Rotational diffusion in a chain of particles

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Abstract
We study the coupled rotational diffusion in a two-particle chain on the basis
of a Smoluchowski equation and calculate time correlation functions that
are measurable in an experiment. This approach might be used to explore
hydrodynamic interactions in the limit where lubrication theory is valid.

1. Introduction

Colloids are widely considered as models for atomic systems [1, 2]. However, a specific
signature of colloidal suspensions is hydrodynamic interactions [3, 4]. Moving colloids
interact with each other through the flow fields that they create. This is a true multi-body
problem which can only be handled by approximate methods such as multipole expansions
for large particle distances (see, e.g., [4, 5]) and lubrication theory when they come close
to each other [6]. Conventionally, hydrodynamic interactions are monitored through their
effect on self-diffusion and collective diffusion in colloidal suspensions [1, 4, 7] but recent
experiments with optical tweezers on a pair of particles [8] also allow a controlled exploration of
hydrodynamic interactions as a function of particle separation, confirming standard approaches
due to Oseen and also Rotne and Prager [3, 4].

Recent work also studied the rotational diffusion of tracer particles [9–11] or colloids
trapped in optical tweezers [12]. An experimental system introduced by Bibette *et al* [13]
suggests the possibility of directly measuring the effect of hydrodynamic interactions on the
rotational diffusion in the limit where lubrication theory is valid. Charged superparamagnetic
particles under the influence of a magnetic field form chains where the particle separation can be
precisely tuned by the magnetic field strength. By labelling the particles with a phosphorescent
dye [11] or by using birefringent colloids [14], rotational diffusion can then be monitored.

This paper investigates rotational diffusion in a two-particle chain theoretically. It
first introduces the Smoluchowski equation to treat rotational diffusion and then discusses
observables to be measured in an experiment.

2. Rotational diffusion and the Smoluchowski equation

Let us first briefly review the rotational diffusion of one particle that can also be considered as a random walk on the unit sphere. The probability density $P(\hat{\nu}, t)$ of finding the particle with an orientation given by the unit vector $\hat{\nu}$ at time t satisfies the Smoluchowski equation [9]

$$\frac{\partial P(\hat{\nu}, t)}{\partial t} = D_0 \nabla_r^2 P(\hat{\nu}, t). \tag{1}$$

This is in complete analogy with translational diffusion. However, instead of the Laplace operator, the square of the nabla operator in angular space ∇_r has to be used, where the index r refers to rotation. Since $\nabla_r = \frac{2\pi i}{h} L$, where L is the angular momentum operator known from quantum mechanics, all the algebra developed for L [15] is also valid for ∇_r. To be concrete, we note that

$$\nabla_r = \hat{\nu} \times \frac{\partial}{\partial \hat{\nu}} = \begin{pmatrix} -\sin\varphi \frac{\partial}{\partial\vartheta} - \frac{\cos\varphi}{\tan\vartheta}\frac{\partial}{\partial\varphi} \\ -\cos\varphi\frac{\partial}{\partial\vartheta} - \frac{\sin\varphi}{\tan\vartheta}\frac{\partial}{\partial\varphi} \\ \frac{\partial}{\partial\varphi} \end{pmatrix}, \tag{2}$$

where ϕ, ϑ are the spherical coordinates used to represent $\hat{\nu}$. The rotational diffusion constant D_0 in equation (1) is related via an Einstein relation to the mobility $\mu_0 = 1/(8\pi\eta a^3)$ for rotational motion, i.e., $D_0 = k_B T \mu_0$. Now, since the operator ∇_r^2 possesses the spherical harmonics $Y_m^l(\hat{\nu})$ as its eigenfunctions, $\nabla_r^2 Y_m^l(\hat{\nu}) = -l(l+1)Y_m^l(\hat{\nu})$, one calculates, with the same method as presented below, the time correlation functions

$$\langle Y_m^{l*}[\hat{\nu}(t)] Y_{m'}^{l'}[\hat{\nu}(0)] \rangle = \frac{1}{4\pi} \delta_{ll'} \delta_{mm'} e^{-l(l+1)D_0 t}. \tag{3}$$

