that we get from our osmotic pressure data, which in fact describes the detailed nature of the "excluded volume".

Contrary to the view that direct electrostatic double-layer interactions make an important contribution in the assembly of DNA helices, the factor-of-2 difference in the decay constants (Figure 3) suggests that they are in fact negligible. They do show up in an important way only indirectly through the entropic work needed to suppress the positional disorder of the chains on their close approach. In fact, given the importance of fluctuations in systems as diverse as bilayers and condensed DNA double helices, one is led to suggest that electrostatic double-layer forces are unlikely ever to appear between flexible molecules without the qualitative enhancement imposed by molecular disorder. Conversely one is now aware of a systematic relation between the disorder and the forces which act to suppress it.

In this connection it is worth noting that the exponential decay of the forces observed here does not have the power law form expected for the steric repulsion between hard flexible rods.[25,32] There seems to be no experimental justification in our data for the assumption, virtually universal in theories of liquid-crystal packing, that charged particles in salt solution can be portrayed as hard particles with an effective radius adjusted according to ionic strength.

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Surface-Interacting Polymers: An Integral Equation and Fractional Calculus Approach

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ABSTRACT: A method due to Feynman and Kac is used to convert the path integral formulation of surface (variable surface dimension) interacting polymers into an equivalent integral equation approach. The integral equation for the surface-interacting chain partition function is determined to be the Volterra analogue of the Fredholm integral equation describing the friction coefficient in the preaveraged Kirkwood–Riseman theory. This approach to surface interacting polymers thus clarifies the close interconnection between the surface interaction and Kirkwood–Riseman theories noted in previous renormalization group calculations. An exact solution of the surface-interacting chain partition function is obtained by using the Riemann–Liouville fractional calculus. Finally, the integral equation and fractional calculus methods are combined to explain some of the most conspicuous features of the renormalization group theory—the mathematical significance of the "crossover exponent", "infrared fixed point", nontrivial "critical exponents", and the pole structure found in the interaction perturbation theory. The integral equation–fractional calculus formalism is also used to examine a point of "critical instability" defining the adsorption threshold and to examine the failure of the renormalization group and eigenfunction expansion methods to describe scaling functions for values of the interaction near the instability point. The critical instability is readily understood on the basis of the Fredholm alternative.

1. Introduction

Recent renormalization group (RG) treatments of surface-interacting[1,2] and hydrodynamically interacting polymers[3,4] indicate a remarkably similar common analytic structure. In many cases the results from one theory can be applied to the other by simply changing the interaction labels.[2] This correspondence holds even when excluded volume is additionally incorporated into the surface and hydrodynamic interaction theories.[2]

The origin of this unity in the underlying mathematical structure of these models of interacting polymers is not immediately evident but is well worth investigating. It is especially useful that the surface-interacting chain theory can be solved exactly so that the accuracy and limitations of the RG ϵ-perturbation results can be unambiguously evaluated.[1,2] The Kirkwood–Riseman integral equation[3,4] for the polymer friction coefficient (preaveraging) can also be solved exactly and compared with the corresponding results from the ϵ-expansion method—but these results will be presented elsewhere.[5] Moreover, the close interconnection between the surface interaction model and the polymer excluded volume models has been discussed previously by Douglas et al.,[1,2] and similar parallels can be drawn between polymer excluded volume and polymer hydrodynamics[5] (see Appendix A). We also discuss (Appendix B) a general result by Darling and Kac[6] which indicates that the unity in the analytic structure of various models of interacting polymers extends significantly beyond the particular models already mentioned. Here we primarily focus on the especially tractable example of surface (variable-dimension surface[1,2]) interacting polymers from a new perspective in order to probe the analytic basis of the common analytic structure found in this broad class of problems. Finally, it should be mentioned that numerous fundamental problems in quantum mechanics,[7] statistical mechanics,[8] probability theory,[6,9] and field theory[10] can be formulated in terms of interacting random walks (i.e., polymers) so that there is significant motivation for understanding the universal "deep structure" of this class of interacting polymer problems.

In section 2 a flexible polymer interacting with a variable-dimension surface is treated by converting the path integral representation of the problem into an equivalent integral equation formulation by using a method due to Feynman and Kac.[7] It is shown that the configurational properties of surface-interacting polymers can be written in terms of Volterra integral equations, which are similar in structure to the Fredholm integral equations commonly encountered in the Kirkwood–Riseman theory of polymer hydrodynamics.[3,4] For example, the integral equation describing the partition function of a surface-interacting chain is the Volterra analogue of the Kirkwood–Riseman integral equation (preaveraging) for the friction coefficient.[3,4] A fractional calculus method is employed to solve the integral equation for surface-interacting chains in section 3, and results obtained by using the path integral formulation of the problem are recovered. Previous calculations by Douglas et al.[4] indicate that the RG ϵ-expansion method and the "ground state dominant" eigenfunction expansion method fail to describe scaling functions in the vicinity of the adsorption threshold, and the reason for this failure has a clear explanation in the integral equation formulation. This approach also makes the mathematical origin of the RG fixed point, the nontrivial critical exponents, and the pole structure observed in perturbation expansions of interacting polymers apparent.

In section 4 we inquire into the mathematical mechanism responsible for the failure of the RG method and other perturbative methods to describe polymer properties beyond certain critical values of the interaction related to the RG fixed points. These critical interaction values define the "adsorption threshold" and "collapse threshold" in the surface-interacting and self-interacting polymer models. It is found that the nonhomogeneous integral equations describing surface-interacting and hydrodynamically interacting polymers have corresponding homogeneous equations which have an important bearing on understanding the mathematical meaning of the "critical instability" and its relation to the RG fixed point. Interestingly, the RG fixed points in the exactly solvable models of surface and hydrodynamically interacting polymers are related to the *smallest magnitude eigenvalues* of the homogeneous integral equation in a limit described below, and the "instability condition" follows from the Fredholm alternative, which requires that the homogeneous and nonhomogeneous integral equations cannot both simultaneously have nontrivial (i.e., non-zero) solutions for a given value of the dimensionless interaction.

2. Integral Equation Formulation of Surface-Interacting Polymers

A long flexible polymer which interacts with a surface through a short-range potential is modeled by a continuous Gaussian chain and an idealized δ function pseudopotential interaction.[1,2,11,12] In order to simplify the algebra below, we fix one of the chain ends to the coordinate origin located on the surface. The chain configuration is specified by a position vector $\mathbf{R}(x)$ at a dimensionless contour distance x along a chain of unit length N and is composed on n Kuhn units of length l. The mean dimensions of the chain are characterized in the absence of surface interactions by the end-to-end distance $\langle \mathbf{R}^2\rangle_{0,\mathrm{f}} \equiv nl^2$ of a "free" chain. It should be apparent that such a model applies only to long flexible chains with a repulsive or weakly attractive surface interaction. Limitations of the model (especially in the limit of strong attractive surface interactions) are described by Douglas et al.[1,2]

In dimensionless energy units of $K_\mathrm{B}T$, the Hamiltonian of the free noninteracting chain is

$$H_0 = (1/2)\int_0^1 \mathrm{d}x\ |\mathrm{d}\mathbf{r}(x)/\mathrm{d}x|^2; \qquad \mathbf{r}(x) = (d/\langle \mathbf{R}^2\rangle_{0,\mathrm{f}})^{1/2}\mathbf{R}(x) \tag{2.1}$$

where $\mathbf{r}(x)$ is a dimensionless position vector. For generality, the dimensionality of the surface can be taken as *continuously variable.* Thus, we speak of a surface of dimension $d_\parallel$ embedded in a space of dimension d. A vector $\mathbf{r}_\parallel(x)$ in reduced units corresponding to (2.1) is defined as the projection of $\mathbf{r}(x)$ onto this surface, and $\mathbf{r}_\perp(x)$ is the projection onto the orthogonal space of dimension $d_\perp$. In this notation the surface interaction contribution H_s to the Hamiltonian H is defined as[1,2]

$$H/K_\mathrm{B}T = H_0 + H_\mathrm{s} \tag{2.2a}$$

$$H_\mathrm{s} = z_\mathrm{s}^{\,0}\int_0^1 \mathrm{d}x\ (2\pi)^{d_\perp/2}\delta[\mathbf{r}_\perp(x)] \tag{2.2b}$$

$$z_\mathrm{s}^{\,0} = (d/2\pi l^2)^{d_\perp/2}\beta_\mathrm{s}^{\,0}n^{\phi_\mathrm{s}}; \quad \phi_\mathrm{s} = \epsilon_\perp/2; \quad \epsilon_\perp = 2 + d_\parallel - d \tag{2.2c}$$

The dimensionless surface interaction $z_\mathrm{s}^{\,0}$ is proportional to the surface cluster integral $\beta_\mathrm{s}^{\,0}$ and to the chain length to the power ϕ_s, the "crossover exponent". Further details can be found in previous papers by Douglas et al.[1,2]

At various points below we refer to polymers interacting through "excluded volume" interactions. Actually, there are many different types of excluded volume interactions, but the most important variety is the "binary" excluded volume interaction specified by the two-parameter model Hamiltonian

$$H_2 = (z_2^{\,0}/2!)\int_0^1 \mathrm{d}x_1 \int_0^1 \mathrm{d}x_2\ (2\pi)^{d/2}\delta[\mathbf{r}(x_1) - \mathbf{r}(x_2)] \tag{2.3a}$$

$$z_2^{\,0} = (d/2\pi l^2)^{d/2}\beta_2^{\,0}n^{\phi_2}; \quad \phi_2 = \epsilon/2; \quad \epsilon = 4 - d \tag{2.3b}$$

where $\beta_2^{\,0}$ is the binary cluster integral and $z_2^{\,0}$ the usual Fixman excluded volume parameter. The term binary refers to the property that two parts of the chain are involved in the interaction. Notice the close analogy between (2.2) and (2.3); indeed, we can think of the H_2 interaction as a kind of polymer surface interaction where *the polymer is its own surface*, or turning the image around the polymer can be thought of as a variety of self-interacting surface. These "analogies" are useful to keep in mind when comparing the physically similar phenomena of surface adsorption and polymer collapse.

