PHYSICAL REVIEW E, VOLUME 64, 011805

Single homopolymers in the relative density representation

H. L. Frisch[1] and J. K. Percus[2,3]
[1]Chemistry Department, State University at Albany, Albany, New York 12222
[2]Courant Institute, New York University, New York, New York 10012
[3]Physics Department, New York University, New York, New York 10003

(Received 22 March 2001; published 26 June 2001)

A single symmetric homopolymer is studied in the grand ensemble of its monomeric units. For an arbitrary external field but next neighbor interactions alone, such a system is represented as a functional of the local density to local fugacity ratio, conjugate to the fugacity, with the excess grand potential as thermodynamic generating function. A sample case in a spherical enclosure is solved, where a complementary exclusion from a spherical volume requires an extension to a grand ensemble of polymers. A preliminary extension is also made in mean field form to non-neighbor interactions, as well as to nonsymmetric interactions.

DOI: 10.1103/PhysRevE.64.011805 PACS number(s): 36.20.−r, 82.60.−s

I. INTRODUCTION

In this paper, we present an exact full analysis of an alternative density functional theory of a single freely jointed polymer chain. In particular, we discuss a chain located in a spherical pore, or on the outside of a spherical surface or plane surface. We will treat further related interactions by a perturbative mean field technique. Previous density functional treatments of polymers in cavities or at walls either were approximations, e.g., based on a Curtin-Ashcroft type weighted density approximation [1], a combined Monte Carlo simulation with a self-consistent density field [2,3], or earlier Cahn-like treatments [4–6].

There is also a very old discussion by Lifschitz [7] of conditions under which a polymeric chain with mean field interactions could collapse to form a globular structure. The technique used has much in common with the presentation that we will adopt, but several differences are apparent. Thus, although we work in a grand ensemble framework, which both simplifies the necessary algebraic manipulations and raises the possibility of collapse even in the absence of long-range interactions, the format that we introduce in the next two sections has relative density [8] as its control variable. This produces a particularly compact representation, some aspects of which are then exemplified, and as is typical of indirect forms—such as standard density functional theory—permits quite painless introduction of further interactions, non-nearest neighbor in this case, at any level of approximation. It also leads naturally to the possibility of nonsymmetric next neighbor interaction, e.g., a definite parity associated with the chain. In the Appendix we present a toy model in which this viewpoint plays a pivotal role.

II. BASIC FORMALISM

We consider the behavior in thermal equilibrium of a single homopolymer with symmetric next neighbor interactions. The interaction ϕ is of binding type, so that the Boltzmann factor $e^{-\beta\phi}\to 0$ at infinite separation. The statistical ensemble employed here is (classical) grand canonical for the monomeric units, controlled in this initial manifestation by the reciprocal temperature β and chemical potential μ, but also by an external potential u which enters the thermodynamics as $\mu(u)=\mu-u(i)$, the argument i denoting all degrees of freedom of the ith monomer. Let us adopt the notation $\langle i|\omega|j\rangle=e^{-\beta\phi(i,j)}$ for the Boltzmann factor regarded as a symmetric matrix, and $\langle i|z|j\rangle=z(i)\delta(i,j)$, where $z(i)=e^{\beta\mu(i)}$ is the externally imposed local fugacity. For idealized point monomers, the arguments $i,j,\ldots$ will represent continuous physical space locations, often designated by r when the argument is to be highlighted.

The situation described here was previously treated [8] in considerable generality in the context of nonbinding interaction, as in a fluid, but we will learn a good deal more by restricting the scope of the system to be studied. The partition function, with the fugacity attached, of an N-element chain is given by

$$\Xi_N=\int z(1)\langle 1|w|2\rangle z(2)\ldots z(N-1)\times\langle N-1|w|N\rangle z(N)\,d1\ldots dN, \tag{2.1}$$

rendered compact by introducing the constant vector $J(i)=1$, so that

$$\Xi_N=\langle J|z(wz)^{N-1}|J\rangle \tag{2.2}$$

for $N\geqslant 1$. Appending $\Xi_0=1$, and observing that an ordered chain does not have equivalent configurations under the permutation of monomers, the full grand partition function $\Xi=1+\Sigma_{N=1}^{\infty}\Xi_N$ becomes

$$\Xi=1+\langle J|z(I-wz)^{-1}|J\rangle, \tag{2.3}$$

where I denotes the identity matrix; the corresponding grand potential is then

$$\Omega=-\frac{1}{\beta}\ln\Xi. \tag{2.4}$$

Now let us attend to the spatial structure of the thermal ensemble. The basic construct is monomer density $n(r)$, obtained by anchoring one monomer at r and dividing by Ξ for normalization,

