Super Gaussian Self-Consistent method for systems with a two–body Hamiltonian

Edward G. Timoshenko[1]

Theory and Computation Group, Centre for Synthesis and Chemical Biology, Conway Institute of Biomolecular and Biomedical Research, Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

Abstract

A new kinetic self–consistent method is presented based on the proposed Gaussian Superposition Principle for computation of ensemble averaged observables of a macromolecule interacting via two–body forces. The latter leads to the derivation of a natural functional closure relation for the 3-point distribution functions (DF), thereby truncating a hierarchy of kinetic equations obtained from the original Langevin equation. The resulting Super Gaussian Self–Consistent (SGSC) equations for the 2-point distribution functions acquire a sufficiently tractable integro–differential form. The SGSC theory strives to yield realistic shapes of various distribution functions for any macromolecule with a generic Hamiltonian involving 2-body interaction potentials, both at equilibrium and during kinetics.

1 Introduction

Models of macromolecules are described by fairly complex Hamiltonians involving both bonded and nonbonded interactions [1]. While computer simulations [2] are proving increasingly powerful in tackling these models, the challenge of resolving the overall problem of determining the macromolecular conformations still remains. The difficulties with overcoming barriers (quasi–nonergodicity), uniformity of sampling the phase space for extended polymer chains (entropic suppression), and the shear task of reaching satisfactory equilibration and acceptable sampling statistics all pose severe problems for equilibrium simulations of macromolecules.

Moreover, kinetic simulations are further exacerbated by the need to limit oneself to ensemble averaging as temporal sampling is no longer allowed, the difficulties with adequate collective 'cluster' motions, and a horrendous timescale problem brought about by the tiny elementary timestep permitted (e.g. about 1 fs for Molecular Dynamics), to mention but a few. There are also various technical limitations and numerical inaccuracies intrinsic to each of the standard techniques such as Monte Carlo, Stochastic and Molecular Dynamics.

Thus, it is quite evident that an adequate theoretical base is really needed [3] to interpret and support any simulation data. Many ingenious theoretical treatments have been developed for polymers at equilibrium over the years[1, 4]. However, in the main, in order to be amenable to analytical analysis, they often have to be either based on rather simplistic models of polymers, or to involve certain approximations with profound consequences for the results. Much less developed and few are the nonequilibrium methods,

[1]Web: http://darkstar.ucd.ie; E-mail: Edward.Timoshenko@ucd.ie

which perform satisfactorily for describing conformational changes of macromolecules. It is often the case, therefore, that a great deal of the description in the polymer area is only qualitatively accurate, but lacking the firm quantitative rigour of other theoretical physical disciplines.

Fundamentally, for the description of kinetics of conformational changes of a macromolecule, one would like to be able to reliably deduce its most detailed statistical–mechanical properties as a function of time given the system's Hamiltonian in terms of a classical force field. As regards the equilibrium state of the macromolecule, it should be simply recoverable as the stationary limit in time of the correct kinetic equations.

An approach to the problem based on the Gaussian self–consistent (GSC) method has been independently developed and applied in somewhat different formulations by our Group [5] and others (see e.g. Refs. [6, 7] and further references therein). Historically, this technique had a predecessor in the Gaussian variational approach for a linear homopolymer chain at equilibrium independently proposed by J. des Cloizeaux [8] and S. Edwards *et al* [9]. Further progress has been made in the years which followed [10] with generalisations to polymers with different chain architectures [11], such as e.g. dendrimers [12], chain stiffness [13], copolymers [14], and multiple chains [15]. However, the method becomes quantitatively inaccurate for nonideal systems even for these observables and, clearly, it is unable to yield realistic radial dependencies of the densities and distribution functions. In particular, the GSC results suffer from an overestimated expansion of the coil in the good solvent, leading to a too large swelling exponent value as the degree of polymerisation increases, whereas an underestimated energy of the globule in the poor solvent. The cause of both deficiencies is quite apparent when comparing the 2-point DF of the GSC and MC. The 2-point DF of GSC has a smooth Gaussian shape extrapolating the true nonmonotonous DF of the nonideal systems. The latter functions have a pronounced power law decrease at the origin, the so–called 'correlation hole', for the coil, whereas an oscillating liquid–like shape with a pronounced peak at the 'first solvation shell' radius for the globule [16].