In addition to the two-parameter-type excluded volume interactions, there are also "higher order" interactions:

$$H_m = (z_m{}^0/m!)\int_0^1 \mathrm{d}x_1 \int_0^1 \mathrm{d}x_2 \ldots \int_0^1 \mathrm{d}x_m \prod_{k=1}^{m-1} \delta[\mathbf{r}(x_{k+1}) - \mathbf{r}(x_k)](2\pi)^{(m-1)(d/2)} \quad (2.4\mathrm{a})$$

$$z_m{}^0 = (d/2\pi l^2)^{d(m-1)/2}\beta_m{}^0 n^{\phi_m}; \quad m \geq 3 \quad (2.4\mathrm{b})$$

$$\phi_m = m - (m-1)(d/2) \equiv (m-1)\epsilon_m/2; \quad \epsilon_m = 2m/(m-1) - d \quad (2.4\mathrm{c})$$

The relevance of the H_s and H_m interactions, of course, depends on the probability of the chain looping back to the surface or itself, respectively, and this property is reflected in the magnitude of the crossover exponents ϕ_s and ϕ_m. Everywhere in the discussion below it is assumed that the crossover exponents ϕ_s and ϕ_m (others in Appendix B) lie in the open interval (0,1) unless otherwise stated. All the models of the interacting polymers exhibit log corrections when the crossover exponents (ϕ_s, ϕ_m, ...) equal zero, and discussion of this special limit is avoided here.

The end vector distribution function is calculated as a weighted average over the Gaussian chain paths (see ref 1 and 2) and is formally written as

$$G(\mathbf{r},z_s{}^0) = \int_{\mathbf{r}'(0)=0}^{\mathbf{r}'(1)=\mathbf{r}} \mathcal{D}[\mathbf{r}'(x)] \exp(-H/K_BT) \quad (2.5)$$

Douglas et al.[1] show that configurational properties of surface-interacting Gaussian polymers can be exactly obtained by perturbatively expanding about the Gaussian chain state. This approach is also discussed by Kosmas[11] using perturbative RG methods with ϵ-expansion, and even earlier calculations along the same line are given by Goovaerts et al.[7] for a closely related quantum mechanical analogue of the surface-interacting polymer model (see Appendix B). The path integral approach is avoided here since the interest is in studying our model from an integral equation perspective.

An alternative to the path integral formulation of surface-interacting polymers involves converting (2.5) into an equivalent differential equation. In particular, the end vector distribution function (not in dimensionless units) for an interacting chain has the path integral representation[13-16]

$$G(\mathbf{R},V) = \int_{\mathbf{R}(0)=\mathbf{0}}^{\mathbf{R}(N)=\mathbf{R}} \mathcal{D}[\mathbf{R}(\tau)] \exp\Big[-(d/2l) \times \int_0^N \mathrm{d}\tau\, |\mathrm{d}\mathbf{R}(\tau)/\mathrm{d}\tau|^2 - \int_0^N \mathrm{d}\tau\, V[\mathbf{R}(\tau)]\Big] \quad (2.6)$$

which can be equivalently written as a diffusion equation[13-16]

$$\left[\frac{\partial}{\partial N} - \frac{l^2}{2d}\nabla^2 + V(\mathbf{R})\right] G(\mathbf{R},V) = \delta(\mathbf{R})\,\delta(N) \quad (2.7)$$

where $V(\mathbf{R})$ is an interaction potential. Closely related equations are frequently encountered in the theory of heat conduction[17] and quantum mechanics, and an exact solution for $G(\mathbf{R},V)$ can often be obtained by using classical mathematical methods (see ref 12 and 16 for a discussion).

Yet another angle for approaching interacting polymers involves converting the diffusion equation (2.7) into an integral equation following the method of Feynman and Kac.[7] This approach is developed here to demonstrate the relation between the Kirkwood–Riseman integral equation and the surface-interacting polymer model described above. It is also especially fruitful for studying *nonperturbative* aspects of the interacting polymer models, which are difficult to extract from the path integral formulation.

If we consider $V(\mathbf{R})\ G(\mathbf{R},V)$ to be a "nonhomogeneous term" in (2.7), then we can use the noninteracting chain (free) Green's function $G^0(\mathbf{R})$ determined by

$$\left[\frac{\partial}{\partial N} - \frac{l^2\nabla^2}{2d}\right] G^0(\mathbf{R}) = \delta(\mathbf{R})\,\delta(N); \quad G(\mathbf{R};V{=}0) \equiv G^0(\mathbf{R}) \quad (2.8)$$

to obtain the full interacting chain Green's function. Multiplying each side of (2.8) by the inverse of the differential operator on the left in (2.8) yields[14,15]

$$G(\mathbf{R},V) = G^0(\mathbf{R}) - \int_0^N \mathrm{d}\tau \int \mathrm{d}^d\mathbf{R}'\ G^0(\mathbf{R}-\mathbf{R}';N-\tau)[V(\mathbf{R}')\ G(\mathbf{R}',\tau';V)] \quad (2.9)$$

which is the Feynman–Kac integral equation.[7] Edwards and Leonard[15] concisely describe the details of the transformation from (2.7) to (2.9).

Already there is a formal resemblance of the integral equation for $G(\mathbf{R},V)$ in (2.9) to integral equations arising in the Kirkwood–Riseman hydrodynamic theory.[18] This resemblance is especially clear when $V(\mathbf{R})$ is a "singular" or "contact potential". For example, in the surface interaction model, where $V(\mathbf{R})$ is a δ function, $\beta_s{}^0\delta(\mathbf{R})$, (2.9) reduces to

$$G(\mathbf{R};V) = G^0(\mathbf{R}) - \beta_s{}^0 \int_0^N \mathrm{d}\tau\ G^0(\mathbf{R},N-\tau)\ G(\mathbf{0},\tau') \quad (2.10)$$

because the δ function "kills off" the position integral in $\mathbf{R}$.

Treatment of the variable-dimension surface requires a minor variation on the theme outlined above. First, define the free chain (noninteracting) end vector distribution function $G(\mathbf{R};V)$ by the product (see ref 1 and 2)

$$G^0(\mathbf{R}) = G_\perp{}^0(\mathbf{R}_\perp)\ G_\parallel{}^0(\mathbf{R}_\parallel) \quad (2.11\mathrm{a})$$

where G^0, $G_\perp{}^0$ and $G_\parallel{}^0$ are equal the usual Gaussian end vector distribution functions in the coordinates, $\mathbf{R}$, $\mathbf{R}_\perp$, and $\mathbf{R}_\parallel$, respectively. Now if the δ function acts on the $\mathbf{R}_\perp$ vector alone, we obtain (see ref 1 and 2)

$$G(\mathbf{R};\delta) = G_\parallel{}^0(\mathbf{R}_\parallel)\ G_\perp(\mathbf{R}_\perp;\delta) \quad (2.11\mathrm{b})$$

where δ denotes the δ potential. The $G_\perp$ contribution to G satisfies the integral equation

$$G_\perp(\mathbf{R}_\perp;\delta) = G_\perp{}^0(\mathbf{R}_\perp) - \beta_s{}^0 \int_0^N \mathrm{d}\tau\ G_\perp{}^0(\mathbf{R}_\perp,N-\tau;\delta)\ G_\perp(\mathbf{0},\tau;\delta) \quad (2.12)$$

which reduces to (2.10) for $\mathbf{R}_\perp = \mathbf{R}$ and $d_\parallel = 0$. It is emphasized that the calculations here refer to penetrable surfaces only.[1,2]

The chain partition function is obtained as

$$Q = \int \mathrm{d}^d\mathbf{R}\ G(\mathbf{R};\delta)$$

and after integrating (2.11) over $\mathbf{R}$, introducing dimensionless variables, and performing some algebra, we obtain a position-independent integral equation for the chain partition function as

$$Q(z_s{}^0) \equiv \psi(x = 1) \quad (2.13\mathrm{a})$$

$$\psi(x) = 1 - \Delta_s \int_0^x [(x-t)^{\epsilon_\perp/2-1}/\Gamma(\epsilon_\perp/2)]\psi(t)\ \mathrm{d}t \quad (2.13\mathrm{b})$$

$$\Delta_s \equiv (z_s^0/u_s^*)\Gamma(1 + \epsilon_\perp/2); \quad u_s^* = \epsilon_\perp/2; \quad \epsilon_\perp \in (0,2) \tag{2.13c}$$

It is easily verified (see below) that a Neumann iterative solution[19,20] of (2.13b) recovers the exact expression for $Q(z_s^0)$ obtained previously by Douglas et al.[1,2] through an explicit Feynman expansion of the path integral for the chain partition function. The infinite-order perturbative result equals

$$Q(z_s^0) = \sum_{k=0}^{\infty} (-\Delta_s)^k/[\Gamma(1 + k\epsilon_\perp/2)] \tag{2.14}$$

where Γ denotes the Γ function. As noted by Douglas et al. (2.14) defines the Mittag–Leffler function $E_{\epsilon_\perp/2}$ of index $\epsilon_\perp/2$.

Darling and Kac[6] have shown that a very large class of interaction potentials gives rise to a partition function that has the Mittag–Leffler function as a *universal limit* for long chains. Since Darling and Kac derived their results in a probability theory context, we summarize some of their main results in Appendix B in terms of more conventional polymer theory notation. It is also indicated in Appendix B that a series closely related to the Mittag–Leffler function arises in the description of the one-particle quantum mechanical density matrix for the general class of homogeneous one-body potentials. These results, which again reveal the underlying structure of the Mittag–Leffler function and its close relatives, can be directly "transcribed" to analogue polymer problems. Next we mention a connection between (2.13b) and its solution, (2.14), to polymer hydrodynamics as advertised above.

