Contact Theorem for Confined Polymeric Chains

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The Boundary Condition

Recently, Miklavic[1] criticized the use of "absorbing" boundary condition (here the term absorbing refers to the random walk nomenclature and should not be mixed with polymer adsorption) which is commonly used in some models of polymer confinement. The point of departure of his criticism appears to be a seeming discrepancy between the contact theorem derived in the framework of an exact statistical mechanical analysis[3] under quite general assumptions and the contact theorem that follows from our own work[2] which seems to disagree with its presumed general form. The disagreement between the two was traced down to the absorbing boundary condition used "traditionally" in connection with the confined polymer problems and was resolved by Miklavic in favor of the contact theorem in its standard form, whereas the absorbing boundary condition was considered to be in error. While we disagree in most respects with the argumentation given by Miklavic, we do recognize that the underlying problem is real and will try to give an outline of its resolution the way we envision it.

The continuous chain (Edwards) model[4] describing the statistics of flexible (or semiflexible) polymeric chains has proved its merits in a wide variety of works that we have no intention to enumerate here. It is based on a path integral representation (for details see ref 7) of the polymer end-to-end distribution function (the polymer Green function)

$$G_\phi(R,R';N) = \int_{R(0)=R'}^{R(N)=R} \mathcal{D}R(n) \times$$
$$\exp\left(-\frac{3}{2l^2}\int_0^N \left(\frac{dR(n)}{dn}\right)^2 dn + \beta \int_0^N \phi(R(n)) \, dn\right) \quad (1)$$

where l is the polymer step length, $\beta = (kT)^{-1}$ the inverse thermal energy, and Nl the total length of the polymeric chain, while ϕ is the external potential acting on the chain. $R(n)$ is the local coordinate of the nth bead along the chain. We should note here that the external potential ϕ can also assume the role of an auxiliary field which, through the Hubbard-Stratonovich transformation (the random field method, ref 4), describes the intrachain interactions. In this case, the partition function contains also an additional averaging over the ensemble of auxiliary fields. This form of the polymer Green function is usually taken as a point of departure for advanced renormalization group analyses.[4]

The path integral representation of the polymer distribution function is equivalent to the following Schrödinger type equation (for details see ref 7)

$$\left[\frac{\partial}{\partial N} - \frac{l^2}{6}\nabla^2 + \beta\phi(R)\right] G_\phi(R,R';N) = \delta(R-R')\delta(N) \quad (2)$$

together with the condition $G_\phi(R,R';N=0) = \delta(R-R')$. In the case of a confined but otherwise ideal (noninteracting) polymer, whose interaction with the bounding surfaces is short range (on the order of the step length of the chain), one can approximate the external potential $\phi(R)$ with $\phi(R) = \kappa\delta(z)$, where z is the coordinate locally perpendicular to the bounding surface located at $z = 0$; thus $R = (z,\rho)$. From eq 2 one obtains that at the surface the Green function satisfies the "radiation" boundary condition

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$$\left[\frac{\partial}{\partial n} - \kappa\right] G_\phi(R,R';N) = 0 \quad (3)$$

where n is the local normal to the surface. κ here stands for the magnitude of the polymer-bounding surface interaction. For $\kappa > 0$, polymer is depleted from the surface region as the interaction between the polymer beads and the bounding surface is repulsive, and for $\kappa < 0$, polymer is adsorbed to the surface since the interaction is attractive. The solution of the problem defined by eqs 1 and 3 can be obtained in closed form

$$G_\phi(Q;z,z';s) = \frac{1}{2[Q^2 + s]^{1/2}}\left[e^{-(z-z')(Q^2+s)^{1/2}} + \right.$$
$$\left. \frac{(Q^2 + s)^{1/2} - \kappa}{(Q^2 + s)^{1/2} + \kappa}e^{-(z+z')(Q^2+s)^{1/2}}\right] \quad (4)$$

with

$$G_\phi(R,R';N) = \mathcal{L}^{-1}\left[\frac{1}{2\pi}\int Q \, dQ \, J_0(Q|\rho - \rho'|)G_\phi(Q;z,z';s)\right] \quad (5)$$

