 in all generality. Figure 6 illustrates an example rescaling the first 10 molecular shells ($M = 10$), and worked out by an even polynomial with linear term retained. All phenomenological coefficients are still reported in the caption, and the agreement between theory and experiment turned out to be rather satisfactory.

We would like to underline that BWR is not clearly the only method to get the configurational TSWP statistics. Once suitably implemented with polymer statistical mechanics, any consistent numerical analysis (i.e., Brownian or molecular dynamics) can certainly be a good candidate to this purpose. However, as this study witnesses itself, the analytical scope of BWR may increase effectiveness with increasing system complexity. As soon as the polymer segments behave more and more realistically and correlations get long-ranged or complex enough, the advantage to handle the configurational statistics by explicit, closed-form expressions may be undoubtedly significant.

Conclusions

1. A covariant Vineyard-like approximation, for the van Hove's function of liquid and chain molecules forming a dilute

polymer solution, has been applied to study the configurational statistics of a single real macromolecule. It defines an extended Gaussian statistics, both involving molecular and macromolecular spacetime scales, and an inverse problem for all total and self-correlation functions implied.

2. From the equivalence between unit number and time raised by Brownian relativity (BWR), static chain configurations can be described by the only statistical features of the liquid phase.

3. Inverting the Vineyard's approximation from the real chain frame carries to a class of solutions linking polymer self-correlation, liquid self-correlation, and total correlation. In particular, the probability distribution function of a true self-avoiding walk polymer (TSWP) is interpreted here as a universal Percus–Yevick behavior.

4. In this description, small-scale repulsions among liquid molecules corresponded to monomer self-repulsions, while oscillations in TSWP correlation functions corresponded to liquid density fluctuations.

5. This statistical problem is analogous to a scattering experiment, where the macromolecule scatters the (correlation and fluctuation) source given by the host liquid. The polymer distribution function turns out to be obeying a sort of static Ornstein–Uhlenbeck's process, generalized to the inclusion of liquid correlations.

Acknowledgment. K. R. Sreenivasan (ICTP Abdus Salam, Director) is kindly acknowledged for previous financial and scientific support.

Appendix

The unknown class of functions $A = A(s, R)$ fulfills four constraints, (i) a boundary condition for the self-correlation change at the origin:

$$\int_0^R A(s, R) ds = -\Delta G_0 \quad (46)$$

the limiting behaviors (eq 14) for the inverse problem, i.e., (ii):

$$\lim_{s \rightarrow 1} [G_{S,1}(R-s)\tilde{h}_1(s) - G_{S,N}(s)\tilde{h}_N(R-s) + A(s, R)] = 0 \quad (47)$$

with (iii):

$$\lim_{s \rightarrow 0} [G_{S,1}(R-s)\tilde{h}_1'(s) + G_{S,N}(s)\tilde{h}_N'(R-s) - G'_{S,1}(R-s)\tilde{h}_1(s) - G'_{S,N}(s)\tilde{h}_N(R-s) + A'(s, R)] = 0 \quad (48)$$

and the differential equation descending from $A_\alpha(R) = 0$, precisely:

$$\lim_{s \rightarrow R} [\alpha A''(s, R) - A(s, R)] = 0 \quad (49)$$

where each function is still regarded being continuous. Condition (i) gives a general constraint on the function area in $(0, R)$, while those in (ii) and (iii) result clearly in a pair of functional behaviors at planes $s = 0$ and $s = 1$. After remembering the conditions on \tilde{h}_K in $s = 0$ ($K = 1, N$) and $\gamma_{N,0} = 0$, they become in fact:

$$A'(0, R) = -G'_{S,N}(0)\tilde{h}_N(R) \quad (50)$$

and:

$$A(1, R) = G_{S,N}(1)\tilde{h}_N(R-1) + G_{S,1}(R-1)\tilde{h}_1(1) \quad (51)$$

With regard to eq 49, it holds at the bisecting line ($s = R$),

yielding:

$$A(s, R) = \varphi(R) \exp\left(-\frac{s}{\sqrt{\alpha}}\right) \quad (s \rightarrow R) \quad (52)$$

where $\varphi(R)$ is an arbitrary function.

Conditions (i–iv) cannot of course determine $A(s, R)$ completely, and translating them in physical consequences may be impossible. The most important point to be made concerns instead their relationship with the total interchain correlation function. In fact, when h_N is not involved in the final equation, eqs 46 and 50–52 do not constrain the inverse problem further. Nevertheless, whenever arbitrary chain numbers would be introduced, these boundary conditions could imply some additional work and be properly accounted for in the polymer distribution function.

References and Notes

- (1) Mezzasalma, S. A. *J. Phys. Chem. B* **2000**, *104*, 4273.
- (2) Dixon, W. G. *Special Relativity*; Cambridge University Press: Cambridge, 1978.
- (3) Weinberg, S. *Gravitation and Cosmology*; John Wiley Sons: New York, 1972.
- (4) Mezzasalma, S. A. *Chem. Phys. Lett.* **2005**, *403*, 334.
- (5) Mezzasalma, S. A. *Ann. Phys.* **2005**, *318*, 408.
- (6) Mezzasalma, S. A. *J. Colloid Interface Sci.* **2002**, *252*, 456.
- (7) Mezzasalma, S. A.; Angioletti, C.; Cesáro, A. *Macromol. Theory Simul.* **2004**, *13*, 44.
- (8) Vineyard, G. H. *Phys. Rev.* **1958**, *110*, 999.
- (9) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed.; Academic Press: London, 1990.
- (10) Mezzasalma, S. A. *Philos. Mag. Lett.* **2005**, *85*, 631.
- (11) Brzezniak, Z.; Zastawniak, T. *Basic Stochastic Processes*; Springer: Berlin, 1999.
- (12) Tikhonov, A. N.; Arsenin, V. Y. *Solutions of Ill-Posed Problems*; Winston and Sons: Washington, D.C., 1977.
- (13) Kirsch, A. *An Introduction to the Mathematical Theory of Inverse Problems*; Springer: New York, 1996.
- (14) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, 1979.
- (15) Boon, J. P.; Yip, S. *Molecular Hydrodynamics*; Dover Publications: New York, 1991.
- (16) Egelstaff, P. A. *An Introduction to the Liquid State*, 2nd ed.; Oxford University Press: Oxford, 1994.
- (17) Goodstein, D. L. *States of Matter*, 2nd ed.; Dover Publications: New York, 1985.
- (18) Nelson, E. *Dynamical Theories of Brownian Motion*, 2nd ed.; Princeton University Press: Princeton, 2001.
- (19) Wertheim, M. S. *Phys. Rev. Lett.* **1963**, *10*, 321.
- (20) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
- (21) Infeld, E.; Rowlands, G. Inverse Scattering Methods. In *Nonlinear Waves, Solitons and Chaos*, 2nd ed.; Cambridge University Press: Cambridge, 2000.
- (22) Welberry, T. R. *Rep. Prog. Phys.* **1985**, *48*, 1543.
- (23) Pearson, A.; Anderson, R. W. *Phys. Rev.* **1993**, *48*, 5865.
- (24) Schafer, L. *Excluded Volume Effects in Polymer Solutions*; Springer-Verlag: Berlin, 1999.
- (25) Amit, D. J.; Parisi, G.; Peliti, L. *Phys. Rev. B* **1983**, *27*, 1635.
- (26) Family, F.; Daoud, M. *Phys. Rev. B* **1984**, *29*, 1506.