Journal of Statistical Physics, Vol. 106, Nos. 1/2, January 2002 (© 2002)

Homopolymers with Intrachain Interactions

J. K. Percus[1]

Received May 4, 2001; accepted August 9, 2001

The system under consideration is a classical homopolymeric chain under an arbitrary external field, and in the grand canonical ensemble of its monomeric units. The ideal case of only symmetric next neighbor interactions is first analyzed in the relative density format. Arbitrary monomer-monomer interactions are introduced in a graphical perturbation series, and the leading order is expressed as a relative density functional with the aid of a sequence of redundant fields under whose variation the thermodynamic potential—here the excess grand potential—is stationary. Various reduction methods are suggested to compress the set of redundant fields of this overcomplete description.

KEY WORDS: Homopolymer; classical chain; thermal equilibrium; relative density; functional; overcomplete description.

1. INTRODUCTION

The theory of externally forced and hence non-uniform simple classical fluids in thermal equilibrium has reached a respectable level of maturity.(1) Complex molecular fluids, with their attendant explosion of phenomenology, are of course a different story, and it is certainly necessary to specify the unique characteristics of the class of systems under investigation. In this discussion, we will have in mind the class of linear chain polymers, so describable at a suitable level of resolution. In fact, we will focus on single polymers, as an entree to the general field. Of course, one knows that under many circumstances, the distinction between interacting long chains and the self-interaction of a very long chain becomes blurred, so that our restriction is not quite as severe as it appears at first sight. At any rate, the number of descriptive parameters available for a long macromolecule is

---

[1] Courant Institute of Mathematical Sciences, and Department of Physics, New York University, 251 Mercer Street, New York, New York 10012; e-mail: jkpl@scires.acf.nyu.edu

0022-4715/02/0100-0357/0

enormous, and so we will focus even further, restricting our attention to homopolymers with symmetric monomeric interactions, i.e., no molecular directional sense.

At a primitive level, imagining only next neighbor interactions, our system is equivalent to a one-dimensional lattice of monomers whose specification (read "degrees of freedom") include such as spatial location. The general situation of this kind (with asymmetric interactions as well) has been studied,[2, 3] although mainly in the context of spatially asymptotically vanishing unit-unit interactions, and we will start in essence by transcribing a portion of this study to the case of binding (asymptotically infinite) interactions, involving an overcomplete representation which has served as a powerful tool in the past.[4] However, our major interest lies in the realistic situation in which, in addition to the binding of next neighbors, one also has interaction between any two monomers, depending on their physical proximity rather than their ordinal distance along the chain. We will do this by extending the traditional Mayer diagram expansion[5] to the case of a permanent backbone coupling the monomeric units, and at the moment carry out the analysis only to low order in the pair interaction strength, suitably defined. This, it develops, is itself a non-trivial undertaking.

2. BACKBONE STATISTICS

We have in mind, as basic structure, an ordered chain of N identical units, and we designate the set of degrees of freedom of unit j simply by (j), representing, e.g., (r_j, θ_j, ϕ_j), the corresponding volume element by dj. An externally specified unit location will usually be denoted by r. Imagining a grand ensemble with monomer number controlled by chemical potential μ, we impose an external potential $u(j)$, or local chemical potential $\mu(j) = \mu - u(j)$, as well as a symmetric next neighbor interaction $\phi(j, j+1)$, where $\phi \to \infty$ as $|r_j| \to \infty$. The Boltzmann factors attached to such a system in thermal equilibrium at reciprocal temperature β will then be

$$\begin{aligned} z(j) &= \exp \beta\mu(j) \\ \langle j|\, w\, |j+1\rangle &= \exp - \beta\phi(j, j+1), \end{aligned} \tag{2.1}$$

and we will interpret w as a matrix, z as a diagonal matrix with diagonal elements $z(j)$: $\langle j|\, z\, |j'\rangle = z(j)\, \delta(j, j')$. Since we are considering only one polymer, its concentration would vanish in an unbounded space, and so we implicitly assume that $u(j)$ is a confining potential, e.g., $u(r) \to \infty$ fast enough as $|r| \to \infty$.[6]