2 The new SGSC method

The intra–chain correlation function is defined as,

$$g_{ij}^{(2)}(r) \equiv \langle \delta(\boldsymbol{x}_i - \boldsymbol{x}_j - \boldsymbol{r}) \rangle = \frac{1}{4\pi r^2} \langle \delta(|\boldsymbol{x}_i - \boldsymbol{x}_j| - r) \rangle \, , \tag{1}$$

We also would need the mean–squared distances between monomers,

$$\mathfrak{D}_{ij} \equiv \frac{1}{3} \langle (\boldsymbol{x}_i - \boldsymbol{x}_j)^2 \rangle = \frac{4\pi}{3} \int_0^\infty r^3 dr \, \mathcal{G}_{ij}(r), \quad \mathcal{G}_{ij}(r) \equiv r \, g_{ij}^{(2)}(r). \tag{2}$$

Next we introduce notations for pairs of indices for brevity,

$$ij \to 1, \quad jk \to 2, \quad ik \to 3, \quad ji \to \check{1}. \tag{3}$$

We proceed from the coarse–grained Langevin equation for the atom coordinates $\boldsymbol{x}_i(t)$,

$$\zeta \frac{d\boldsymbol{x}_i}{dt} = -\frac{\partial H}{\partial \boldsymbol{x}_i} + \boldsymbol{\eta}_i. \tag{4}$$

We can restrict ourselves by a 2-body Hamiltonian H and a Gaussian (white) noise,

$$H = \sum_{j<k} V_{jk}(|\boldsymbol{x}_j - \boldsymbol{x}_k|), \qquad \left\langle \eta_i^\alpha(t)\, \eta_j^\beta(t') \right\rangle = 2k_B T\zeta\, \delta^{\alpha\beta}\, \delta_{ij}\, \delta(t-t'). \tag{5}$$

The exact equation can be derived with help of Fluctuation–Dissipation Theorem,

$$\zeta \frac{dg_{ij}^{(2)}(\boldsymbol{r})}{dt} \;=\; 2k_B T \frac{\partial^2 g_{ij}^{(2)}(\boldsymbol{r})}{\partial \boldsymbol{r}^2} + \left\langle \frac{\partial G_{ij}^{(2)}(\boldsymbol{r})}{\partial \boldsymbol{r}} \left(\frac{\partial H}{\partial \boldsymbol{x}_i} - \frac{\partial H}{\partial \boldsymbol{x}_j} \right) \right\rangle. \tag{6}$$

This eq. involves 3-point DF and leads to a kinetic hierarchy analogous to that of BBGKY (Bogoliubov, Born, Green, Kirkwood and Yvon) derived from the Liouville eq. [17, 18],

$$I_{ij} \equiv \left\langle \frac{\partial G_{ij}^{(2)}(\boldsymbol{r})}{\partial \boldsymbol{r}} \left(\frac{\partial H}{\partial \boldsymbol{x}_i} - \frac{\partial H}{\partial \boldsymbol{x}_j} \right) \right\rangle, \quad I_{ij}^{(dir)} = \frac{2}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial V_{ij}(r)}{\partial r}\, g_{ij}^{(2)}(r) \right), \tag{7}$$

$$g_{ijj}^{(3)}(\boldsymbol{r}, \boldsymbol{r}') = g_{ij}^{(2)}(r)\, \delta(\boldsymbol{r}'), \qquad g_{iji}^{(3)}(\boldsymbol{r}, \boldsymbol{r}') = g_{ij}^{(2)}(r)\, \delta(\boldsymbol{r} + \boldsymbol{r}'). \tag{8}$$

$$I_{ij}^{(indir)} = \sum_{k \neq i,j} \int d\boldsymbol{r}' \left(V_{jk}(\boldsymbol{r}') \frac{\partial^2 g_{ijk}^{(3)}(\boldsymbol{r}, \boldsymbol{r}')}{\partial \boldsymbol{r} \partial \boldsymbol{r}'} - V_{ik}(\boldsymbol{r}') \frac{\partial^2 g_{jik}^{(3)}(-\boldsymbol{r}, \boldsymbol{r}')}{\partial \boldsymbol{r} \partial \boldsymbol{r}'} \right). \tag{9}$$