Here $\hat{\nu}(t)$ means orientation of the particle at time t and the symbol $*$ means complex conjugate. For small times, one shows with the help of equation (3) (for details, see below) that the square of the angular displacement of $\hat{\nu}$ exhibits the typical diffusive behaviour:

$$\langle |\hat{\nu}(t) - \hat{\nu}(0)|^2 \rangle \approx 4D_0 t. \tag{4}$$

We now concentrate on a chain of two particles of radius a whose centres are connected by the vector r. For simplicity, we only consider their rotational diffusion, i.e., we disregard any coupling to translational motion. In particular, we take the particles' separation r as fixed, e.g., by assuming that fluctuations around the equilibrium separation, governed by the two-particle potential, are negligibly small. The coupled rotational diffusion is described by self-diffusion tensors $D_{11} = D_{22}$ for particles 1 and 2, respectively, and the tensors $D_{12} = D_{21}$ encoding the hydrodynamic interactions between particle 1 and 2. As in the one-particle case, these quantities are related to mobilities by an Einstein relation, $D_{ij} = k_B T \mu_{ij}$. The mobilities μ_{ij} connect the torque T_j on particle j with the angular velocity ω_i of particle i: $\omega_i = \mu_{ij} T_j$. Due to Lorentz's reciprocal theorem [3], they fulfil $\mu_{ij} = \mu_{ji}^t$, where t means transposed matrix. If, in addition, the particles are identical, $\mu_{ij} = \mu_{ji}$. The uniaxial symmetry of the two-particle chain determines the form of D_{ij}:

$$D_{ij} = D_{ij}^\perp \mathbf{1} + \Delta D_{ij} \hat{r} \otimes \hat{r} \qquad \text{with } \Delta D_{ij} = D_{ij}^\parallel - D_{ij}^\perp, \tag{5}$$

where $\mathbf{1}$ means the unit tensor, $\hat{r} = r/r$ and $\otimes$ means the tensor product. The constants $D_{ij}^\parallel$ and $D_{ij}^\perp$ refer, respectively, to rotational diffusion about the two-particle axis $\hat{r}$ and a direction perpendicular to it. The related mobilities as a function of reduced particle distance r/a are plotted in figure 1. The library HydroLib [16] allows one to calculate their values ranging from small particle distances where lubrication theory has to be applied to large distances where expansions into a/r are applicable. For comparison, the Rotne–Prager approximation is also
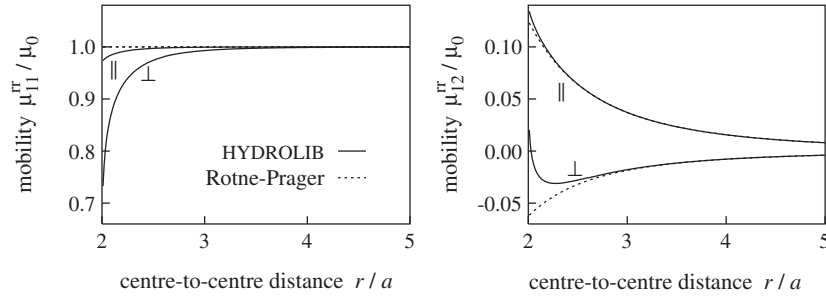
Figure 1. The rotational mobilities of the two-particle chain in units of $\mu_0 = 1/(8\pi\eta a^3)$ as a function of reduced centre-to-centre distance r/a. Full lines: values calculated with numerical library HydroLib; dotted lines: the Rotne–Prager approximation.

shown. Both graphs of figure 1 illustrate that the Rotne–Prager approximation works well for centre-to-centre distances larger than $3a$. To see noticeable deviations of the mobilities $\mu_{11}^{rr\|}$ and $\mu_{11}^{rr\perp}$ from the single-particle value $\mu_0 = 1/(8\pi\eta a^3)$ (the index rr refers directly to the rotational degree of freedom), the particles have to be close. Note that the mobilities in both graphs stay finite when the particles approach contact at $r = 2a$; the derivatives of the perpendicular coefficients, however, are singular.