Our system is not invariant under any permutation of monomer indices (aside from a complete reversal), and so the grand partition function is taken as

$$\begin{aligned}\Xi &= 1+\int z(1)\,d1+\cdots\\ &\quad+\int\cdots\int z(1)\langle 1|\,w\,|2\rangle\,z(2)\langle 2|\,w\,|3\rangle\cdots z(N)\,d1\cdots dN+\cdots\\ &= 1+\langle 1|\,z(I-wz)^{-1}\,|1\rangle,\end{aligned}\tag{2.2}$$

where 1 is the vector of all 1's. It follows that in obvious notation, the monomer density is given by

$$\begin{aligned}n(r)/z(r) &= (1/\Xi)\,\delta\Xi/\delta z(r)\\ &= \langle 1|\,(I-zw)^{-1}\,|r\rangle\langle r|\,(I-wz)^{-1}\,|1\rangle/\Xi,\end{aligned}\tag{2.3}$$

or defining

$$\psi(r) = \langle r|\,(I-wz)^{-1}\,|1\rangle/\Xi^{1/2}\tag{2.4}$$

and taking account of the symmetry of w, that

$$n(r)/z(r) = \psi(r)^2,\tag{2.5}$$

as well as

$$\Xi = 1+\Xi^{1/2}\langle 1|\,z\,|\psi\rangle.\tag{2.6}$$

There is the tacit assumption in (2.2)–(2.4) that $I-wz$ is not singular, since this would in a finite system correspond to a condensation of the monomers.

The crucial relation (2.4) is certainly simple enough, but for arbitrary z is not much more explicitly amenable to solution than the inverse of an arbitrary matrix. It has the advantage of producing a one-point function, and we don't want to lose this. A convenient way to put the structure in nominal closed form is by adopting an overcomplete description,(4) i.e., for the system defined by w, represent its state by both z and ψ, and Ξ too, although they are hardly independent. In detail, we write (2.4) as

$$\psi - wz\psi = \Xi^{-1/2}\,1,\tag{2.7}$$

modify this to $(z-zwz)\,\psi-\Xi^{-1/2}z1=0$, and observe that the latter may be written as

$$\delta/\delta\psi(r)|_{z,\Xi}\ [\tfrac{1}{2}\langle\psi|\ z-zwz\ |\psi\rangle-\langle 1|\ z\ |\psi\rangle]/\Xi^{1/2}=0. \tag{2.8}$$

But also

$$\left.\frac{\delta}{\delta z(r)}\right|_{\psi,\Xi}\left[\frac{1}{2}\langle\psi|\ z-zwz\ |\psi\rangle-\Xi^{-1/2}\langle 1|\ z\ |\psi\rangle\right]$$

$$=\frac{1}{2}\psi(r)^2-\psi(r)\langle r|\ wz\ |\psi\rangle-\psi(r)/\Xi^{1/2} \tag{2.9}$$

which by virtue of (2.7) reduces to $-\frac{1}{2}\psi(r)^2$. Thus we recognize that

$$\text{if}\quad \beta\Omega=\langle\psi|\ z-zw\ |\psi\rangle-2\Xi^{-1/2}\langle 1|\ z\ |\psi\rangle+g(\Xi)$$

$$\text{then}\quad \delta\beta\Omega/\delta\psi(r)|_{z,\Xi}=0$$

$$\delta\beta\Omega/\delta z(r)|_{\psi,\Xi}=-n(r)/z(r). \tag{2.10}$$

Since the grand potential $\Omega=-\frac{1}{\beta}\ln\Xi$ can be defined by the property that

$$\delta\beta\Omega=-\int(n(r)/z(r))\,\delta z(r)\,dr, \tag{2.11}$$

it follows that (2.10) will indeed represent $\beta\Omega$ if we can guarantee that

$$\partial\beta\Omega/\partial\Xi|_{z,\psi}=0. \tag{2.12}$$

This requires that $0=g'(\Xi)+\langle 1|\ z\ |\psi\rangle/\Xi^{3/2}=g'(\Xi)+[(\Xi-1)/\Xi^{1/2}]/\Xi^{3/2}$, or $g(\Xi)=-1/\Xi-\ln\Xi$ (to within an additive constant) and hence that

$$\beta\Omega=\langle\psi|\ z-zwz\ |\psi\rangle-2\Xi^{-1/2}\langle 1|\ z\ |\psi\rangle-1/\Xi-\ln\Xi. \tag{2.13}$$

The stationarity of $\beta\Omega$ with respect to ψ and Ξ has resolved its overcompleteness.