For any observable A, we formulate the Gaussian Superposition Principle (GSP),

$$\left\langle A(\{\boldsymbol{x}_i(t) - \boldsymbol{x}_j(t)\}) \right\rangle = \prod_{i<j} \int d\boldsymbol{y}_{ij}\, f_{ij}^t(|\boldsymbol{y}_{ij}|) \left\langle A(\{\boldsymbol{x}_i^{(0)}(t) - \boldsymbol{x}_j^{(0)}(t) - \boldsymbol{y}_{ij} \sqrt{\mathcal{D}_{ij}(t)}\}) \right\rangle_0, \tag{10}$$

where $\langle \ldots \rangle_0$ denotes the averaging over the Gaussian noise via the GSC method,

$$\zeta \frac{d\boldsymbol{x}_i^{(0)}}{dt} = -\frac{\partial H^{(0)}}{\partial \boldsymbol{x}_i^{(0)}} + \boldsymbol{\eta}_i, \qquad H^{(0)} = \sum_{j<k} K_{jk} \boldsymbol{x}_j^{(0)}\, \boldsymbol{x}_k^{(0)}, \tag{11}$$

The variables $\boldsymbol{y}_{ij}$ are dimensionless and $\mathcal{D}_{ij}$ are the MS distances of the GSC method,

$$\mathcal{D}_{ij}(t) \equiv \frac{1}{3} \left\langle \left(\boldsymbol{x}_i^{(0)}(t) - \boldsymbol{x}_j^{(0)}(t) \right)^2 \right\rangle_0. \tag{12}$$

The functions f_{ij} for any ij satisfy the normalisation conditions,

$$\int d\boldsymbol{y}_{ij}\, f_{ij}^t(|\boldsymbol{y}_{ij}|) = 1. \tag{13}$$

In application to $g_{ij}^{(2)}$, we can hence produce the decomposition,

$$g_{ij}^{(2)}(r,t) = \int d\boldsymbol{y}\, (2\pi \mathcal{D}_{ij}(t))^{-3/2} \exp\left(-\frac{\left(\boldsymbol{r} - \boldsymbol{y}\sqrt{\mathcal{D}_{ij}(t)} \right)^2}{2\mathcal{D}_{ij}(t)} \right) f_{ij}^t(y). \tag{14}$$

Next, let us introduce the rescaled variables and functions,

$$\hat{r}_{ij} \equiv \frac{r}{\sqrt{\mathcal{D}_{ij}}}, \quad g_{ij}^{(2)}(r) \equiv \frac{\hat{g}_{ij}^{(2)}(\hat{r}_{ij})}{\mathcal{D}_{ij}^{3/2}}, \quad y\, f_{ij}(y) \equiv \mathcal{F}_{ij}(y), \quad \hat{r}_{ij} \hat{g}_{ij}^{(2)}(\hat{r}_{ij}) \equiv \hat{\mathcal{G}}_{ij}(\hat{r}_{ij}). \tag{15}$$

We can rewrite above Eq. as an equivalent 1-D decomposition,

$$\hat{\mathcal{G}}_{ij}(\hat{r}_{ij}) = \int_{-\infty}^{\infty} dy\, \frac{\exp\left(-\frac{(\hat{r}_{ij}-y)^2}{2}\right)}{(2\pi)^{1/2}}\, \mathcal{F}_{ij}(y). \tag{16}$$

Mathematically, this Eq, is the Gauss transformation (GT),

$$G(x) = \mathfrak{G}[F](x) \equiv \int_{-\infty}^{\infty} dy\, \frac{\exp\left(-\frac{(x-y)^2}{2}\right)}{(2\pi)^{1/2}}\, F(y) = \exp\left(\frac{1}{2}\frac{d^2}{dx^2}\right) F(x), \tag{17}$$

$$F(x) = \mathfrak{G}^{-1}[G](x) = \exp\left(-\frac{1}{2}\frac{d^2}{dx^2}\right) G(x). \tag{18}$$