1063-651X/2001/64(1)/011805(5)/$20.00

$$n(r)=(1/\Xi)z(r)\,\delta\Xi/\delta z(r) \tag{2.5}$$

[equivalent, of course, to $n(r)=-\delta\Omega/\delta\mu(r)$]. Using the general relation $\delta A^{-1}=-A^{-1}\delta A A^{-1}$, Eqs. (2.3) and (2.5) yield, at once,

$$n(r)=\frac{1}{\Xi}\langle J|(I-zw)^{-1}|r\rangle z(r)\langle r|(I-wz)^{-1}|J\rangle, \tag{2.6}$$

which by the symmetry of w can be written as

$$n(r)/z(r)=\psi(r)^2/\Xi,$$

$$\text{where}\quad \psi(r)=\langle r|(I-wz)^{-1}|J\rangle \tag{2.7}$$

We also note, from Eq. (2.3), that

$$\Xi=1+\langle J|z\psi\rangle. \tag{2.8}$$

III. v REPRESENTATION

Although Eqs. (2.7) and (2.8) complete our required description, their use of fugacity $z(r)$ as control field is unsuitable for many extensions and applications. A thoroughly studied alternative is that of expressing the system characteristics in terms of density functionals, but we will opt for an intermediary strategy, involving a less common Legendre transform, that corresponding to the relative density (relative to an ideal gas),

$$v(r)=n(r)/z(r) \tag{3.1}$$

as independent control variable [8]. Since

$$\delta\Omega=-\int n(r)\,\delta\mu(r)\,dr=(-1/\beta)\int n(r)\,\delta z(r)/z(r)\,dr=$$

$$(-1/\beta)\int n(r)[\delta n(r)/n(r)-\delta v(r)/v(r)]dr,$$

we have

$$\delta(\beta\Omega+N)=\delta\beta\Omega^{\mathrm{ex}}=\int z(r)\,\delta v(r)\,dr,$$

or

$$z(r)=\delta\beta\Omega^{\mathrm{ex}}/\delta v(r). \tag{3.2}$$

$\beta\Omega^{\mathrm{ex}}$ serves as thermodynamic potential in a v representation, with $z(r)$ as a conjugate field. An overwhelming advantage of this formalism is, as we will see in a moment, that we can set up an explicit form for the functional $\beta\Omega^{\mathrm{ex}}[v]$ in which, as opposed to Eq. (2.3), only inverses of fixed matrices appear.

Actually, it will be convenient to write $\beta\Omega^{\mathrm{ex}}$ redundantly in terms of Ξ as well, so that we will want to have

$$\delta\beta\Omega^{\mathrm{ex}}[v,\Xi]/\delta v(r)=z(r),$$

$$\partial\beta\Omega^{\mathrm{ex}}[v,\Xi]/\partial\Xi=0, \tag{3.3}$$

which both determine Ξ and guarantee that $\delta\beta\Omega^{ex}=\int z(r)\,dv(r)\,dr$. Enforcing Eqs. (3.3) is no problem. We rewrite Eq. (2.7) as

$$(I-wz)\psi=J,\quad v=\psi^2/\Xi, \tag{3.4}$$

and then $z\psi=w^{-1}(\psi-J)$ implies that

$$z=v^{-1/2}w^{-1}(v^{1/2}-\Xi^{-1/2}J). \tag{3.5}$$

From the first of Eqs. (3.3), it follows that

$$\beta\Omega^{\mathrm{ex}}=\int(v^{1/2}(r)-\Xi^{-1/2})\langle r|w^{-1}|r'\rangle$$

$$\times(v^{1/2}(r')-\Xi^{-1/2})\,dr\,dr'+f(\Xi), \tag{3.6}$$

where $f(\Xi)$ is to be determined by the second of Eqs. (3.3), which reads

$$\begin{aligned}0&=f'(\Xi)+\Xi^{-3/2}\int\langle r|w^{-1}|r'\rangle\\&\quad\times(v^{1/2}(r')-\Xi^{-1/2})\,dr\,dr'\\&=f'(\Xi)+\Xi^{-2}\langle r|w^{-1}|\psi-J\rangle\\&=f'(\Xi)+\Xi^{-2}(\Xi-1).\end{aligned}$$