The overcompleteness of (2.13) is actually more than absolutely necessary, but validating this remark requires a change of viewpoint. The quantity

$$v(r)\equiv n(r)/z(r) \tag{2.14}$$

which, as the ratio of density and ideal gas density, we may refer to as relative density is (as in (2.3)) conjugate to $z(r)$ with $\beta\Omega$ as appropriate thermodynamic potential. Let us now go from a $\{z(r)\}$ control description to a $\{v(r)\}$ description.$^{(3)}$ This requires expressing $z(r)$ in terms of $\{v(r)\}$ and Legendre transforming to

$$\begin{aligned}\beta\Omega + \int v(r)\, z(r)\, dr &= \beta\Omega + \int n(r)\, dr \\ &\equiv \beta\Omega^{ex},\end{aligned} \tag{2.15}$$

the excess (over ideal gas) grand potential. Now of course, we have

$$\delta\beta\Omega^{ex} = \int z(r)\, \delta v(r)\, dr, \tag{2.16}$$

so that $\delta\beta\Omega^{ex}/\delta v(r) = z(r)$, while $\delta\beta\Omega^{ex}/\delta\psi(r) = 0$, $\delta\beta\Omega^{ex}/\partial\Xi = 0$. An equivalent description is that

$$\delta\Omega^{ex} = -\int n(r)\, \delta\mu^{ex}(r)\, dr, \tag{2.17}$$

where $\mu^{ex}(r) = \mu(r) - (1/\beta)\, n(r)$.

From (2.9), we have $v(r) = -\psi(r)^2 + 2\psi(r)(wz\psi(r) + \Xi^{-1/2})$, so that

$$z(r)\, \psi(r) = \frac{1}{2}\, w^{-1} \left(\frac{v(r)}{\psi(r)} + \psi(r) - 2\Xi^{-1/2} \right). \tag{2.18}$$

Substituting into (2.15), written via (2.13) as

$$\beta\Omega^{ex} = \langle\psi|\, z - wz\, |\psi\rangle - 1/\Xi - \ln \Xi \tag{2.19}$$

yields

$$\beta\Omega^{ex} = \frac{1}{4} \left\langle \frac{v}{\psi} + \psi - 2\Xi^{-1/2} 1 \right| w^{-1} \left| \frac{v}{\psi} + \psi - 2\, \Xi^{-1/2}\, 1 \right\rangle - 1/\Xi - \ln \Xi. \tag{2.20}$$

But then $\delta\beta\Omega^{ex}/\delta\psi = 0$ tells us that $-v/\psi^2 + 1 = 0$, so $\psi = v^{1/2}$, leading to the final result

$$\beta\Omega^{ex} = \langle v^{1/2} - \Xi^{-1/2} 1|\, w^{-1}\, |v^{1/2} - \Xi^{-1/2} 1\rangle - 1/\Xi - \ln \Xi. \tag{2.21}$$

As a matter of fact, Ξ is readily eliminated from (2.21) by solving $\partial\beta\Omega^{ex}/\partial\Xi = 0$ and substituting, but we will retain the simpler form (2.21).

3. LEADING ORDER PAIR INTERACTION

The grand partition function (2.2) represents a system with only next neighbor forces. However, forces $-\nabla\tilde{\phi}$ that are physically short range can couple sites that are ordinarily far apart on the chain, giving rise to much of the interesting phenomenology associated with the system. We will now append such pair forces in a perturbative fashion, modeling our treatment after that of Mayer for imperfect fluids. We introduce the Mayer f-function

$$\langle i|\, f\, |j\rangle = e^{-\beta\tilde{\phi}(i,j)} - 1, \tag{3.1}$$

so that the grand partition function now reads

$$\Xi = 1 + \sum_{N=1} \int \prod_{1}^{N} z(i) \prod_{1}^{N-1} \langle i|\, w\, |i+1\rangle \prod_{1 \leqslant i < j \leqslant N} (1 + \langle i|\, f\, |j\rangle)\, d1 \cdots dN. \tag{3.2}$$