where $\mathcal{L}^{-1}$ stands for the inverse Laplace transform acting on the variable s. The above form of the Green function can be used as a starting point for the analysis of polymer adsorption problem ($\kappa < 0$) due to short-range surface adsorbing potential,[8] a case which was investigated recently in connection with membrane curvature energy.[9] [The behavior of eq 5 is very different for positive and negative values of κ. This is clearly evident from the fact that for negative κ the second term in brackets has a singularity at $Q = (\kappa^2 - s)^{1/2}$.] Since the polymer cannot penetrate the wall, there is a discontinuity in the Green function and/or its derivatives right at the wall for any finite $\kappa > 0$. However, as κ is progressively increased the value of the Green function at the wall continuously approaches zero. Thus, in the limit $\kappa \to \infty$, the radiation boundary condition (3) continuously reaches the absorbing limit, $G_\phi(Q;z=0,z';s) = 0$, describing a polymeric chain completely excluded from the wall. In this limit, the Green function remains continuous across the wall, turning to zero right at the wall itself. The absorbing limit can thus be reached in a continuous fashion. It thus follows, contrary to the conclusion reached by Miklavic, that the Green function can remain continuous even across a discontinuous (infinite) potential barrier.

The singular repulsive potential at the wall affects also the monomer (density) distribution, defined as

$$\rho_\phi(r) = \frac{\int\int d^3R \, d^3R' \int_0^N dn \, G_\phi(R,r;N-n)G_\phi(r,R';n)}{\int\int d^3R \, d^3R' \, G_\phi(R,R';N)} \quad (6)$$

that vanishes right at (and outside) the walls. Let us call, following Joanny et al.,[9] the monomer concentration very near, but not exactly at the wall, ρ_s (the definition will become clear in what follows). In the continuous chain model, the short-range potential $\phi(z)$ is in fact "fuzzy" over a length $\Delta z \sim l$ (the step length) close to the surface, since the continuous model is insensitive to the spatial variations in the external potential below this scale. The physical meaning of the delta function distribution of the external wall-polymer potential is thus that the short-range repulsive wall potential vanishes for separations larger than $z \sim l$. We can therefore define the contact concentration in the continuous model as

$$\rho_s = \lim_{l\to 0} \rho_\phi(z \sim l) \quad (7)$$

if the bounding surface is at $z = 0$. We shall see later on that this quantity does not vanish and in fact represents the contact density entering the standard contact theorem of statistical mechanics. The structure of the above equation is such that it

relates the *physical* contact density (left side) to the specified limit of the density in the *continuous model* close to the wall (right side). The two are not the same because of the nature of the steeply varying short-range potential at the wall. If the wall potential would be smooth on the scale of the step length, the contact density would, of course, correspond exactly to the continuous model density right at the wall. One should also note that while $\rho_\phi(z=0)$ is insensitive to other (adsorbing) long-range wall-polymer potentials (it is in fact constant and equal to zero), their characteristics would distinctly affect ρ_s. This is most clearly seen with charged polymers where long-range electrostatic attraction between the polymer beads and the wall promotes adsorption of the chain to the surface.[2]

The above definition of the contact density is quite general but has different implications for different models of the polymeric chains. In the lattice mean-field theories,[5] ρ_s would simply correspond to the monomer density in the first lattice plane just beyond the wall. In the polyelectrolyte Poisson-Boltzmann approximation,[6] the contact density would be identified directly with the density right at the wall (if the polymer beads are of vanishing extension).

The Contact Theorem

We now approach the problem of the evaluation of forces acting on the bounding surfaces confining the polymer, or what amounts to the same thing, the evaluation of the pressure ($\mathcal{P}$) acting in the system. In what follows, we shall limit ourselves to the ground-state dominance limit where all local physical properties of the polymer reach a well-defined limit for $N \to \infty$. We shall also assume that the external field ϕ depends only on the transverse coordinate ($\phi(\mathbf{r}) = \phi(z)$) and has a short-range (singular) repulsive contribution (of the type discussed in the previous section) superimposed on a long-range interaction of a general form. In this case, the polymer Green function assumes the approximate form