The integral equation for the surface-interacting chain partition function given in (2.13) is to be contrasted with the integral equation describing the polymer hydrodynamic radius in the Kirkwood–Riseman (KR) theory in the preaveraging approximation.[12,18,21,22] The preaveraged KR expression for the friction coefficient f_{KR} (proportional to the hydrodynamic radius) is defined through a Fredholm[19] integral equation

$$f_{\mathrm{KR}} = n\hat{\zeta}\int_0^1 \mathrm{d}x\ \Phi(x) \tag{2.15a}$$

$$\Phi(x) = 1 - \Delta_{\mathrm{H}}\int_0^1 [|x - t|^{(\epsilon/2)-1}/(\Gamma(\epsilon/2))]\Phi(t)\ \mathrm{d}t \tag{2.15b}$$

$$\Delta_{\mathrm{H}} = h2^{\epsilon/2}\Gamma(\epsilon/2); \quad \epsilon = 4 - d; \quad \epsilon \in (0,2) \tag{2.15c}$$

where $\hat{\zeta}$ is the bead friction coefficient. The h parameter is the usual dimensionless hydrodynamic interaction parameter[21,23]

$$h = (\hat{\zeta}/2d\pi\eta_s)[(d - 1)/2^{\epsilon/2}(d - 2)]n^{\phi_H}, \quad \phi_{\mathrm{H}} = \epsilon/2 \tag{2.16a}$$

$$h(d{=}3) = [(\hat{\zeta}/\eta_s)/(12\pi^3)^{1/2}]n^{1/2} \tag{2.16b}$$

$$h^*(\epsilon) \equiv 2^{-\epsilon/2}(1 + \epsilon/2)(\epsilon/4); \quad h^*(d{=}3) = 0.265 \tag{2.16c}$$

with η_s the solvent viscosity. Note that (2.15b) is the Fredholm analogue[19] of the Volterra equation (2.13b) describing the surface interacting polymer if $d_\parallel$ is taken equal to $d_\parallel = 2$. Further observe that (2.15b) and (2.13b) are *singular* integral equations[19] since the kernels $(x - t)^{\phi_s - 1}/\Gamma(\epsilon_\perp/2)$ and $|x - t|^{\phi_H - 1}/\Gamma(\epsilon/2)$, respectively, diverge when $x = t$.

3. Solution of Integral Equation for a Surface-Interacting Chain Obtained by Using Fractional Calculus

To get a deeper insight into the analytic structure of $Q(z_s^0)$ and other related properties we consider the solution of (2.13b) from a different perspective which makes the mathematical significance of the concepts critical dimension, *dimensional-dependent critical exponents*, *fixed* points, etc., more transparent. In addition, the method allows for a simple and elegant solution of (2.13b) using operational calculus. First, it is necessary to develop a little background material defining the rudiments of the fractional calculus methods.

A. Fractional Calculus. The integral operator in (2.13b) defines the Reimann–Lioville fractional differential integral operator I_x^α, whose "action" on a function $f(x)$ is defined by an average of $f(x)$ as[24]

$$I_x^\alpha f(x) = \int_0^x \frac{(x - t)^{\alpha-1}}{\Gamma(\alpha)} f(t)\ \mathrm{d}t \tag{3.1}$$

The function $f(x)$ is defined to be zero for $x < 0$ and is chosen from a class of functions such that the operation is ensured to exist. There are numerous pitfalls of technical detail associated with restrictions on α and the class of admissable functions. These details are simply avoided at this point, and the reader is referred to ref 24 for points of rigor.

The operator I_x^α defines fractional order differentiation and integration (negative and positive α, respectively) as a continuous semigroup of operators and forms the basis of a simple operational calculus. The main properties of the I_x^α operator are as follows:[24]

"exponent rule"

$$I_x^\alpha I_x^\beta f = I_x^{\alpha+\beta} f \tag{3.2a}$$

commutativity

$$I_x^\alpha I_x^\beta f = I_x^\beta I_x^\alpha f \tag{3.2b}$$

identity and left-inverse operations

$$I_x^0 f = I_x^{-\alpha} I_x^\alpha f = f \tag{3.2c}$$

eigenvalue equation of Euler

$$(x^{-\alpha} I_x^\alpha)x^m = [\Gamma(m + 1)/\Gamma(m + 1 + \alpha)]x^m \tag{3.2d}$$

The reader is warned that the kernel of the I_x^α operator becomes "singular" for $\alpha \le 0$, especially for $\alpha = 0$ and the negative integers. Taking the limit $\alpha \to 0^+$, for example, involves a delicate balance of divergences, and $(x - t)^{\alpha-1}/\Gamma(\alpha)$ is a δ function sequence

$$\lim_{\alpha\to 0^+} (x - t)^{\alpha-1}/\Gamma(\alpha) \to \delta(x-t) \tag{3.3a}$$

so that (3.2c) is interpreted as the limit

$$\lim_{\alpha\to 0^+} I_x^\alpha f(x) = \int_0^x \delta(x-t)f(t)\ \mathrm{d}t = f(x) \tag{3.3b}$$

Similarly, taking α to have negative integer values gives the derivatives of $f(x)$ in terms of the usual elementary calculus notions of the local variation of f at x. The more global definition of differentiation and integration applies when α is negative and noninteger, and the variable α serves to interpolate between the integer derivatives. Further details may be found in ref 24. The fractional calculus based on I_x^α gives numerous insights into the analytic structure reflected in integral equations of the type (2.13b) as well as providing a powerful computational tool. For example, it is simple to develop "strong coupling" and "weak coupling" series solutions of (3.13b) by using only simple algebra and (3.2).

B. Solution of Integral Equation. Introducing (3.1) into (3.13b) gives a simple operational definition of our integral equation as

$$(1 + \Delta_s I_x^{\epsilon_\perp/2})\psi = 1 \quad (3.4)$$

Dividing both sides by the terms in parentheses gives the exact formal solution

$$\psi(x) = 1/(1 + \Delta_s I_x^{\epsilon_\perp/2}) \quad (3.5)$$

which upon expansion of the denominator yields the small coupling expansion

$$\psi(x) = \sum_{k=0}^{\infty} (-\Delta_s)^k I_x^{k\epsilon_\perp/2} \quad (3.6a)$$

Interpreting the operator I_x^α to act on the function unity, (3.2d), yields

$$I_x^{k\epsilon_\perp/2} = I_x^{k\epsilon_\perp/2}(1) = x^{k\epsilon_\perp/2}/\Gamma(1 + k\epsilon_\perp/2) \quad (3.6b)$$

which upon combining with (3.6a) and taking $x = 1$ at the end of the calculation gives the exact result (2.14). Alternatively, we may develop the "strong coupling expansion" for large positive z_s^0 by formally dividing the numerator and denominator of (3.5) by $\Delta_s I_x^{\epsilon_\perp/2}$ to obtain

$$\psi(x) = (\Delta_s I_x^{\epsilon_\perp/2})^{-1}/[1 + (\Delta_s I_x^{\epsilon_\perp/2})^{-1}] \quad (3.7)$$

Expanding (a "Neumann series[20] of the third kind") the denominator and interpreting the operator $I_x^{\epsilon_\perp/2}$ as above gives ($x = 1$)

$$Q(z_s^0) \sim [1/(z_s^0/u_s^*)\Gamma(1 + \epsilon_\perp/2)] \times \left[1 - \frac{\Gamma(1 - \epsilon_\perp/2) + O[(z_s^0)^2]}{(z_s^0/u_s^*)\Gamma(1 + \epsilon_\perp/2)}\right] \quad (3.8a)$$

which is the exact asymptotic expansion given by Douglas et al.[1] for the corrections to scaling about the $z_s^0 \to \infty$ limit. Just about any large-scale property of interest can be obtained by this simple operational algebra.

The $z_s^0 \to \infty$ limit implies a nontrivial critical exponent γ_s for surface-interacting chains that is defined through the scaling relation[1,2,11]

$$Q \sim n^{\gamma_s - 1}; \quad z_s^0 \to \infty \quad (3.8b)$$

Since z_s^0 scales (see (2.4)) as $n^{\epsilon_\perp/2}$, we have from (3.8a) the exact relation

$$\gamma_s - 1 = -\epsilon_\perp/2 \text{ (exact)} \quad (3.8c)$$

Note that the critical exponent γ_s in (3.8b) and the correction to scaling series in (3.8a) are generated by the action of the fractional differentiation operator in (3.7).

C. Further Fractional Calculus Manipulations. Fractional calculus also has convenient application to the manipulation of Feynman expansions obtained alternatively from the perturbation expansion of the path integral formulation of interacting polymers. For example, Douglas et al.[1] calculate the surface-interacting chain partition function $Q(z_s^0)$ as (see (3.4b)–(3.6) of ref 1)

$$Q(z_s^0) = 1 - z_s^0 \int_0^1 \mathrm{d}x\, x^{-d_\perp/2} + (z_s^0)^2 \int_0^1 \mathrm{d}x' \int_0^x \mathrm{d}x\, x^{-d_\perp/2}(x' - x)^{-d_\perp/2} + O[(z_s^0)^2] \quad (3.9)$$

Introduction of the definition of I_x^α into (3.9) yields an operator expansion

$$Q(z_s^0) = 1 - z_s^0 I_x^1 x^{-d_\perp/2} + z_s^0 I_x^1 \Gamma(1 - d_\perp/2) I_x^{1-d_\perp/2} x^{-d_\perp/2} + O[(x_s^0)^2]; \quad x = 1 \quad (3.10)$$

with $x = 1$ taken at the end of the calculation. Note that (3.2d) implies

$$I_x^1 x^{-d_\perp/2} = \Gamma(\epsilon_\perp/2) I_x^{\epsilon_\perp/2} \quad (3.11)$$

which along with the group property (3.2b) allows us to write $Q(z_s^0)$ as (3.5) to order $(z_s^0)^2$. By induction we can infer the general term (3.6a) and arrive at (3.4a) and the Volterra integral equation (2.13b) by a different route.