Similarly, the GSP of the 3-point DF gives the expression,

$$g^{(3)}_{ijk}(\boldsymbol{r},\boldsymbol{r}') = \int\int d\boldsymbol{y}d\boldsymbol{y}'\, \frac{f_{ij}(y)\, f_{jk}(y')}{((2\pi)^2\,\Delta_{ijk})^{3/2}}\, \exp\Big(-\frac{1}{2\Delta_{ijk}}\Big[(\boldsymbol{r}-\boldsymbol{y}\sqrt{D_{ij}})^2\mathcal{D}_{jk}$$
$$-2(\boldsymbol{r}-\boldsymbol{y}\sqrt{D_{ij}})(\boldsymbol{r}'-\boldsymbol{y}'\sqrt{D_{jk}})\mathcal{D}_{ij,jk} + (\boldsymbol{r}'-\boldsymbol{y}'\sqrt{D_{jk}})^2\mathcal{D}_{ij}\Big]\Big), \tag{19}$$

where $\Delta_{ijk} > 0$ and the correlation coefficients $\mathcal{D}_{ij,jk}$ are,

$$\Delta_{ijk} \equiv \mathcal{D}_{ij}\,\mathcal{D}_{jk} - \mathcal{D}^2_{ij,jk}, \tag{20}$$

$$\mathcal{D}_{ij,jk} \equiv \frac{1}{3}\Big\langle \left(\boldsymbol{x}^{(0)}_i - \boldsymbol{x}^{(0)}_j\right)\left(\boldsymbol{x}^{(0)}_j - \boldsymbol{x}^{(0)}_k\right)\Big\rangle_0 = -\frac{1}{2}\left(\mathcal{D}_{ij} + \mathcal{D}_{jk} - \mathcal{D}_{ik}\right). \tag{21}$$

From above Eq. we deduce the following closure relation,

$$g^{(3)}_{ijk}(\boldsymbol{r},\boldsymbol{r}') = \exp\Big(\mathcal{D}_{ij,jk}\frac{\partial^2}{\partial\boldsymbol{r}\,\partial\boldsymbol{r}'}\Big)\, g^{(2)}_{ij}(r)\, g^{(2)}_{jk}(r'). \tag{22}$$

Properties of this SGSC closure relation include:

$$\mathfrak{D}_{ij,jk} = \mathcal{D}_{ij,jk} = \frac{1}{3}\int\int d\boldsymbol{r}d\boldsymbol{r}'\,(\boldsymbol{r}\boldsymbol{r}')\, g^{(3)}_{ijk}(\boldsymbol{r},\boldsymbol{r}'). \tag{23}$$

$$\int d\boldsymbol{r}'\, g^{(3)}_{ijk}(\boldsymbol{r},\boldsymbol{r}') = g^{(2)}_{ij}(r), \qquad \int d\boldsymbol{r}\, g^{(3)}_{ijk}(\boldsymbol{r},\boldsymbol{r}') = g^{(2)}_{jk}(r'). \tag{24}$$

Moreover, the proposed SGSC closure satisfies the correspondence condition, i.e. it recovers the exact GSC closure relation if $g^{(2)\,Gau}_{ij}(r) = (2\pi\mathcal{D}_{ij})^{-3/2}\exp(-r^2/(2\mathcal{D}_{ij}))$. Note that to obtain the latter distribution we simply have to choose $f^{Gau}_{ij}(\boldsymbol{y}) = \delta(\boldsymbol{y})$.

An important feature of this theory is the 1-D reduction of the 3-point DF,

$$\mathcal{I}_{12} \equiv \int d\,\overset{\triangle}{\boldsymbol{r}'}\,\frac{\partial^2 g^{(3)}_{12}(\boldsymbol{r},\boldsymbol{r}')}{\partial\boldsymbol{r}\,\partial\boldsymbol{r}'} = \frac{2\pi}{rr'}\,\Xi\Big(\mathcal{D}_{1,2}\frac{\partial}{\partial r}\frac{\partial}{\partial r'}\Big)\frac{\partial}{\partial r}\frac{\partial}{\partial r'}\, r g^{(2)}_1(r)\, r' g^{(2)}_2(r'), \tag{25}$$

where $\Xi(z) \equiv \int_{-1}^{1} da\, a\, e^{a\,z}$. The resulting SGSC equation for the 2-point DF functions are,

$$\zeta\frac{d\mathcal{G}_1(r)}{dt} = 2k_BT\frac{\partial^2\mathcal{G}_1(r)}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\Big(r\frac{\partial V_1(r)}{\partial r}\,\mathcal{G}_1(r)\Big) \tag{26}$$
$$+2\pi\sum_{k\neq i,j}\int_0^{\infty} dr'\,\Big[r'\,V_2(r')\,\Xi\Big(\mathcal{D}_{1,2}\frac{\partial}{\partial r}\frac{\partial}{\partial r'}\Big)\frac{\partial}{\partial r}\frac{\partial}{\partial r'}\mathcal{G}_1(r)\,\mathcal{G}_2(r') + ((1,2)\leftrightarrow(\check{1},3))\Big].$$