$$G_\phi(\mathbf{r},\mathbf{r}';N) \approx \psi(z)\,\psi(z')e^{-E_N N} \qquad (8)$$

where the eigenfunctions $\psi(z)$ are now normalized in such a way that

$$\rho_\phi(z) = \psi^2(z) \quad \text{with} \int \rho_\phi(z)\,dz = N/S \qquad (9)$$

where S is the total area of the bounding surface. In the ground-state dominance limit, the equation defining the Green function eq 2 assumes the form of an eigenvalue equation

$$\frac{l^2}{6}\frac{d^2\psi(z)}{dz^2} + E_N\psi(z) - \beta\phi(z) = 0 \qquad (10)$$

where additionally the eigenfunctions have to satisfy the absorbing boundary condition, $\psi(z=0) = 0$. We have thus decoupled the effects of the wall-polymer potential into a short-range part (affecting the boundary condition) and the remaining long-range part. After some manipulations we can derive from the eigenvalue equation the following relation

$$\frac{d}{dz}\left[\frac{l^2}{6}\left(\frac{d\psi(z)}{dz}\right)^2 + E_N\psi^2(z) - \beta\phi(z)\,\psi^2(z)\right] = -\beta\frac{d\phi(z)}{dz}\psi^2(z) \qquad (11)$$

The force per unit bounding surface area can be written[9] as the average force, acting on the unit surface area

$$\mathcal{P} = -\left\langle\frac{\partial\phi(z)}{\partial z}\right\rangle = -\int\frac{\partial\phi(z)}{\partial z}\rho_\phi(z)\,dz \qquad (12)$$

where $\rho_\phi(z)$ is the monomer density distribution. Using eq 11 and the definition of the force per unit bounding surface area,

we are led to the following conclusion

$$\mathcal{P} = -\int_0^\infty\frac{\partial\phi(z)}{\partial z}\rho_\phi(z)\,dz = kT\frac{l^2}{6}\left(\frac{d\psi(z)}{dz}\right)^2_{z=0} \qquad (13)$$

This is the required relation expressing the force equilibrium in the system. We have derived this relation before but with somewhat different argumentation[2] (starting from the variational principle for the free energy). Since it expresses the pressure in the system in terms of statistical mechanical averages right at the wall, it could be termed a contact theorem. On the other hand, the exact statistical mechanical analysis, as rightly pointed out by Miklavic,[1] leads to a different form of the contact theorem,[3] viz.

$$\mathcal{P} = kT\rho_\phi(z=0^+) \qquad (14)$$

with some variations in the case of long-range (Coulombic) interactions between the particles, when the contact theorem assumes the form $\mathcal{P} = kT\rho_\phi(z=0^+) - (\sigma^2/2\epsilon\epsilon_0)$, where σ is the surface charge density at the impenetrable wall and other symbols have their standard meaning. In the above relation, $\rho(z=0^+)$ stands for the one particle (or monomer in the case of polymeric chains) density right outside the bounding wall. Superficially, there thus appears to be a fundamental inconsistency between the contact theorem as applied to simple fluids and as applied to polymers in the continuous chain approximation. Miklavic tried to resolve this puzzle by claiming that it is due to the "unphysical" ("absorbing") boundary condition in the case of a confined polymer ($\rho_\phi(z=0) = 0$). In our view, the resolution of the conundrum is of a different yet more fundamental type.

What is in fact the limit $\rho_\phi(z=0^+)$ in the case of a continuous chain polymer? In the continuum (Edwards) model, the molecular details below the scale defined by the steplength are not resolved. Thus, also the external potential confining the polymer is in fact spread over a length $\Delta z \sim l$. The appropriate surface limit of the monomer density in the continuum model should thus be $\rho_\phi(z=0^+) = \rho_\phi(z\sim l)$. In fact, in the frame of the ground-state dominance one obtains the following relation

$$\mathcal{P} = kT\frac{l^2}{6}\left(\frac{d\psi(z)}{dz}\right)^2_{z=0} \approx kT\psi^2\left(z=\frac{l}{6^{1/2}}\right) =$$
$$kT\rho_\phi\left(z=\frac{l}{6^{1/2}}\right) = kT\rho_s \qquad (15)$$

The ρ_s introduced above is the same as the one introduced in the context of the boundary condition. The form of the contact theorem for polymeric chains described in the framework of the continuous chain model thus coincides with its form derivable on general grounds from statistical mechanics. Just as in the case of the boundary condition one has to be aware of the coarse-graining underlying the continuous chain model.