The perturbation expansion for polymer excluded volume can also be conveniently manipulated by using fractional differential operators. For example, the mean square end-to-end distance $\langle \mathbf{R}^2 \rangle$ perturbation expansion for a polymer with binary excluded volume interactions can be written as a perturbation expansion in terms of the Fixman parameter z_2^0 and I_x^α (see (3.5) of ref 1)

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 [(1 - z_2^0 I_x^2[(1 - x)x^{-d/2}] + \ldots)/(1 - z_2^0 I_x^2 x^{-d/2} + \ldots)]; \quad x = 1 \quad (3.12a)$$

and expanding the denominator gives

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 [1 + z_2^0 I_x^2 x^{1-(d/2)} + O[(z_2^0)^2]]; \quad x = 1 \quad (3.12b)$$

which, upon interpretation using (3.2d) and taking $x = 1$, reduces to the standard expression

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 [1 + z_2^0 (2/\epsilon)/(1 + \epsilon/2) + O[(z_2^0)^2]]; \quad \epsilon \in (2,4) \quad (3.12c)$$

It is apparent that the ϵ pole structure of the perturbation expansion reflects the action of the fractional differential operators on the $x^{-d/2}$ terms, which derive from the Gaussian chain probability of ring closure. This is also apparent in (3.10), where the $x^{-d_\perp/2}$ terms derive from the probability that a chain loops back to a surface.

D. Universal Structure of RG Scaling Functions. A comparison of the scaling functions derived from the RG theory for a wide class of properties and types of interactions indicates remarkable similarities. The labels on the interaction change and certain mathematically obscure constants, the RG "fixed points", vary, but the structure of the scaling functions is quite universal. The question is whether this regularity is derived as an artifact of the RG perturbative formalism or whether it is indicative of a fundamental universal structure in the exact scaling functions. This problem is conveniently addressed in the case of surface-interacting polymers, where exact and RG solutions are available for comparison, and the fractional calculus provides a convenient tool for exploring this type of question. In the next section we investigate the mathematical significance of the RG fixed point and its role in determining a condition of instability where the polymer adsorbs onto a surface or "collapses" into itself.

Before the precise relation between the RG scaling functions and the exact scaling functions for surface-interacting chains is illustrated, it is necessary to support the contention of a universal analytic structure derived from the RG theory. For example, the RG result to order ϵ for the end-to-end distance $\langle \mathbf{R}^2 \rangle$ for a polymer with excluded volume is equal (see (2.3)):

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 (1 + z_s^0/u_2^*)^{(2\nu-1)/\phi_2} [1 + a_R^2 u_2^* \lambda_2 + O(\epsilon^2)] \quad (3.13a)$$

$$(2\nu - 1)/\phi_2 = 1/4 + O(\epsilon); \quad \phi_2 = \epsilon/2; \quad a_R^2 = -1 + O(\epsilon) \quad (3.13b)$$

$$\lambda_2 = (z_2^0/u_2^*)/(1 + z_2^0/u_2^*); \quad u_2^* = \epsilon/8 + O(\epsilon^2); \quad \epsilon \in (0,2) \quad (3.13c)$$

Quite generally, any static radial property P scaling as a radius to the power m, $P \sim \mathbf{R}^m$, has a generic scaling form[16,27,28]

$$P = P_0 (1 + z_2^0/u_2^*)^{(m/2)(2\nu-1)/\phi_2} [1 + a_p u_2^* \lambda_2 + O(\epsilon^2)]; \quad m \neq 0 \quad (3.14)$$

where P_0 and a_p depend on branching architecture (linear, ring, star, comb) and the particular property calculated. P_0 indicates P in the Gaussian chain ($z_2{}^0 = 0$) limit.

The partition function of a polymer with excluded volume, $Q(z_2{}^0)$, corresponds to (3.14) in the $m = 0$ limit and has some special features which make it less universal than the class of large-scale static radial properties. To first order in ϵ the partition function $Q(z_2{}^0)$ is equal

$$Q = Q_0 \delta\mu (1 + z_2{}^0/u_2{}^*)^{(\gamma-1)/\phi_2}[1 + a_Q u_2{}^* \lambda_2 + O(\epsilon^2)] \quad (3.15a)$$

$$(\gamma - 1)/\phi_2 = 1/4 + O(\epsilon); \quad a_Q = 1 + O(\epsilon) \quad (3.15b)$$

where Q_0 is the partition function of the noninteracting ($z_2{}^0 = 0$) chain. The "nonuniversal" contribution $\delta\mu$ (see Cherayil et al.[29] for a discussion of this term) and Q_0 are dependent on the small-scale structure of the polymer. The exponent γ and the constant a_Q are "universal" for linear polymers but vary with chain architecture and with the proximity to an interface.[29] We now compare these results to those of other models of interacting polymers.

Calculations of the effect of ternary interactions ($z_3{}^0$ in (2.4)) on the molecular dimensions follow a similar pattern as the binary interaction. For example, the first order in the $\epsilon_3 = 3 - d$ renormalization group expression for end-to-end distance $\langle \mathbf{R}^2 \rangle$ under θ conditions (vanishing second virial coefficient) is

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 [1 + b_{\mathbf{R}^2} u_3{}^* \lambda_3 + O(\epsilon_3{}^2)] \quad (3.16a)$$

$$\lambda_3 = (z_3{}^0/u_3{}^*)/(1 + z_3{}^0/u_3{}^*); \quad b_{\mathbf{R}^2} = -1.9 + O(\epsilon_3) \quad (3.16b)$$

$$u_3{}^* = \epsilon_3/44\pi + O(\epsilon_3{}^2); \quad \epsilon_3 = 3 - d; \quad \epsilon_3 \in (0,1) \quad (3.16c)$$

Treatment of higher order interactions $z_m{}^0$ (see (2.4)) are like a broken record, and the same structure is obtained aside from the interaction labels. See Cherayil et al.[30] for the case of ternary interactions in the $\epsilon_3 \to 0^+$ limit.

RG calculations for a surface-interacting chain based on the Hamiltonian (2.2) again yield similar results. For direct comparison, the end-to-end distance $\langle \mathbf{R}^2 \rangle$ and the partition function $Q(z_s{}^0)$ of a chain terminally attached to an interacting surface are[1,2]

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 [1 + C_{\mathbf{R}^2} u_s{}^* \lambda_s + O(\epsilon_\perp{}^2)] \quad (3.17a)$$

$$\lambda_s = (z_s{}^0/u_s{}^*)/(1 + z_s{}^0/u_s{}^*); \quad C_{\mathbf{R}^2} = d_\perp/d \quad (3.17b)$$

$$u_s{}^* = \epsilon_\perp/2; \quad \epsilon_\perp = 2 + d_\parallel - d \quad (3.17c)$$

$$Q = Q_0 (1 + z_s{}^0/u_s{}^*)^{(\gamma_s - 1)/\phi_s} + O(\epsilon^2) \quad (3.18a)$$

$$(\gamma_s - 1)/\phi_s = -1; \quad \phi_s = \epsilon_\perp/2 \quad (3.18b)$$

Finally, we briefly note that the RG result for the friction coefficient $f_{\mathrm{KR}}/f_{\mathrm{KR}}(h \to 0)$ equals (see Appendix B)

$$f_{\mathrm{KR}}(h)/f_{\mathrm{KR}}(h \to 0) = (1 + h/h^*)^{-1} + O(\epsilon^2) \quad (3.19)$$

which is identical with Q/Q_0 in (3.18a) aside from the interaction labels. The pattern of similarity between the models should be evident.

We now contrast the perturbative RG results for the polymer–surface interaction with the *exact* operational calculations to get some insight into the mathematical origin of the universal analytic structure in this class of problems. From (3.5) the partition function of a surface interacting chain is

$$Q(z_s{}^0) = 1/(1 + \Delta_s I_x{}^{\epsilon_\perp/2})|_{x=1} \quad (3.20)$$

Taking the limit of $\epsilon_\perp$ small, corresponding to the working assumption of the RG ϵ-perturbation theory, yields (see (2.13b) and (3.2c))

$$\Delta_s \approx z_s{}^0/u_s{}^*; \quad I_x{}^{\epsilon_\perp/2} \approx 1; \quad \epsilon_\perp \approx 0^+ \quad (3.21)$$

which in combination with (3.20) gives

$$Q(z_s{}^0) \approx 1/(1 + z_s{}^0/u_s{}^*); \quad \epsilon_\perp \approx 0^+ \quad (3.22)$$

This is exactly the first order in ϵ RG result (3.18a). The RG prediction for the Kirkwood–Riseman integral equation (2.15b) is derived in Appendix B by using essentially the same operational calculus argument.[5] From these examples we see that the RG theory exploits the singular nature of the interaction kernel near the critical dimension where $\epsilon_\perp$ is small (see (3.3b)). The ϵ-expansion method is an expansion in the "singularity strength" of the interaction kernel.

The above analysis, indicating a connection of the perturbative RG scaling functions and the exact theory in an operational calculus formulation, suggests a number of nontrivial generalizations of the conventional RG theory in situations where the model is not exactly solvable. Consider, for example, the leading contribution of the excluded volume effect on $\langle \mathbf{R}^2 \rangle$ in (3.13a) given by

$$\langle \mathbf{R}^2 \rangle \sim \langle \mathbf{R}^2 \rangle_0 (1 + z_s{}^0/u_s{}^*)^{(2\nu-1)/\phi_2}; \quad \epsilon \approx 0^+ \quad (3.23a)$$

and observe that because $(2\nu - 1)/\phi_2$ is positive and generally noninteger the scaling function for $\langle \mathbf{R}^2 \rangle$ in (3.23a) becomes imaginary for $z_2{}^0 < -u_2{}^*$. Of course, there are all kinds of difficulties in defining the two-parameter model for negative $z_2{}^0$, but let us put these problems aside for a moment. If we formally reverse the process of going from (3.20) to (3.22) and (see (3.12a)) replace $z_2{}^0/u_2{}^*$ by $(z_2{}^0/u_2{}^*)I_x{}^{\epsilon/2}$, we obtain

$$\langle \mathbf{R}^2 \rangle \approx \langle \mathbf{R}^2 \rangle_0 [1 + (z_2{}^0/u_2{}^*) I_x{}^{\epsilon/2}]^{(2\nu-1)/\phi_2}|_{x=1}; \quad \epsilon \approx 0^+ \quad (3.23b)$$

which upon expansion and interpretation of the $I_x{}^{\epsilon/2}$ operator gives

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 \sum_{k=0}^{\infty} \begin{bmatrix} \delta \\ k \end{bmatrix} (z_s{}^0/u_s{}^*)^k / \Gamma(1 + k\epsilon/2);$$

$$\delta = (2\nu - 1)/\phi_2; \quad \epsilon \approx 0^+ \quad (3.23c)$$

Such a formal procedure might prove effective in extending the RG results into the regime $z_2{}^0 \leq -u_2{}^*$, where there is no present effective method of calculating scaling functions. Note that this procedure leads to exact results in the surface adsorption model.