The expansion of (3.2) in products of the $\langle i|\, f\, |j\rangle$ is easier to organize, and harder to simplify, than that for the corresponding fluid, in which the backbone $\prod_{1}^{N-1} \langle i|\, w\, |i+1\rangle$ is missing. A typical term in the expansion has the form $\prod_k z(k) \prod_k \langle k|\, w\, |k+1\rangle \prod_{(i,j) \in G} \langle i|\, f\, |j\rangle$, where the graph G refers *only* to f-links and denotes an ordered set (e.g., lexicographically ordered) of ordered f-links $(i < j)$, with vertices imagined as ordered integers on the real axis. By a connected graph $G \subset G_c$ *in this context* we will mean a graph for which no vertex exists that divides G into two non-overlapping (but perhaps touching) left and right subgraphs. Now define $\langle i|\, C\, |j\rangle$ by summing up the contributions of connected graphs with left vertex i and right vertex $j > i$, in the sense that

$$\langle i|\, C\, |j\rangle = \sum_{G \subset G_c} \int \prod_{k=i+1}^{j-1} z(k) \prod_{k=1}^{j-1} \langle k|\, w\, |k+1\rangle \prod_{(k,\ell) \in G} \langle k|\, f\, |\ell\rangle \prod_{k=i+1}^{j-1} dk. \tag{3.3}$$

Here G_c includes the degenerate case $\langle 1|\, w\, |z\rangle$ with no f-link at all. Equation (3.2) then clearly decomposes into

$$\begin{aligned}\Xi &= 1 + \int z(1)\, d1 + \int z(1) \langle 1|\, C\, |2\rangle\, z(2)\, d1\, d2 \\ &\quad + \int z(1) \langle 1|\, C\, |2\rangle\, z(2) \langle 2|\, C\, |3\rangle\, z(3)\, d1\, d2\, d3 + \cdots \\ &= 1/\langle 1|\, z(I - Cz)^{-1}\, |1\rangle. \end{aligned} \tag{3.4}$$

In this study, we will confine our attention to the beginning of the expansion of $\langle 1|\, C\, |2\rangle$ in f-links, which will involve only a minor diagram resummation. There are further classes of diagrams that yield easily in principle and Dyson-type relations that systematize the procedure; these will be reported in the future. For the present, we proceed only through first order terms in f, analogous to stopping at second virial order in the fluid case.$^{(5)}$ To this order, amounting to retaining only subchains bound by single arbitrary-neighbor interactions:

$$\begin{aligned}\langle 1|\, C\, |2\rangle &= \langle 1|\, w\, |2\rangle + \langle 1|\, f\, |2\rangle \Big(\langle 1|\, w\, |2\rangle + \int \langle 1|\, w\, |3\rangle\, z(3) \langle 3|\, w\, |2\rangle\, d3 \\ &\qquad + \int \langle 1|\, w\, |3\rangle\, z(3) \langle 3|\, w\, |4\rangle\, z(4) \langle 4|\, w\, |2\rangle\, d3\, d4 + \cdots \Big) \\ &= \langle 1|\, w\, |2\rangle + \langle 1|\, f\, |2\rangle \langle 1|\, w(I - zw)^{-1}\, |2\rangle, \end{aligned} \tag{3.5}$$

so that, using the convention

$$\langle 1|\, a \wedge b\, |2\rangle = \langle 1|\, a\, |2\rangle \langle 1|\, b\, |2\rangle, \tag{3.6}$$

we have

$$\Xi = 1 + \langle 1|\, z(I - [w + f \wedge w(I - zw)^{-1}]\, z)^{-1}\, |1\rangle. \tag{3.7}$$

One can also restrict f to non-next neighbor interactions, which slightly changes the structure of (3.5).

Technically, the $f \wedge g$ term in (3.5) breaks the simple connectedness of the path from 1 to 2, and hence its representation as a matrix product. It is therefore convenient to represent $\langle 1|\, f\, |2\rangle$, highly non-uniquely, in the bilinear form

$$\langle 1|\, f\, |2\rangle = \sum_\alpha \chi_\alpha^*(1)\, f_\alpha\, \chi_\alpha(2), \tag{3.8}$$

where α must cover the range of f but is otherwise unrestricted. The symmetry of $\langle 1|\, f\, |2\rangle$ tells us that

$$\langle 1|\, f\, |2\rangle = \sum_\alpha \chi_\alpha(1)\, f_\alpha\, \chi_\alpha^*(2), \tag{3.9}$$

as well, and the reality of $\langle 1|\, f\, |2\rangle$ that f_α may be taken as real. If we introduce the diagonal matrix