Thus, $f(\Xi)=-1/\Xi-\ln\Xi$ to within an additive constant, and we conclude that, in obvious notation,

$$\beta\Omega^{\mathrm{ex}}[v,\Xi]=-\ln\Xi-\frac{1}{\Xi}+(v^{1/2}-\Xi^{-1/2})$$

$$\times w^{-1}(v^{1/2}-\Xi^{-1/2}). \tag{3.7}$$

IV. CONFINED SYSTEMS

For the dual purposes of understanding Eqs. (3.7) and being aware of potential dangers, the direct formulations (2.7) and (2.8) in the form preceding Eq. (3.5), are quite sufficient. Suppose, in particular, that the polymer is inside a cavity denoted by Λ; then, from $z\psi=w^{-1}(\psi-1)$, we can write

$$w^{-1}(\psi-1)=0\quad\text{for}\ r\in\overline{\Lambda},$$

$$(w^{-1}-z_0)(\psi-1)=z_0\quad\text{for}\ r\in\Lambda, \tag{4.1}$$

where z_0 is the imposed fugacity, and of course $\psi\rightarrow 1$ asymptotically. A simple interaction for which w^{-1} is very accessible is the Yukawa or shielded Coulomb form

$$\langle r|w|r'\rangle=Ae^{-K|r-r'|}/|r-r'| \tag{4.2}$$

(corresponding to the trapping potential $\beta\phi(r,r')=K|r-r'|+\ln|r-r'|-\ln A$, which makes sense if mean next neighbor separations are large enough). Equation (4.2) is the Green's function for the Helmholtz operator, and so

$$w^{-1}=\frac{1}{4\pi A}(K^2-\nabla^2), \tag{4.3}$$

meaning of course that

$$\langle r|w^{-1}|r'\rangle=(1/4\pi A)(K^2-\nabla^2)\,\delta(r-r').$$

Thus we can write

$$\begin{aligned}(K^2-\boldsymbol{\nabla}^2)(\psi-1)&=0 \quad \text{for} \quad r\in\overline{\Lambda},\\ (K'^2-\boldsymbol{\nabla}^2)(\psi-1)&=K^2-K'^2 \quad \text{for} \quad r\in\Lambda,\end{aligned} \tag{4.4}$$

where $K'^2=K^2-4\pi A z_0$, and, with connection conditions obtained by integrating across the boundary, $\partial\Lambda{:}\,\psi-1$ and $\hat{n}\cdot\boldsymbol{\nabla}(\psi-1)$ are continuous across $\partial\Lambda$.

Consider the special case of a spherical cavity of radius a. Setting

$$\phi(r)=r[\psi(r)-1], \tag{4.5}$$

we have

$$\begin{gathered}K^2\phi(r)-\phi''(r)=0, \quad r\geqslant a\\ K'^2\phi(r)-\phi''(r)=(K^2-K'^2)r, \quad r\leqslant a\\ \phi(r),\phi'(r) \quad \text{continuous across} \quad r=a,\end{gathered} \tag{4.6}$$

solvable routinely to yield, inside the cavity,

$$\phi(r)=\frac{K^2-K'^2}{K'^2}\left(r-\frac{1+Ka}{K\sinh K'a+K'\cosh K'a}\sinh K'r\right) \quad \text{for} \quad r\leqslant a. \tag{4.7}$$