4. Instability and the Adsorption and Collapse Thresholds

A. Instability Condition. Although the renormalization group provides a powerful method for calculating the solution properties of flexible interacting polymers,[16,28] it can only be applied in its present form to a limited range of temperatures and concentrations. For example, the theory is *not applicable* to the description of polymer adsorption and polymer "collapse" from attractive polymer–polymer interations, and it cannot describe the polymer coexistence curve and phase separation. It is found that there are certain critical values of the interactions at which the results of the RG theory strongly diverge and beyond which the theory becomes meaningless. Douglas and Freed[26] first studied this phenomenon by trying to extend the RG theory to describe polymer collapse at infinite dilution. These heuristic calculations indicated a critical value of the excluded volume interaction given by

$$z_2{}^0 \approx -u_2{}^*; \quad u_2{}^* = \epsilon/8 + O(\epsilon^2) \quad (4.1a)$$

where the RG scaling functions become singular.

The RG "fixed point" u_2^*, is calculated perturbatively as the nontrivial zero of the Gell-Mann–Low β function following a standard field theoretic recipe (see ref 16). Although the method of calculating u_2^* is well-known, the mathematical significance of this parameter is rather obscure, and from the perspective of the path integral approach to interacting polymers there does not seem to be any obvious significance for a critical value of z_2^0 associated with u_2^*. There are also basic questions[31] about the existence and uniqueness of the RG fixed point which are difficult to address given the perturbative nature of the RG ϵ-expansion method. These problems are not just academic when we realize that all dimensionless properties calculated by using the RG theory (critical exponents, etc.) are calculated as a function of the RG fixed point.

Comparison between the Douglas and Freed calculation[26] and experimental data for contracting polymers gave reasonably good agreement in the rather narrow regime between the θ point and the critical value of the interaction given in (4.1a), which empirically seemed to define a "collapse threshold" beyond which considerable contraction occurred. More recent experimental data by Chu et al.[32] indicate that the scaling curves are rather complicated below the θ point, and a "bifurcation" into a family of curves is observed. Interestingly, the splitting of the scaling curves observed by Chu et al. occurs[32] at nearly a *universal* value of z_2^0 below the θ point, which closely coincides with the condition of (4.1a).

Unfortunately, there are numerous complicating physical effects (ternary interactions, short-range interactions along the chain, etc.) which make it difficult to unambiguously compare theoretical calculations for polymer collapse with experimental data. To understand the mathematical side of the problem, Douglas et al.[1,2] considered the exactly solvable surface-interacting polymer model specified by (2.1) in order to test the accuracy and limitations of the RG theory. Interestingly, the RG description of polymer adsorption showed the same type of singular behavior as in the polymer collapse problem, yielding a critical value of the surface interaction z_s^0 related to the RG fixed point $u_s^* = \epsilon_\perp/2$ as

$$z_s^0 \approx -u_s^* \tag{4.1b}$$

This condition defines an "adsorption threshold" in analogy with the "collapse threshold" introduced earlier.[1,2,26] Douglas et al.[2] also observed that the scaling functions for surface-interacting chains in the eigenfunction expansion approach become divergent as the "adsorption threshold" (4.1b) is approached for values of z_s^0 less than $-u_s^*$. This qualitative behavior can be seen in the eigenfunction expansion of the surface-interacting chain partition function $Q(z_s^0)$, which is given by[1]

$$Q(z_s^0) \sim (2/\epsilon_\perp) \exp(-E_s n); \quad z_s^0 < -u_s^* \tag{4.2a}$$

$$-E_s n = |-(z_s^0/u_s^*)\Gamma(1 + \epsilon_\perp/2)|^{1/\phi_s}; \quad \phi_s = \epsilon_\perp/2 \tag{4.2b}$$

where the continuum contributions to the eigenfunction expansion are neglected. In the model (2.1) there is only one eigenvalue, E_s, for the adsorbed chain.[1] Observe that the eigenvalue E_s is a *function* of the surface interaction z_s^0 and that for $z_s^0 \ll -u_2^*$ we have $E_s \sim O(1)$, but as z_s^0 approaches $-u_s^*$ the eigenvalue E_s approaches zero, $E_s(z_s^0 \approx -u_s^*) \sim O(1/n)$, and the partition function becomes a rapidly varying function in this limit. The corresponding rapid variation of the mean dimensions of the polymer chain for $z_s^0 \approx -u_s^*$ is illustrated in Figure 2 of Douglas et al.[1]

Another qualitatively important feature is the temperature dependence of E_s, which can be inferred from (4.2b) and the definition of z_s^0 in (2.2) as

$$E_s \sim (\beta_s^0)^{1/\phi_s}; \quad \beta_s^0 \sim (T - \theta_A); \quad T \approx \theta_A \tag{4.2c}$$

where constant prefactors are neglected and where θ_A is the "adsorption θ point" at which β_s^0 vanishes.[1,2,12] As discussed in Douglas et al.,[1] the exponent $1/\phi_s$ defines the order of the adsorption phase transition in a generalization of the Ehrenfest definition using the I_x^α operator.

Detailed comparison[1,2] between the approximate RG ϵ-expansion and eigenfunction expansion calculations against the exact scaling functions indicate that the "stability condition" (4.1b) obtained from the RG theory defines a point where the perturbative methods cannot follow the strong variation of the scaling functions. It is also evident from the analysis of Douglas et al.[1] that the presence of the "singular" behavior at $z_s^0 \approx -u_s^*$ has an important impact on the shape of the crossover curves even in the regime of repulsive polymer–surface interactions, where the RG theory is applied without difficulty (see Figure 2 of Douglas et al.[1]). This leads us to further inquire into the mathematical mechanism underlying the stability conditions (4.1a) and (4.1b) and into the meaning of the RG fixed point by using a nonperturbative method. In the next section it is shown that the stability condition (4.1b) is determined by an eigenvalue equation with the RG fixed point related to a particular eigenvalue.

B. Adsorption Threshold. The homogeneous Volterra equation corresponding to (2.13b) is equal to

$$\hat{\psi}(x) = -\Delta_s \int_0^x [(x - t)^{(\epsilon_\perp/2)-1}/\Gamma(\epsilon_\perp/2)]\, \hat{\psi}(t) \equiv -\Delta_s I_x^{\epsilon_\perp/2} \hat{\psi}(x) \tag{4.3}$$

where $\hat{\psi}(x)$ denotes the solution of (4.3) in distinction from the nonhomogeneous equation (2.13b). There are general theorems[19] which indicate that Volterra integral equations with integrable kernels do not have nontrivial (i.e., nonzero) eigenfunctions. However, in the limit $\epsilon_\perp \to 0^+$ the kernel of (4.3) becomes singular, and these theorems *no longer apply*. Indeed, for $\epsilon_\perp \to 0^+$ the eigenfunction solutions are the class of continuous bounded functions on the interval $(0, \infty)$ since $I_x^{\epsilon_\perp/2}$ is an identity operator and the kernal is a δ function. The eigenvalue condition in (4.3) corresponds to

$$\lim_{\epsilon \to 0^+} -\Delta_s = 1 \tag{4.4a}$$

which along with the definition of Δ_s in (2.13c) yields

$$z_s^0 \approx -u_s^*; \quad u_s^* \equiv \epsilon_\perp/2 \tag{4.4b}$$

We then see that the RG fixed point u_s^* corresponds to an eigenvalue of an associated integral equation (see ref 5). The Fredholm alternative[19] implies that if the homogeneous equation (4.3) has a solution for some value of z_s^0, then (2.13b) may have no nontrivial solution. Now if $\epsilon_\perp$ is small then (4.3) "almost" has eigenvalue solutions, and the scaling functions become rapidly varying for values of z_s^0 corresponding to the stability condition (4.1b). A similar "singular" behavior commonly occurs in the solution of nonhomogenous Fredholm equations when the dimensionless coupling parameter (e.g., Δ_H in (2.15)) is near an eigenvalue of the homogeneous equation.[19] In fact, the homogeneous analogue of (2.15b) has an infinite number of eigenvalues at which f_{KR} diverges.[5] The structure of this spectrum will be discussed elsewhere, but here we note that the condition $h \approx -h^*$ with h^* the RG fixed point characterizes the smallest magnitude eigenvalue of this spectrum.[5] Again we find that the RG fixed point is associated with an eigenvalue, and it is conjectured that this is quite generally the case.