$$\langle 1|\, \chi_\alpha\, |2\rangle \equiv \chi_\alpha(2)\, \delta(1, 2), \tag{3.10}$$

then

$$f \wedge g = \sum_{\alpha} f_{\alpha} \chi_{\alpha}^{+} g \chi_{\alpha}, \tag{3.11}$$

so that

$$I - Cz = I - wz - \sum_{\alpha} f_{\alpha} \chi_{\alpha}^{+} (I - wz)^{-1} wz \chi_{\alpha}, \tag{3.12}$$

and

$$\Xi = 1 + \langle 1 | \, z \left(I - wz - \sum_{\alpha} f_{\alpha} \chi_{\alpha}^{+} (I - wz)^{-1} wz \chi_{\alpha} \right)^{-1} | 1 \rangle. \tag{3.13}$$

Using the general

$$\delta A^{-1} = -A^{-1} \, \delta A \, A^{-1}, \tag{3.14}$$

as we have done before, and threading through the operation $\delta / \delta z(r)$, we therefore have the extended profile relation

$$\begin{aligned} n(r)/z(r) &= \Xi^{-1} \, \delta \Xi / \delta z(r) \\ &= \Xi^{-1} [\langle 1 | \, (I - zC)^{-1} \, | r \rangle \langle r | \, (I - Cz)^{-1} \, | 1 \rangle \\ &\quad + \sum_{\alpha} f_{\alpha} \langle 1 | \, (I - zC)^{-1} \, \chi_{\alpha}^{+} zw (I - zw)^{-1} \, | r \rangle \\ &\quad \times \langle r | \, wz (I - wz)^{-1} \, \chi_{\alpha} (I - Cz)^{-1} \, | 1 \rangle] \end{aligned} \tag{3.15}$$

4. OVERCOMPLETE FUNCTIONAL

Again, the notations $(I - zw)^{-1}$ and $(I - zC)^{-1}$ conceal our inability to deal explicitly with arbitrary z, and again, an overcomplete representation offers an avenue of relative escape. We follow the procedure of Section 2. Define

$$\begin{aligned} \psi &= \Xi^{-1/2} (I - Cz)^{-1} \, 1 \\ \psi_{\alpha} &= (I - wz)^{-1} \, wz \chi_{\alpha} \psi, \end{aligned} \tag{4.1}$$

so that

$$n(r)/z(r)=\psi(r)^2+\sum_\alpha f_\alpha\psi_\alpha^*(r)\,\psi_\alpha(r). \tag{4.2}$$

Now

$$\begin{aligned}\psi_\alpha-wz\psi_\alpha&=wz\chi_\alpha\psi\\ \psi-wz\psi-\sum_\alpha f_\alpha\chi_\alpha^+\psi_\alpha&=\Xi^{-1/2}1.\end{aligned} \tag{4.3}$$

f_α is real, and so, taking the real part of the second relation, we rewrite (4.3) as

$$\begin{aligned}(w^{-1}-z)\,\psi_\alpha-z\chi_\alpha\psi&=0\\ 2z(I-wz)\,\psi-\sum_\alpha f_\alpha(z\chi_\alpha^+\psi_\alpha+z\chi_\alpha\psi_\alpha^*)-2\Xi^{-1/2}z1&=0\end{aligned} \tag{4.4}$$

Eqs. (4.4) are in fact equivalent to (4.3), as is readily verified by solving for ψ and comparing with (4.1) and (3.12). In terms of the functional (the hermitian scalar product is now implicit)

$$\begin{aligned}\Lambda=&\langle\psi|\,z-zwz\,|\psi\rangle-2\Xi^{-1/2}\langle 1|\,z\,|\psi|\rangle\\ &-\sum_\alpha f_\alpha\langle\psi|\,z\,|\chi_\alpha\psi_\alpha^*+\chi_\alpha^+\psi_\alpha\rangle+\sum_\alpha f_\alpha\langle\psi_\alpha|\,(w^{-1}-z)\,|\psi_\alpha\rangle,\end{aligned} \tag{4.5}$$

we see that

$$\begin{gathered}\delta\Lambda/\delta\psi_\alpha^*(r)|_{z,\psi,\Xi}=0,\qquad \delta\Lambda/\delta\psi_\alpha(r)|_{z,\psi,\Xi}=0,\\ \delta\Lambda/\delta\psi(r)|_{z,\{\psi_\alpha\},\Xi}=0\end{gathered} \tag{4.6}$$