There remains the question of the range of validity of the continuous chain contact theorem, eq 13, if one relaxes the ground-state dominance as well as the mean-field restraint. The procedure to derive the contact theorem in this general case is rather formal, based on the full expression for the Green's function, eq 1, where the averaging over auxiliary fields, if the intrachain interactions are present, is done last (see the discussion in the Appendices D and F of ref 4). We do not want to reproduce the whole of the derivation at this point, since it does not add much to what has already been said in connection with the ground-state dominance contact theorem but will rather concentrate on some of its crucial steps. First of all one has

$$\rho_c = \left\langle\rho_\phi\left(z\sim\frac{l}{6^{1/2}}\right)\right\rangle_\phi \approx \frac{l^2}{6}\left\langle\frac{\partial\Psi(\mathbf{r};n)}{\partial z}\frac{\partial\Psi^\dagger(\mathbf{r};n)}{\partial z}\right\rangle_\phi \qquad (16)$$

where Ψ is a Gaussian random field (a disorder field[12]) which in

the ground-state dominance limit ($N \gg 1$) becomes equal to ψ. The Gaussian random field Ψ is introduced to represent the Green function in a simple form (see ref 4 for details). The derivatives with respect to the transverse coordinate z are taken at the bounding surface. Also one can derive the following result[2]

$$\left\langle \frac{\partial\Psi(\mathbf{r};n)}{\partial z}\frac{\partial\Psi^{\dagger}(\mathbf{r};n)}{\partial z}\right\rangle_{\phi} = -\frac{9}{l^{4}}\left\langle \left(\frac{dz(n)}{dn}\right)^{2}\right\rangle_{\phi} \qquad (17)$$

where the correct interpretation of the symbolically written square of the derivative of z with respect to n at the surface is $(dz(n)/dn)$ $\rightarrow (z_{n+1} - z_n)(z_n - z_{n-1})$. [Similar relations can be derived in the functional integral formulation of quantum mechanics and are thoroughly discussed in ref 13. They can be obtained by starting from a discretized representation of the Green function eq 1 and evaluating the indicated derivatives.] Thus, we finally get for the general form of the contact theorem for sterically excluded polymers in the continuous chain limit

$$\mathcal{P} = -\frac{3kT}{2l^{2}}\left\langle \left(\frac{dz(n)}{dn}\right)^{2}\right\rangle_{z=0} \qquad (18)$$

where the averaging in the last term is done over the polymer configurations, over the position along the polymeric chain and over the auxiliary fields ϕ. The term on the right-hand side of the above relation appears to be nothing but the (zz) component of the polymer stress tensor ($\mathbf{T}_{ik}$) in the continuous chain representation,[11] evaluated at the bounding surface, thus making eq 18 particularly transparent from the mechanical point of view since it asserts that $\mathcal{P} = -\mathbf{T}_{ik}\mathbf{n}_k$, where $\mathbf{n}_k = (0, 0, 1)$; i.e., it is a unit vector in the z direction. [Note that the definition of $(dz(n)/dn)^2$ as a symmetrized square of the first derivative leads to a possibility that if the polymer chain snakes its way mostly along the bounding surface, $(z_{n+1} - z_n)(z_n - z_{n-1})$ will be on the average negative, making the pressure, eq 18, positive (i.e., repulsive in the case of two apposed surfaces confining the polymer).] The ground-state dominance limit of the contact theorem can now be obtained also directly from eq 18 in the form of eq 13.

The conclusion that follows from the above discussion is that, for a continuous model polymeric chain excluded from the bounding surface through a short-range delta-like potential, the correct form of the contact theorem is given by eq 18. This form is also completely consistent with the general form of the contact theorem, eq 14, if one interprets the contact density in view of the coarse-graining inherent in the chain Hamiltonian eq 1, entering the continuous chain representation.

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