The connection between the RG fixed point and an associated eigenvalue also explains another puzzling feature observed in Douglas et al.'s detailed comparison between perturbative and exact calculations in the surface interaction problem.[1,2] Successive orders of the surface interaction perturbation theory at low order strongly diverge at a critical value of $z_s^0 = u_s^*$ (see Figure 2 of Douglas et al.), and a similar phenomenon is observed[1] in the two-parameter perturbation expansion for $z_2^0 \approx u_2^*$ and in the KR hydrodynamic interaction theory for $h \approx h^*$. We can readily understand this qualitative behavior of the perturbation expansions from the classical theory of integral equations, which implies that the radius of convergence of the Neumann series for a nonhomogeneous Fredholm equation is limited by the smallest magnitude eigenvalue of the associated homogeneous equation.[19] The qualitative significance of the splitting of the interaction perturbation theory becomes apparent if we recall the connection between the smallest magnitude eigenvalue and the RG fixed point mentioned above. It should be noted that the standard Fredholm theory strictly applies only to integral equations whose kernels are "smoother" than the singular type integral equations typically describing interacting polymers. Many of the results of the Fredholm theory can be extended to weakly singular integral equations, but this technical issue is avoided here.[19]

Another qualitatively important property of the interacting polymer perturbation theory is the convergence of the perturbation expansion, which is critically dependent on the degree of singularity of the kernel in the integral equation describing the interaction. For example, the perturbation expansion in the surface interaction model (2.1) has an infinite radius of convergence when the crossover exponent ϕ_s (see (2.2)) is positive, $\phi_s \in (0,1)$, corresponding to a "weakly singular", kernel but the radius of convergence shrinks to zero for ϕ_s negative[1] corresponding to an "intrinsically singular" kernel.[19] In particular, the coefficients in the surface interaction perturbation theory for negative ϕ_s grow at a factorial rate in a fashion quite similar to that encountered in the two-parameter model of polymer excluded volume.[1]

Conclusion

The conversion of the path integral formulation of interacting polymers into an equivalent integral equation approach provides numerous insights into the universal analytic structure of the scaling functions derived for many types of interactions. While the mathematical significance of the fixed points, critical exponents, etc., is rather obscure in the path integral approach, these parameters are readily understood from the perspective of singular integral equation theory. For example, the crossover exponent in the surface-interacting chain and Kirkwood–Riseman theories characterizes the degree of singularity of the integral equation with the critical dimension corresponding to a crossover point between a weakly singular and intrinsically singular kernel.[19] The renormalization group fixed point calculated from the nontrivial zero of the Gell-Mann–Low β function[1] is found to be related to the smallest magnitude eigenvalue of an associated eigenvalue integral equation. The pole structure found in the interaction perturbation theory again reflects the degree of singularity of the integral equation kernel.

The integral equation approach to surface-interacting polymers is not only useful for understanding the deeper mathematical significance of results obtained alternatively from the path integral formulation in conjunction with the RG theory but also enables us to understand the failure of the RG theory to describe polymers with attractive interactions. The search for such an extension of the present theory is fundamental for the description of polymer collapse from self-attractive interactions, polymer adsorption with excluded volume interactions, and the polymer coexistence curve.

Typically the scaling curves obtained from the perturbative RG theory "blow up" at critical values of the dimensionless interaction. In the integral equation approach we see that these critical conditions can be understood on the basis of the Fredholm alternative—applied somewhat loosely to the singular type equations describing interacting polymers. By studying the relation between the exact solution of the integral equation for surface-interacting polymers and the corresponding result in the RG theory, we see that the ϵ-expansion perturbation theory exploits the strongly singular nature of the kernel, which at the critical dimension is equal to a δ function. In Appendix B it is shown that in the Kirkwood–Riseman theory the kernel likewise becomes a δ function. Some arguments are given to "reverse" the approximations of the RG theory in order to recover the exact theory, and these arguments are generalized to the excluded volume problem.

The recurrent theme of the present paper is that the various theories of interacting polymers (surface, excluded volume, hydrodynamic interactions), as well as a much larger body of physics and mathematics, exhibit a high degree of universality in their analytic structure. Beyond the mathematical interpretation of this universal structure, which can be obtained by adopting the integral equation perspective, we may inquire more deeply into why and how this universal structure manifests itself. The threads of these questions are further pursued in the Appendixes.

Appendix A. Some Ill-Understood Connections between Polymer Hydrodynamics and Excluded Volume Theories

The close interconnection between the two-parameter and surface-interacting polymer models is discussed briefly by Douglas et al.[2] and again in the main text. Given these parallels and the close correspondence between polymer hydrodynamics and surface-interacting polymers, we might also expect a connection between the analytic structures of the hydrodynamic[2,3] and excluded volume theories. This correspondence indeed exists and is very useful for gaining further insight into the analytic structure of the excluded volume model—although the relation between the models is not quite as transparent in this instance beyond a similarity of analytic structures obtained after RG calculations.

A. Penetration Function. The second virial coefficient in the two-parameter model (see ref 16, 21, and 28) describes the cooperative interference between the segments of one chain and those of another. For a small excluded volume interaction we have

$$A_2 \sim N_A(n^2\beta_2^0)/2!M^2; \quad \beta_2^0 \to 0 \qquad \text{(A.1)}$$

with M the molecular weight of the polymer, β_2^0 the binary cluster integral, and N_A Avogadro's number. This result corresponds to each segment of each chain interacting independently to give the factor of n^2 volume exclusion interferences. We might call this the freely penetrating limit.

When β_2^0 is not vanishingly small the chains can no longer penetrate each other to the same degree, and it is this effect that is calculated perturbatively by using the two-parameter model of excluded volume. The large excluded volume interaction limit is obvious in retrospect. As the chain swells the local excluded interaction eventually saturates (in mathematical terms a fixed point is reached) so that one polymer chain largely excludes the presence of the other. This leads to the scaling relation

$$A_2 \sim N_A\langle \mathbf{R}^2\rangle^{d/2}/M^2 \tag{A.2}$$

where the volume of the independently interacting chain segments ($n^2\beta_2^0/2!$) of one chain is replaced by the average volume pervaded by the coil ($\langle \mathbf{R}^2\rangle^{d/2}$) as a whole. The penetration function describes the "crossover" between the limiting situations (A.1) and (A.2) and is defined by

$$\Psi(z_2^0) = (d/2\pi)^{d/2}A_2(2!M^2/N_A)(6\langle S^2\rangle)^{-d/2} \tag{A.3}$$

where $\langle S^2\rangle^{1/2}$ is the radius of gyration of the polymer. The constant of proportionality in (A.3) is defined so that $\Psi(z_2^0) = z_2^0 + O[(z_2^0)^2]$ with z_2^0 defined in (2.3b).

The RG estimate of the penetration function $\Psi(z_2^0)$ to the first order in ϵ equals[33]

$$\Psi(z_2^0) = \Psi^*(z_2^0/u_2^*)/[1 + z_2^0/u_2^*] + O(\epsilon^2) \tag{A.4a}$$

$$\Psi^* = \epsilon/8 + O(\epsilon^2); \quad u_2^* = \epsilon/8 + O(\epsilon^2) \tag{A.4b}$$

Note that the magnitude of the RG fixed point u_2^* controls the rate at which the excluded volume interaction saturates and that the asymptotic value of Ψ^* is intimately connected with the RG fixed point u_2^*. In second order, Ψ^* equals[33]

$$\Psi^* = \epsilon/8 + (4 \ln 2 + 77/12)(\epsilon/8)^2 + O(\epsilon^3) \tag{A.4c}$$

$$\Psi^*(d{=}3) = 0.269$$

and the scaling function becomes slightly more complicated than in (A.4a).

B. Hydrodynamic Penetration Function. The integral equation in (2.15) describes a physical situation rather analogous to the interpenetration of polymer coils, and this similarity is reflected in the mathematics describing the friction coefficient of an isolated coil. Equation 2.15b describes the "penetration" of the solvent flow field into the polymer coil.[3,21] For weak hydrodynamic interaction

$$f_{KR} = n\zeta + O(h^2); \quad h \to 0 \tag{A.5}$$

corresponding to the "free-draining" limit where each bead along the chain backbone exerts an independent frictional force to give a total friction given by (A.5).[3,21] The integral equation (2.15b) describing the cooperative hydrodynamic disturbance of the beads is obtained by considering the balance of forces in the fluid within the Kirkwood–Riseman preaveraging theory.[3,21] The result of strong hydrodynamic interaction again yields an obvious limiting situation where the coil as a whole behaves effectively as a Stokes sphere (d dimensions) having a radius on the order of the radius of gyration. In d dimensions we then expect

$$f_{KR} \sim \langle S^2\rangle_0^{(d-2)/2} \tag{A.6}$$

which is found in the explicit solution of (2.15b).[3,4] In analogy with the virial coefficient penetration function, we may define a dimensionless hydrodynamic penetration function $\Psi_H \sim f_{KR}/\langle S^2\rangle_0^{(d-2)/2}$ with the constant of proportionality defined such that

$$\Psi_H(h) = h + O(h^2) \tag{A.7a}$$

A RG calculation based on (2.15b) gives the result[4]

$$\Psi_H = \Psi_H^*(h/h^*)/(1 + h/h^*) + O(\epsilon^2) \tag{A.7b}$$

where the fixed point value ($h \to \infty$) of the hydrodynamic penetration function Ψ_H^* equals $\Psi_H^* = h^*$ (see (2.16c)). Note that in three dimensions $\Psi_H^*(d{=}3) = 0.265$ and that the scaling functions in (A.4a) and (A.7b) *have the same form aside from the interaction labels.*

The physical connection between the polymer second virial coefficient and the friction coefficient is that they are both virial coefficients, or in field theoretic language vertex functions, describing the interaction of the individual chain segments and their surroundings. However, beyond a superficial comparison of the output scaling functions, obtained after turning the cranks of the interaction perturbation theory and the RG ϵ-expansion method, the underlying mathematical origin of the observed similarity remains obscure. It would be very interesting if the polymer excluded volume problem could be cast into an integral equation formulation which could recover the ϵ-perturbation results order by order. Such a formulation, even if restricted to a self-consistency type approximation, might allow the nonperturbative treatment of polymer collapse and other basic problems where there are attractive polymer–polymer interactions.

In connection with an integral equation formulation of the second virial coefficient, we note a very interesting related work by Edwards[34] which treats the self-energy of an electron in quantum electrodynamics (QED). At a purely mathematical level the RG analysis involved in QED is quite analogous to that encountered in polymer physics, and similar Feynman diagrams are encountered in both calculations. The physical connection becomes clear if we think of the configurational paths of polymer as being analogous to the dynamical trajectories of the electrons. Edwards[34] was able to transform the QED description of the vertex function describing the electron self-interaction into an approximate integral equation of the singular Fredholm type which he then proceeded to solve nonperturbatively. He also observed at this early date a relation between renormalizability and the strength of the singularity of the integral equation kernel.[34]

Appendix B. Fractional Calculus Approaches to Polymer Hydrodynamics

The nonperturbative solution[5] to the Kirkwood–Riseman integral equation (2.15b) involves an eigenfunction expansion method. An alternative scheme involves the use of the fractional calculus. To proceed we may introduce the "adjoint" fractional differential operator K_x^α, the "Weyl operator" (see ref 24), which is denoted

$$K_x^\alpha f(x) = \int_x^\infty \mathrm{d}t\,[(t-x)^{\alpha-1}/\Gamma(\alpha)]\,f(t) \tag{B.1}$$

For technical reasons the function $f(x)$ is taken to vanish outside the interval (0,1), and we restrict values of α and class of functions $f(x)$ so that the integral in (B.1) has meaning.