The functional Λ is very close to the desired generating potential. We first observe that

$$\begin{aligned}\delta\Lambda/\delta z(r)|_{\psi,\{\psi_\alpha\},\Xi}=&\,\psi(r)^2-2\psi(r)\,wz\psi(r)-2\Xi^{-1/2}\psi(r)\\ &-\sum_\alpha f_\alpha\psi(r)(\chi_\alpha\psi_\alpha^*+\chi_\alpha^+\psi_\alpha)(r)-\sum_\alpha f_\alpha\psi_\alpha^*(r)\,\psi_\alpha(r),\end{aligned} \tag{4.7}$$

which by virtue of the second of (4.3) and its conjugate reduces precisely to $-\psi(r)^2 - \sum_\alpha f_\alpha \psi_\alpha^*(r)\, \psi_\alpha(r)$ and hence to $-n(r)/z(r)$. In other words, we have $\delta\Lambda|_\Xi = -\int n(r)/z(r)\, \delta z(r)\, dr$. Since $\partial\Lambda/\partial\Xi \equiv \Xi^{-3/2} \int z(r)\, \psi(r)\, dr = (\Xi - 1)/\Xi^2$, as in the case of Section 2, we conclude that

$$\beta\Omega[z, \psi, \{\psi_\alpha\}, \Xi] = \Lambda - \ln \Xi - 1/\Xi. \tag{4.8}$$

For potential reduction of the overcompleteness of (4.8), we again switch from a z to a $v = n/z$ representation. This requires

$$\begin{aligned}\beta\Omega^{ex} &= \Lambda - \int z(r)\, \frac{\delta\Lambda}{\delta z(r)}\, dr - \ln \Xi - 1/\Xi \\ &= \langle\psi|\, zwz\, |\psi\rangle + \sum_\alpha f_\alpha \langle\psi_\alpha|\, w^{-1}\, |\psi_\alpha\rangle - \ln \Xi - 1/\Xi. \end{aligned} \tag{4.9}$$

But (4.7), in the form

$$\begin{aligned} v(r) = {}& 2\psi(r)\, wz\psi(r) + \sum f_\alpha \psi_\alpha^*(r)\, \psi_\alpha(r) \\ & - \psi(r)^2 + \sum f_\alpha \psi(r)[\chi_\alpha \psi_\alpha^*(r) + \chi_\alpha^+ \psi_\alpha(r)] + 2\Xi^{-1/2}\, \psi(r), \end{aligned} \tag{4.10}$$

allows us to eliminate z in favor of v, resulting in

$$\begin{aligned} \beta\Omega^{ex} = {}& \sum f_\alpha \langle\psi_\alpha|\, w^{-1}\, |\psi_\alpha\rangle - \ln \Xi - 1/\Xi \\ & + \frac{1}{4} \Big\langle \frac{v - \sum f_\alpha \psi_\alpha^* \psi_\alpha}{\psi} + \psi - 2\Xi^{-1/2}\ 1 - \sum f_\alpha (\chi_\alpha \psi_\alpha^* + \chi_\alpha^+\ \psi_\alpha)\, |w^{-1}| \\ & \times \frac{v - \sum f_\alpha \psi_\alpha^* \psi_\alpha}{\psi} + \psi - 2\Xi^{-1/2}\ 1 - \sum f_\alpha (\chi_\alpha \psi_\alpha^* + \chi_\alpha^+\ \psi_\alpha) \Big\rangle \end{aligned} \tag{4.11}$$

Elimination of $\psi(r)$ from (4.11) is again routine. From $\delta\Omega^{ex}/\delta\psi(r) = 0$, we have $1 - \frac{v}{\psi^2} + \sum f_\alpha \frac{\psi_\alpha^* \psi_\alpha}{\psi^2} = 0$, precisely as in (4.2). Thus, $\psi = (v - \sum f_\alpha \psi_\alpha^* \psi_\alpha)^{1/2}$ and we can therefore rewrite (4.11) as