Consequently,

$$n(r)=(z_0/\Xi)\,\psi(r)^2,$$

where

$$\psi(r)=\frac{K^2}{K'^2}-\frac{K^2-K'^2}{K'^2}\frac{1+Ka}{K\sinh K'a+K'\cosh K'a}\times\frac{\sinh K'r}{r} \quad \text{for} \quad r\leqslant a \tag{4.8}$$

and

$$\Xi=1+z_0\int_0^a\psi(r)d^3r.$$

There are now two regimes to study. If $4\pi A z_0<K^2$, K' is real, and $\psi(r)$ decreases as r increases to a, but $\psi(r)>1$ throughout. At the crossover given by $K'=0$,

$$\psi(r)=1+\frac{\frac{1}{2}-\frac{1}{6}Ka}{1+Ka}(Ka)^2-\frac{1}{6}(Kr)^2\geqslant 1.$$

But then, for $4\pi A z_0>K^2$, we can set $K'=iK''$ to obtain

$$\psi(r)=-\frac{K^2}{K''^2}+\frac{K^2+K''^2}{K''^2}\frac{1+Ka}{K\sin K''a+K''\cos K''a}\frac{\sin K''r}{r}, \tag{4.9}$$

again a decreasing function of r as long as $K\sin K''a+K''\cos K''a>0$. However, this decays from

$$\psi(0)>\frac{K^2+K'^2}{K''^2}\frac{\left(1-\cos K''a\right)+Ka\left(1-\dfrac{\sin K''a}{K''a}\right)}{K\sin K''a+K''\cos K''a}, \tag{4.10}$$

which becomes arbitrarily large as K'' is varied, so that $K\sin K''a+K''\cos K''a\to 0$. Beyond this condensation, the grand ensemble ceases to be meaningful: as one readily verifies, the eigenvalues of zw are given here by

$$\tan[K''(\lambda)a]/[K''(\lambda)a]=-1/Ka, \tag{4.11}$$

where $K''(\lambda)^2=4\pi A z_0/\lambda-K^2$, or

$$\lambda=4\pi A z_0/(K''(\lambda)^2-K^2), \tag{4.12}$$

and the threshold for $\lambda=1$ is precisely at the first vanishing of $K\sin K''a+K''\cos K''a$ (occurring for $\pi/2<K''a<\pi$).

V. UNCONFINED SYSTEMS

An opposite situation is that of indefinite confinement. Suppose that the polymer is constrained to be outside the sphere $r\leqslant a$, but that the spherical surface has a ''glue'' layer, so that

$$z(r)=z_0\theta(r-a)+\gamma\delta(r-a). \tag{5.1}$$

This setup is a bit different. We cannot have a single polymer ensemble because, with the infinite space available, it will always evaporate away. But we can for example imagine a fluid of noninteracting polymers, with asymptotic monomer concentration controlled by the same fugacity we have already included. For such a system, the grand potential will be $\Xi_{\mathrm{ToT}}=1+\Xi+1/2!\,\Xi^2+1/3!\,\Xi^3+\cdots$, or

$$\Xi_{\mathrm{ToT}}=\exp\Xi, \tag{5.2}$$

and so the only change will be that now $n(r)=z(r)(\delta/\delta z(r))\ln\Xi_{\mathrm{ToT}}=z(r)\,\delta\Xi/\delta z(r)$. Hence, with the same notation as before for z, v, ψ, Eq. (2.7) must be replaced by

$$n(r)=z(r)\psi(r)^2, \tag{5.3}$$

but nothing else will change.

Now we can proceed. From $z\psi=w^{-1}(\psi-1)$, or $(1/4\pi A)(K^2-\nabla^2)(\psi-1)=(z_0\theta(r-a)+\gamma\delta(r-a))\psi$, we have, in the previous notation,

$$\begin{gathered}K^2\phi(r)-\phi''(r)=0, \quad r<a\\ K'^2\phi(r)-\phi''(r)=(K^2-K'^2)r, \quad r>a\\ \phi(a^+)=\phi(a^-) \quad \text{but} \quad \phi'(a^+)-\phi'(a^-)=-4\pi A\gamma a.\end{gathered} \tag{5.4}$$

Again, the solution is routine, and we find that

$$r>a:\ \phi(r)=K^2/K'^2 + \frac{4\pi A\gamma a-(K^2/K'^2-1)(Ka\coth Ka-1)}{K\coth Ka+K'} \times\frac{e^{-K(r-a)}}{r}. \qquad (5.5)$$