It would appear that the composition operator Ξ generates a seemingly intractable series involving the radial derivatives of all orders. However, this operator is closely related to the translation operator. By expressing the potential $rV_2(r)$ as the Laplace transform of its original one can rewrite this as,

$$U_{1,2}^{(indir)} = \int_{-\infty}^{\infty} \tau \, d\tau \, \hat{\mathcal{G}}_1^{[1]}(\hat{r}_1 + \Gamma\tau) \int_0^{\infty} d\hat{r}_2 \, \mathfrak{V}_2(\hat{r}_2, |\tau|, \mathcal{D}_2) \, \hat{\mathcal{G}}_2^{[1]}(\hat{r}_2), \tag{27}$$

where the derivative $\hat{\mathcal{G}}_1^{[1]}$ is understood to be an even function and we have introduced,

$$\mathfrak{V}_2(\hat{r}_2, |\tau|, \mathcal{D}_2) \equiv \int_{|\tau|}^{\infty} \frac{ds}{s^2} \frac{\mathfrak{L}^{-1}[rV_2](s/\sqrt{\mathcal{D}_2})}{\mathcal{D}_2} \exp\left(-s\hat{r}_2\right). \tag{28}$$

Since $\mathfrak{I}_{ij}$ is not an observable as it can not be represented via an average of some function of monomer coordinates, it is not clear how to obtain an evolution equation for it. The same difficulty exists for $\mathcal{D}_{ij}$, which we still need to know in order to express the correlation coefficients $\mathcal{D}_{ij,jk}$ involved in the closure relation. The most obvious thought is to require the Gaussian quantities $\mathcal{D}_{ij}$ to satisfy a quasi–Gaussian equation similar to Eq. (17) in Ref. [19], which involves the derivatives of the instantaneous mean energy,

$$\begin{aligned} \frac{\zeta}{2}\frac{d\mathcal{D}_{ij}}{dt} &= 2k_BT + \sum_k (\mathcal{D}_{ik} - \mathcal{D}_{jk})(W_{ik} - W_{jk}), && (29) \\ W_{ik}(t) &\equiv -\frac{2}{3}\frac{\partial \mathcal{E}}{\partial \mathcal{D}_{ik}(t)}, \qquad \mathcal{E} \equiv \langle H \rangle = 4\pi \sum_{j'<k'} \int_0^{\infty} r^2 dr \, V_{j'k'}(r) \, g_{j'k'}^{(2)}(r). && (30) \end{aligned}$$

Here we use the full mean energy as the integral of the Gaussian function with the 2-body potential would diverge. After a lengthy algebra the final two equations become,

$$\begin{aligned} \frac{\zeta}{2}\frac{d\mathfrak{D}_1}{dt} &= X_1, \qquad \frac{\zeta}{2}\frac{d\mathcal{D}_1}{dt} = Y_1, && (31) \\ X_1 &\equiv 2k_BT + 2A_1 + \sum_{k\neq i,j} (\mathcal{D}_{1,2}B_2 + \mathcal{D}_{\check{1},3}B_3), && (32) \\ Y_1 &\equiv 2k_BT + 2A_1 - \sum_{k\neq i,j} (\mathcal{D}_{1,2}\frac{A_2}{\mathcal{D}_2} + \mathcal{D}_{\check{1},3}\frac{A_3}{\mathcal{D}_3}), && (33) \\ A_1 &\equiv \frac{4\pi}{3}\int_0^{\infty} dr \, V_1(r)\frac{\partial(r^2\mathcal{G}_1)}{\partial r}, \qquad B_1 \equiv \frac{4\pi}{3}\int_0^{\infty} dr \, r \, V_1(r)\frac{\partial^2\mathcal{G}_1}{\partial r^2}. && (34) \end{aligned}$$