$$\begin{aligned} \beta\Omega^{ex} &= -\ln \Xi - 1/\Xi + \sum f_\alpha \langle\psi_\alpha|\, w^{-1}\, |\, \psi_\alpha\rangle + \langle\Psi|\, w^{-1}\, |\Psi\rangle, \\ \text{where}\quad \Psi &= \left(v - \sum f_\alpha \psi_\alpha^* \psi_\alpha\right)^{1/2} - \Xi^{-1/2} - \frac{1}{2} \sum f_\alpha (\chi_\alpha \psi_\alpha^* + \chi_\alpha^+ \psi_\alpha), \end{aligned} \tag{4.12}$$

an evident generalization of (2.21). A more compact form, in terms of an indefinite (real) metric $A \cdot B = \sum f_\alpha A_\alpha B_\alpha$, is

$$\beta\Omega^{ex} = -\ln \Xi - 1/\Xi + \int w^{-1}(12)\, \psi^*(1) \cdot \psi(2)\, d1\, d2 + \langle \Psi |\, w^{-1}\, | \Psi \rangle$$

$$\text{where } \Psi = (v - \psi^* \cdot \psi)^{1/2} - \Xi^{-1/2} - \operatorname{Re} \psi^* \cdot \chi \text{ and } \chi^*(1) \cdot \chi(2) = \langle 1 |\, f\, | 2 \rangle. \tag{4.13}$$

5. CONCLUDING REMARKS

The expression (4.12), and its variational consequences, constitute the formulation desired. However, there are two obvious complications. First is that there are an enormous number of functions $\{\psi_\alpha\}$ to deal with—although the expression (4.13) suggests several possibilities for doing so. Second, the actual form of (4.12) is not unique, since only the relation (3.8) among the $\{f_\alpha\}$ and $\{\chi_\alpha\}$ has to be satisfied. A variational ansatz such as $\psi_\alpha = \chi_\alpha\, \phi$, valid according to (4.1) if each χ_α is slowly varying, with a common ϕ, addresses both of these problems.

In this approximation (choosing ϕ as real), (4.12) is replaced by the much simpler

$$\beta\Omega^{ex} = -\ln \Xi - 1/\Xi + \langle \phi |\, f \Lambda w^{-1}\, | \phi \rangle + \langle \Psi |\, w^{-1}\, | \Psi \rangle$$

$$\text{where } \Psi = (v - g\phi^2)^{1/2} - g\phi - \Xi^{-1/2} \text{ and } g = \langle r |\, f\, | r \rangle, \tag{5.1}$$

very much in the mold of (2.13). The consequences of (5.1) have yet to be delineated.

Summing up, our tacit objective has been to get a feeling for the fashion in which analysis of polymer chains with long-range interactions, ordinally speaking, might proceed, rather than developing systematic brute force techniques for the purpose. We have focussed upon variational approaches of the density functional type, with their obvious close association with a thermodynamic viewpoint. This means that at most one-point fields are legitimate intermediaries, and the "algebraic" problems are related to this requirement. In particular, we found that even at the equivalent of a second order virial correction with respect to non-neighbor pairs, a whole set of one-point quantities is called for, which must thereafter be reduced in some sequential fashion, of which we only examined leading order. Nonetheless, the concepts we were forced to introduce are of much greater applicability, and we are in the process of applying them to the case of non-symmetric next-neighbor interactions (already considered in ref. 3) which in fact offers a formal avenue of entree to given heteropolymeric ordering as well. The consequences will be reported in a future communication, in the context of a systematic diagram resummation of which only leading order has been presented here. We are also in the process of developing exactly solvable (but of course very special) models to serve as analytic checks on suggested approximations, as well as a number of strictly numerical comparisons.

ACKNOWLEDGMENTS

A portion of this research was carried out at the Institute of Theoretical Physics, University of California, Santa Barbara, supported in part by NSF Grant PHY99-07949.

REFERENCES

1. See, e.g., D. Henderson (ed.), *Fundamentals of Inhomogeneous Fluids* (Dekker, 1992).
2. J. K. Percus, Higher spin one-dimensional Ising lattice in arbitrary external field, *J. Math. Phys.* **23**:1162 (1982).
3. J. K. Percus, Non-uniform classical fluid mixture in one-dimensional space with next neighbor interactions, *J. Statist. Phys.* **89**:249 (1997).
4. J. K. Percus and L. Šamaj, Exact free energy functionals for non-simply connected lattices, *J. Statist. Phys.* **77**:421 (1994)
5. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, 1986).
6. H. L. Frisch and J. K. Percus, Single homopolymers in the relative density representation, *Phys. Rev. E* **64**:011805 (2001).