Interestingly, there is a transition from depletion to accumulation next to the surface at a characteristic value of γ (or of z_0 at fixed γ). This is seen more clearly if we take the limit $\psi_1(z)$ of $\psi(a+z)$ as $a\rightarrow\infty$, thereby converting the sphere to a planar surface with z its outward direction. Doing so, then

$$\psi_1(z)=\frac{K^2}{K'^2}+\frac{4\pi A}{K+K'}\left(\gamma-\frac{Kz_0}{K''^2}\right)e^{-K'z}; \qquad (5.6)$$

thus the switch occurs at $\gamma=Kz_0/K+K'$, and the asymptotic monomer density is $n(\infty)=z_0(K/K')\psi$. Note that here, the system collapses as $K'\rightarrow 0$.

VI. EFFECT OF LONG-RANGE FORCES

It is the one-dimensional ordering of monomers, and corresponding spatial separation of next neighbor monomer interactions, that leads to the simplicity of the above analysis. But the physical interactions are of two kinds: the next neighbor binding that we have accounted for, and the (at least) pair forces due to physical proximity which need not be ordinal proximity. This situation is of course inherently much more complex, but we can make inroads in mean field fashion. Suppose that we append to the interaction

$$\Delta\phi=\tfrac{1}{2}\sum_{i\neq j}\overline{\phi}(i,j)=\tfrac{1}{2}\int\hat{n}_2(1,2)\overline{\phi}(1,2)d1\,d2,$$

where (6.1)

$$\hat{n}_2(r,r')=\sum_{i\neq j}\delta(r_i-r)\delta(r_j-r')$$

is the microscopic pair distribution. Since the grand potential serves as a universal generating functional we have for the expectation $n_2=\langle\hat{n}_2\rangle$,

$$\frac{\delta\beta\Omega}{\delta\beta\overline{\Omega}(1,2)}=\frac{1}{2}n_2(1,2), \qquad (6.2)$$

so, for weak $\overline{\phi}$, we can write

$$\beta\Omega=\beta\Omega_0+\tfrac{1}{2}\int n_{20}(1,2)\beta\overline{\phi}(1,2)d1\,d2. \qquad (6.3)$$

In the mean field approximation, density fluctuations are neglected, and we have simply

$$\beta\Omega=\beta\Omega_0+\tfrac{1}{2}\int n_0(1)n_0(2)\beta\overline{\phi}(1,2)d1\,d2, \qquad (6.4)$$

where the subscript 0 refers uniformly to the $\overline{\phi}=0$ expressions.

We have seen that, for pure chains,

$$n=vz=v/\psi w^{-1}(\psi-J)=v^{1/2}/\Xi^{1/2}w^{-1}(\Xi^{-1/2}v^{1/2}-1) =v^{1/2}w^{-1}(v^{1/2}-\Xi^{-1/2}).$$

Hence, we can generalize Eq. (3.7) to the approximation

$$\beta\Omega^{\mathrm{ex}}[v,\Xi]=-\ln\Xi-\frac{1}{\Xi}+(v^{1/2}-\Xi^{1/2}) \times\left(w^{-1}+\frac{1}{2}w^{-1}v^{1/2}\beta\overline{\phi}v^{1/2}w^{-1}\right) \times(v^{1/2}-\Xi^{-1/2}), \qquad (6.5)$$

where $v^{1/2}$ is diagonal when used as an operator. Since $(w+\Delta)^{-1}=w^{-1}-w^{-1}\Delta w^{-1}+\cdots$, we have in effect made the replacement

$$w\rightarrow w-\tfrac{1}{2}v^{1/2}\beta\overline{\phi}v^{1/2} \qquad (6.6)$$

of the next neighbor Boltzmann factor, subject to the warning that Eq. (6.6) is v dependent so that this will not be the only change in the profile equation for $z(v)$. Part of the change of Eq. (6.6) is obvious: since the added interaction also appears between next neighbors, there is a direct change $w=e^{-\beta\phi}\rightarrow e^{-\beta(\phi+\overline{\phi})}=w-\beta\overline{\phi}w\ldots$, but this is only one of several components of the modification.