The function $\Phi(x)$ in (2.15b) can be determined as the solution of the operator equation

$$[1 + \Delta_H(K_x^{\epsilon/2} + I_x^{\epsilon/2})]\Phi(x) = 1 \tag{B.2}$$

which is formally equal to

$$\Phi(x) = (1 + \Delta_H(K_x^{\epsilon/2} + I_x^{\epsilon/2}))^{-1} \tag{B.3}$$

Expanding the denominator and integrating over x (see (2.15a)) generate the usual Neumann series expansion for the friction coefficient, explicitly

$$\Phi(x) = \sum_{k=0}^{\infty}(-\Delta_H)^k(K_x^{\epsilon/2} + I_x^{\epsilon/2})^k \tag{B.3a}$$

The calculation of Oono et al.[22] corresponds to a calculation of this series to the $k = 1$ term.

To make direct contact with previous calculations it is useful to introduce an alternate hydrodynamic interaction variable $z_H{}^0$ proportional to h in (2.1b). Following Wang et al.[3,4] we define $z_H{}^0$ as

$$h = 2^{-\epsilon/2}(1 + \epsilon/2)z_H{}^0/2 \tag{B.4a}$$

with the corresponding hydrodynamic fixed point $u_{H,0}{}^*$

$$u_{H,0}{}^* = \epsilon/2 + O(\epsilon^3) \tag{B.4b}$$

such that $z_H{}^0/u_{H,0}{}^* = h/h^*$. The variable Δ_H in (2.15b) then equals

$$\Delta_H = (z_H{}^0/2u_{H,0}{}^*)\Gamma(2 + \epsilon/2) \tag{B.4c}$$

We can obtain the approximate RG results for f_{KR} and Kirkwood's classical double-sum approximation[3,21] for f_{KR} by noting that (see (3.19)–(3.21))

$$\Delta_H \approx z_H{}^0/2u_H{}^*; \qquad I_x{}^{\epsilon/2} \approx 1; \qquad K_x{}^{\epsilon/2} \approx 1; \qquad \epsilon \approx 0^+ \tag{B.5}$$

so that (B.3a) becomes

$$\Phi(x) \approx 1/(1 + z_H{}^0/u_H{}^*); \quad \epsilon \approx 0^+ \tag{B.6a}$$

$$f_{KR} \approx n\hat{\zeta}/(1 + z_H{}^0/u_H{}^*); \quad \epsilon \approx 0^+ \tag{B.6b}$$

This is *exactly* Kirkwood's double-sum result in d dimensions[3,21] and the first order in ϵ result obtained in the RG theory.[3,4] Allessandrini has shown that for $z_H{}^0 \rightarrow \infty$ the approximate expression (B.6) is accurate to within 2% over the range $\epsilon \in (0,2)$ in comparison with the exact *preaveraged* Kirkwood–Riseman theory (see also ref 23). It is easily shown[5,19] that (B.6) is an exact solution of the integral equation (2.13a) for $\epsilon = 2$ (i.e., $d = 2$) over the whole range of $z_H{}^0$. The determination of the exact expression of $f_{KR}(z_H{}^0)$ over the full range of $z_H{}^0$ is significantly more complicated [$\epsilon \in (0,2)$] than the simple expression (B.6).[5] See also Wang et al.,[3] where preaveraging corrections to the polymer friction coefficient are determined by using the ϵ-expansion perturbation theory and the RG method.

We also briefly mention that there is a more general but rather undeveloped variety of fractional calculus appropriate to the Fredholm-type integral equations which typify polymer hydrodynamics theory. This theory directly manipulates the composite operator

$$A_x = I_x{}^{\epsilon/2} + K_x{}^{\epsilon/2} \tag{B.7}$$

For example, Trigt[35] describes a method for constructing $A_x{}^{-1}$ which then allows the direct calculation of Φ in the limit $\Delta_H \rightarrow \infty$. This method could have many useful applications in polymer hydrodynamics calculations. See Trigt[35] for important applications of (B.7) in the context of neutron transport and radiative transfer problems.

Appendix C. Universal Limiting Form of Interacting Polymer Partition Functions

The result (2.14) for the partition function of a surface-interacting polymer is apparently closely related to a general theorem obtained by Darling and Kac (DK) regarding a *universal* limiting ($n \rightarrow \infty$) form of the partition function for a broad class of interaction potentials.[6] Now if we transcribe to the notation of the Gaussian chain model with a pseudopotential interaction we can directly apply DK's results to a polymer context.

Darling and Kac[6] calculate the partition function of a Gaussian chain interacting through a very general interaction

$$H_\Omega = \beta_\Omega{}^0 \int_0^N V_\Omega[\mathbf{R}(\tau)]\,\mathrm{d}\tau \tag{C.1}$$

where the potential $V_\Omega[\mathbf{R}(\tau)]$ is defined under the condition that the expansion coefficients in the perturbation series are finite. The method of calculation by DK exactly parallels the calculation of the partition function for the surface interacting chain by Douglas et al. (see (3.4) of ref 1 and compare with DK's evaluation of $\mu_m(t)$). The existence (i.e., finiteness) of the perturbation coefficients in the series for the partition function puts "growth constraints" on the potential obtained from the integration of the potential over all space subject to certain weighting factors. These details are summarized in DK, and suffice it to say here that the class of potentials considered is "very general".

The calculation of DK indicates the remarkable result that the partition function for this very general class of potentials approaches a *universal function* for long chains

$$Q(\beta_\Omega{}^0) = \sum_{k=0}^{\infty}(-\Delta_{Dk})^k/\Gamma(1 + k\alpha); \quad 0 < \alpha < 1, n \rightarrow \infty \tag{C.2a}$$

$$\Delta_{DK} \sim \beta_\Omega{}^0 n^\alpha g(n) \tag{C.2b}$$

where $g(n)$ is a slowly varying function.[6] The $\beta_\Omega{}^0$ parameter, the "coupling constant", has been added here for convenience; (C.2a) is a Mittag–Leffler function of index α.

One of the sticky points in DK's calculation is the meaning of the α index in (C.2b), which arises as a consequence of their "growth constraints" on the potential V_Ω. It is clear in the retrospect of modern RG calculations that α specifies the crossover exponent (see (2.4) and below). Note that (C.2a) has exactly the same form as the particular example of the surface interaction partition (see (2.14)) where α is replaced by the surface interaction crossover exponent $\epsilon_\perp/2$.

The theorem of Darling and Kac[6] leading to the universal limiting form of the partition function (C.2) is stated in such general terms that it is difficult to appreciate its full ramifications. In order to flesh out the practical interpretation of the theorem it would certainly be worthwhile to explore certain explicit classes of potentials to which (C.2) applies as a universal long-chain limit. As mentioned above, the motivation for introduction of the growth parameter α seems rather vague (at a physical not mathematical level) in the work of DK, and a logical direction to pursue the DK theory is to consider classes of potentials giving rise to a dimensionless interaction parameter scaling as a power of the chain length. This immediately leads us to the class of homogeneous potentials.

Homogeneous potentials are characterized by their invariance of functional form under a dilation of scale. Specifically, if we have an interaction potential of the form

$$H_I = \beta_{\mathrm{Hom}} \int_0^N V_{\mathrm{Hom}}[\mathbf{R}(\tau)]\,\mathrm{d}\tau \tag{C.3a}$$

then a homogeneous potential of index h obeys the similarity relation

$$V_{\mathrm{Hom}}(\lambda\mathbf{R}) = \lambda^h V_{\mathrm{Hom}}(\mathbf{R}) \tag{C.4}$$

In general V_{Hom} can depend on many coordinates $\mathbf{R}(\tau)$, in which case we refer to V_{Hom} as a many-body potential. If V_{Hom} depends on a single position coordinate $\mathbf{R}(\tau)$ as explicitly indicated in (C.4), then it is said to be a one-body potential.

It is an important fact that many of the relevant interaction potentials arising in polymer science are of the homogeneous type. A well-known example is the polymer excluded volume interaction defining the two-parameter model (see (2.3)). In addition to this type of two-body interaction there are many-body excluded volume interactions, long-range polyelectrolyte interactions, the polymer–surface interaction and its many body generalizations, etc.[16] Homogeneous potentials have the simple (but unique) property that once dimensionless units are introduced into the interaction Hamiltonian the dimensionless interaction scales as a simple power of the chain length n. The exponent of n, the crossover exponent, ϕ, plays a critical role in the theory since it characterizes how the relative strength of an interaction is affected by chain length. If ϕ is positive, the interaction grows with chain length; for negative ϕ it dies away. Typically (but not always) the homogeneity power of the potential depends on the dimension so that ϕ is a function of the dimension, and a critical dimension is defined by the value of d at which ϕ vanishes. Interactions with positive ϕ are relevant, negative ϕ are irrelevant, and the $\phi = 0$ case is termed marginal.