3 Conclusion

Here I have shown how one can extend the Gaussian self–consistent (GSC) approach for describing conformational changes of a macromolecule so that the Gaussian limitation is surpassed. Obviously, a Gaussian shape of the monomer—monomer distribution functions (DFs) is correct only for an ideal molecule characterised by a set of arbitrarily connected harmonic springs. Such Gaussian chain, or more generally a Gaussian network, being exactly solvable, plays an important rôle similarly to other ideal systems in Statistical Mechanics. The GSC method is based on finding a trial Gaussian network, involving virtual harmonic springs between all of the monomers, which fits best the mean–squared (MS) inter–monomer distances with respect to the true system Hamiltonian. Such a trial network is described by a quadratic trial Hamiltonian, and hence by a linear trial stochastic ensemble associated with it, leading to an unrealistic Gaussian shape of DFs.

Clearly, any physically reasonable shape of DF can be represented as a linear superposition of shifted Gaussian functions of the same width, which is known mathematically as Gauss transformation (GT). Therefore, given the true shape of DF, one can invert the GT in order to find the superposition amplitudes $f^t_{ij}(r)$. The idea of the SGSC method is to find such amplitudes in a self–consistent manner proceeding from the nonlinear Langevin equation by optimising the 2-point DFs, similar to how the GSC method optimises the MS distances between monomers. This is accomplished as follows. First, one starts by rigorously deriving a hierarchy of equations for DFs from the Langevin equation similarly to the BBGKY hierarchy obtained from the Liouville equation [17, 18]. Second, we write the 3-point DF as a double linear superposition of the reference Gaussian 3-point DFs with the same decomposition amplitudes as for the 2-point DF, which, in fact, constitutes a natural functional closure relation for the 3-point function in terms of the 2-point functions. Such a closure truncates the infinite hierarchy and produces a closed set of the SGSC equations for the 2-point DFs. Remarkably, this generic closure relation, which is valid for any 2-body potential, happens to possess all of the properties required by Statistical Mechanics. Furthermore, it turns out to be also mathematically well tractable, leading in a *tour de magie* to the 1-dimensional reduction and, consequently, to an elegant final equation by exploiting the intimate relation of the closure to the translation operator. We know that the latter operator is of great significance in Quantum Mechanics. In particular, the symbol formulation of Quantum Mechanics, which is expressed in terms of functions over the classical phase space, has the convolution operator for two observables, which looks very similar to the SGSC closure relation.

If we extend the above superposition method to any observable in our theory, we would naturally arrive to the general form of the Gaussian Superposition Principle (GSP), which expresses any observable of the SGSC theory as a linear superposition of the observables obtained from the reference Gaussian (GSC) method. One can ask perhaps how the GSP corresponds to the Superposition Principle in Quantum Mechanics, which is considered to be one of its cornerstones. Any Quantum Mechanical system is described by a linear equation in the Hilbert space and thus superpositions of elementary solutions emerge as a simple consequence of linearity. The current application of the superposition idea to a highly nonlinear Langevin equation is much more subtle. In fact, what we do here is attempting to construct a good approximation for ensemble averaged observables by expressing them via a linear superposition of the elementary approximants obtained from a reference Gaussian theory. This is done by determining the decomposition amplitudes, which optimise the 2-point DFs with respect to the true nonlinear Langevin equation. Yet, despite this rather different context, the formal analogies with Quantum Mechanics in various parts of the present formalism are quite striking and unforeseen.

Interestingly, the final SGSC equation is a parabolic type integro–differential equation, which has terms analogous to those of the Fokker–Planck equation [20]: the entropic term is similar to the diffusive part, whereas the direct interactions term is similar to the drift part of the Fokker–Planck equation. The remaining indirect interactions term involves an integral bearing some similarity to the collision integral in the Boltzmann[21] and, particularly, in the Landau equations. We know that the latter integral equations have been very successful in describing a rich physical behaviour of various complex systems, but these equations are generally difficult to solve analytically. One would hope that the proposed SGSC equation could play a fundamental rôle for the kinetics of conformational changes of a macromolecule in solution over long timescales, akin to the rôle played by the Boltzmann equation for the kinetics of gas phase.

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