For computational purposes, the relative density form [Eq. (6.5)] is most suitable. It is only necessary to rewrite the profile equation (3.3) at fixed imposed fugacity in the strictly stationary form

$$\delta\left[\beta\Omega^{\mathrm{ex}}[v,\Xi]-\int v(r)z(r)dr\right]=0, \qquad (6.7)$$

parametrize v, and vary the parameters. Of course, an obvious strategy is to use a $\overline{\phi}=0$ reference solution such as Eq. (4.8), and (with its $r>a$ extension as well) convert its parameters to effective ones to be determined by stationarity. Sample results will be reported in a future communication.

ACKNOWLEDGMENTS

This research was supported in part by NSF Grant Nos. DMR 9623224 and CHE 9708562. J. K. P. would like to thank the Institute for Theoretical Physics, University of California, Santa Barbara for its hospitality during the completion of this paper (the research was supported in part by the National Science Foundation under Grant No. PHY99-07949), and the authors gratefully acknowledge the assistance of S. Pasqual in performing the numerical work that motivated several portions of the paper.

APPENDIX: NONSYMMETRIC INTERACTION

A polymer of identical monomers need not have even parity, e.g., site A on one monomer interacts with site B of its neighbor. Then the Boltzmann factor $w(r,r')$ will not be symmetric, and the general strategy must be modified. Let us see how this works from the profile point of view [9], relegating energetic considerations [8] to the future. Equation (2.3) is still valid,

$$\Xi = 1 + \langle J | z(I - wz)^{-1} | J \rangle, \tag{A1}$$

but Eqs. (2.6)–(2.8) now become

$$n(r)/z(r) = \hat{\psi}(r)\psi(r)/\Xi,$$

where

$$(I - wz)\psi(r) = J, \quad (I - w^T z)\hat{\psi}(r) = J, \tag{A2}$$

and

$$\Xi = 1 + \langle J | z\psi \rangle = 1 + \langle J | z\hat{\psi} \rangle.$$

Then, defining $\phi = \psi/\Xi$ and $\hat{\phi} = \hat{\psi}/\Xi$, z can be eliminated to give, in brief notation

$$\phi - w\frac{n}{1 + w^T n/\phi} = 1, \quad \hat{\phi} - w^T \frac{n}{1 + wn/\hat{\phi}} = 1, \tag{A3}$$

and the major task is to solve for ϕ and $\hat{\phi}$. Several solvable cases of discrete systems were examined long ago [9]. Prototypical is that in which

$$w(x,x') = A\delta(x' - x - 1), \tag{A4}$$

representing a one-dimensional lattice gas on an integer lattice. Here we have

$$\phi(x) = \frac{An(x+1)}{1 + an(x)/\phi(x)} + 1, \tag{A5}$$

and, similarly for $\hat{\phi}$, two instantly solvable quadratic relationships, equivalent to previous solutions [10] of this model.

---

[1] A. Yethiraj, J. Chem. Phys. **109**, 3289 (1998).

[2] A. Yethiraj and C. E. Woodward, J. Chem. Phys. **102**, 5499 (1994).

[3] J. B. Hooper, J. D. McCoy, and J. G. Curro, J. Chem. Phys. **112**, 3090 (2000); J. B. Hooper, M. T. Pioggi, J. D. McCoy, and F. Weinhold, *ibid.* **112**, 3094 (2000), and papers cited therein.

[4] I. Schmidt and K. Binder, J. Phys. II **46**, 1631 (1985).

[5] S. K. Nath, J. D. McCoy, J. D. Curro, and A. Saunders, J. Polym. Sci., Part B: Polym. Phys. **33**, 2307 (1985).

[6] K. F. Freed, J. Chem. Phys. **105**, 10572 (1996).

[7] I. M. Lifschitz, Sov. Phys. JETP **55**, 2408 (1968); also see L. A. Blumenfeld, *Problems of Biological Physics* (Springer-Verlag, Berlin, 1981).

[8] J. K. Percus, J. Stat. Phys. **89**, 249 (1997).

[9] J. K. Percus, J. Math. Phys. **23**, 1142 (1982).

[10] J. K. Percus, J. Stat. Phys. **16**, 299 (1977).