The class of homogeneous one-body potentials encompasses power law type potentials, generalized functions such as δ functions. Derivatives of δ functions and certain fractal functions are not described here. Introducing dimensionless units for the potential (C.4) yields

$$H_{\mathrm{Hom}} = z_{\mathrm{Hom}}{}^{0} \int_0^1 (d/2\pi)^{h/2} V_{\mathrm{Hom}}[\mathbf{r}(x)]\, \mathrm{d}x \qquad \text{(C.5a)}$$

$$z_{\mathrm{Hom}}{}^{0} = (d/2\pi)^{-h/2} \beta_{\mathrm{Hom}}{}^{0} n^{\phi_{\mathrm{Hom}}}; \qquad \phi_{\mathrm{Hom}} = \epsilon_{\mathrm{Hom}}/2; \qquad \epsilon_{\mathrm{Hom}} = 2 + h \qquad \text{(C.5b)}$$

The Kuhn length is taken to be unity, $l = 1$, for notational simplicity. The surface interaction model (2.1) is a special example of (C.5) corresponding to a δ function pseudopotential acting on the coordinates $\mathbf{r}(x)$ so that the homogeneity power is $h = d_{\parallel} - d$ with $d_{\parallel}$ the surface dimension. There are numerous situations where a polymer embedded in a medium of nonhomogeneous density can be modeled as effectively lying in a power law potential determined by the density correlation function of the background, and this provides part of the background motivation for the present discussion.

A convenient formalism for calculating the perturbation expansion for the class of homogeneous one-body potentials $V_{\mathrm{Hom}}[\mathbf{R}(\tau)]$ is given by Goovaerts et al.,[7] who develop their methods in the context of solving certain related quantum mechanical problems starting from Feynman's path integral.[13] Fortunately, Goovaerts et al.[7] used the density matrix approach where the transcription to the equivalent polymer problem is particularly straightforward (see ref 16). From (2.13) of Goovaerts and Devreese[7a] we can simply write down the perturbation expansion for Q for the *entire class of homogeneous one-body potentials* as

$$Q(z_{\mathrm{Hom}}{}^{0}) = \sum_{m=0}^{\infty} C_m (-z_{\mathrm{Hom}}{}^{0})^m / \Gamma(1 + m\epsilon_{\mathrm{Hom}}/2) \qquad \text{(C.6a)}$$

$$C_m \equiv I(m,\epsilon_{\mathrm{Hom}}) / (2\pi)^{((h/2)+d)m} 2^{hm/2} \qquad \text{(C.6b)}$$

$$I(m,\epsilon_{\mathrm{Hom}}) = \int \frac{\mathrm{d}^d\mathbf{k}_1\, \hat{f}(\mathbf{k}_1)}{1 + \mathbf{k}_1{}^2} \int \frac{\mathrm{d}^d\mathbf{k}_2\, \hat{f}(\mathbf{k}_2)}{1 + (\mathbf{k}_1 + \mathbf{k}_2)^2} \cdots \int \frac{\mathrm{d}^d\mathbf{k}_m\, \hat{f}(\mathbf{k}_m)}{1 + (\mathbf{k}_1 + \mathbf{k}_2 + \ldots + \mathbf{k}_m)^2} \qquad \text{(C.6c)}$$

with $f(\mathbf{k})$ the Fourier transform of the homogeneous potential

$$f(\mathbf{k}) = \int \mathrm{d}^d\mathbf{R}\; e^{i\mathbf{k}\cdot\mathbf{R}} V_{\mathrm{Hom}}[\mathbf{R}] \qquad \text{(C.6d)}$$

Some of the constants in the Goovaerts et al.[7] Hamiltonian, corresponding to (2.1), are different, and there is a necessary reinterpretation of parameters involved in mapping the quantum mechanical density matrix into the equivalent polymer problem. This notational detail, as well as a generalization to d dimensions, is attended to in (2.13). ϵ_{Hom} is restricted to positive values and further technical restrictions can be found in ref 7.

The expansion (C.6a) can easily be checked against the result of Douglas et al.[1,2] given in (2.14). For δ function $\delta[\mathbf{R}(\tau)]$ in the d dimension, we have $f(\mathbf{k}) = 1$, and the integrals in (C.6d) factor into a simple product

$$C_m(\delta \text{ potential}) = (2\pi)^{-((h/2)+d)m} 2^{-hm/2} \left[\int \mathrm{d}^d\mathbf{k}/(1 + \mathbf{k}^2) \right]^m \qquad \text{(C.7a)}$$

Evaluation of the integral gives

$$\left[\int \mathrm{d}^d\mathbf{k}/(1 + \mathbf{k}^2) \right]^m = (\pi^{d/2}\Gamma[(2 - d)/2])^m \qquad \text{(C.7b)}$$

Insertion of (C.7b) into (C.7a) and noting $h = -d$ for the d-dimensional δ potential yield

$$C_m(\delta \text{ potential}) = [\Gamma(\epsilon_{\mathrm{Hom}}/2)]^m \qquad \text{(C.8)}$$

where $\epsilon(\delta;h=-d) = 2 - d$. Combining (C.8) and (C.6a) gives (2.14) for $d = 0$. Generalization to the variable $d_{\parallel}$ follows by replacing d by $d_{\parallel}$ in the above argument.

Calculation for the general power law $V_p = |\mathbf{R}|^p$ should, in principle, be possible, although the determination of the C_m coefficients becomes involved as we proceed to higher orders in perturbation theory. The coefficients of C_m for a power law potential are obtained by calculating the Fourier transform of $|\mathbf{R}|^p$, which for reference is[58]

$$f_p(\mathbf{k}) = (\Gamma[(p + d)/2] 2^{p+d} \pi^{d/2} / \Gamma(-p/2)) k^{-(p+d)} \qquad \text{(C.9)}$$

Values of p at which the Γ function "blows up" are excluded. After inserting (C.9) into (C.6d), we then find the leading term is proportional to

$$C_1(|\mathbf{R}|^p) \propto \Gamma[(p + d)/2]/\epsilon_p; \quad \epsilon_p = 2 + p \qquad \text{(C.10)}$$

which is consistent with the usual pole structure in ϵ_p found in the perturbation expansions of homogeneous potentials such as the two-parameter model of excluded volume (see (C.4)). Note that the expansion parameter ϵ_p depends on dimension only because the homogeneity power of the potential depends on the dimension.

To make further progress with calculating the general expansion (C.6), it is convenient to specialize to relatively simple cases like the δ function interaction given above. For example, the d-dimensional Coulomb potential $V_{\mathrm{Coul}} = |\mathbf{R}|^{2-d}$ in $d = 3$ is calculated by Goovaerts and Devreese,[7a] and after some notation transcription we obtain the elegant result

$$Q(z_{\mathrm{Coul}}{}^{0}) = 1 + \sum_{m=1}^{\infty} [-z_{\mathrm{Coul}}{}^{0}]^m C_m / \Gamma(1 + m(\epsilon/2)); \qquad \epsilon = 4 - d,\ \epsilon \in (2,4) \qquad \text{(C.11a)}$$

$$z_{\mathrm{Coul}}{}^{0}(d{=}3) = (d/2\pi)^{1/2} \beta_{\mathrm{Coul}}{}^{0} n^{\phi_2}; \quad \phi_2 = \epsilon/2 \qquad \text{(C.11b)}$$

$$C_m(d{=}3) = 2^2(1 - 2^{2-m})\zeta(m-1); \quad \phi(d{=}3) = 1/2 \qquad \text{(C.11c)}$$

where $\zeta(m-1)$ is the Riemann ζ function. In Goovaerts and Devreese's calculation[7] the coupling constant $\beta_{\mathrm{Coul}}{}^{0}$ is equal to $-e^2$ where e is the charge on an electron. Observe the underlying mathematical structure of the Mittag–Leffler function in (C.11a) and (C.11c): for a repulsive interaction the Coulomb potential has a critical dimension of four just as in the polymer excluded volume.

References and Notes

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(5) The solution to (2.15b) can be obtained as an expansion in the eigenfunctions of the homogeneous analogue of (2.15b) given by $\hat{\Phi}_k(x) = (h_{k*}) \int_{-1}^{1} |x - t|^{\phi_H - 1} \hat{\Phi}_k(t)$, $\phi_H = \epsilon/2$, following Hilbert-Schmidt theory as *generalized* to treat a weakly singular kernel.[19] For the physical range of interest, $\phi_H \in 0,1)$, the kernel is compact in the function space $L^2(0,1)$ and positive so that the $\hat{\Phi}_k$ form a complete denumerable set of eigenfunctions in $L^2(0,1)$. The derivation of the solution to (2.15b) over the entire range of h is involved and will be presented elsewhere, but here it is worth pointing to a couple of relevant features. First, if we assume a simple constant variational trial function in the integral equation above, we find the estimate for the smallest eigenvalue of the homogeneous equation $h_1{}^*$ is equal to the RG fixed point $h^*(\epsilon)$ in (2.16c). A numerically generated solution to homogeneous integral equation indicates that $h_1{}^*$ (numerical, ϵ) equals the RG fixed point $h^*(\epsilon)$ to an accuracy of 0.5% or better over the range $\epsilon \in (0,2)$. Thus, we have $h_1{}^* \simeq h^*$ to high accuracy, and again we find an interpretation of the RG fixed point in terms of an eigenvalue equation. (See Section III.3). Second, the solution to (2.15b) is far more complicated than any explicit calculation has ever indicated. This can be seen by examining the eigenfunction spectrum $h_k{}^*$, which has the asymptotic dependence $[k \to \infty; \epsilon \in (0,2); k > 1]$ $h_k{}^* \sim \Gamma(1 - \epsilon/2) \sin(\epsilon\pi/4) (\pi/2)^{\epsilon/2}[k - (1 + \epsilon/4)/2]^{\phi_H} + O(k^{-d/2})$, derived by using a generalization of Wiener-Hopf theory: Ukai, S. *J. Math. Phys.* **1971**, *12*, 83. See also: Kac, M. *Mich. Math. J.* **1955**, *3*, 141. The Fredholm alternative (see ref 19) requires that the solution to (2.15b) "blows up" for values of h at every single value of $(-h_k{}^*)$ leading to a rather kinky structure of f_{KR}, which is entirely missed in approximate analytic solutions to (2.15b) given in the literature. Observe that the spectrum specified by $h_k{}^*$ compresses as $\epsilon \to 0^+$ while for $\epsilon \to 2$ all the eigenvalues $h_k{}^*$, *except* $h_1{}^*$, approach infinity. The mathematical structure of the eigenvalue spectrum is quite rich. An approximate solution to (2.15 b) is given in Appendix B by a fractional calculus method.
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