The Smoluchowski equation determines the temporal evolution of the probability density $P(\hat{\nu}_1, \hat{\nu}_2, t)$ of finding particles 1 and 2 with respective orientations given by $\hat{\nu}_1$ and $\hat{\nu}_2$ at time t [4, 9]:

$$\frac{\partial P(\hat{\nu}_1, \hat{\nu}_2, t)}{\partial t} = \hat{L}_S P(\hat{\nu}_1, \hat{\nu}_2, t), \tag{6}$$

where

$$\hat{L}_S = \nabla_{r1} \cdot D_{11}\nabla_{r1} + \nabla_{r2} \cdot D_{22}\nabla_{r2} + 2\nabla_{r1} \cdot D_{12}\nabla_{r2} \tag{7}$$

denotes the Smoluchowski operator that is a generalization of $D_0\nabla_r^2$ in the single-particle equation (1). Since the two particles are identical and with the help of equation (5), it is rewritten as

$$\hat{L}_S = D_{11}^\perp(\nabla_{r1}^2 + \nabla_{r2}^2) + \Delta D_{11}\left(\frac{\partial^2}{\partial\varphi_1^2} + \frac{\partial^2}{\partial\varphi_2^2}\right) + 2D_{12}^\perp\nabla_{r1} \cdot \nabla_{r2} + 2\Delta D_{12}\frac{\partial}{\partial\varphi_1}\frac{\partial}{\partial\varphi_2} \tag{8}$$

where $\partial/\partial\varphi_i$ is the z component of ∇_{ri} with $\hat{z} \| r$. In analogy to the wavefunction determined from Schrödinger's equation in quantum mechanics, the time evolution of the probability density $P(\hat{\nu}_1, \hat{\nu}_2, t)$ is known in principle when eigenvalues and eigenfunctions of the Smoluchowski operator are known. Due to the analogy with the angular momentum algebra, the eigenvectors of the unperturbed problem, i.e., particles not coupled by hydrodynamic interactions ($D_{12}^\perp = \Delta D_{12} = 0$), are just products of two spherical harmonics: $\Phi(\hat{\nu}_1, \hat{\nu}_2) = Y_{m_1}^{l_1}(\hat{\nu}_1)Y_{m_2}^{l_1}(\hat{\nu}_2)$. They are even eigenfunctions of the last term in the second line of equation (8). The operator $\nabla_{r1} \cdot \nabla_{r2}$, however, mixes the eigenfunctions of the unperturbed problem. How this is done can be calculated with the help of 'ladder operators' introduced in full analogy to the angular momentum algebra [15]:

$$\nabla_r^\pm = \nabla_{rx} \pm i\nabla_{ry}. \tag{9}$$

Applied to spherical harmonics, they yield

$$\nabla_r^\pm Y_m^l(\hat{\nu}) = i\sqrt{l(l+1) - m(m \pm 1)}Y_{m\pm1}^l(\hat{\nu}) = ic_{lm}^\pm Y_{m\pm1}^l(\hat{\nu}). \tag{10}$$

We rewrite the crucial term $\nabla_{r1} \cdot \nabla_{r2}$ of $\hat{L}_S$ with the help of

$$\nabla_{rx} = \tfrac{1}{2}(\nabla_r^+ + \nabla_r^-) \qquad \text{and} \qquad \nabla_{ry} = \frac{1}{2i}(\nabla_r^+ - \nabla_r^-) \tag{11}$$

as

$$\nabla_{r1} \cdot \nabla_{r2} = \frac{1}{2}(\nabla_{r1}^+ \nabla_{r2}^- + \nabla_{r1}^- \nabla_{r2}^+) + \frac{\partial}{\partial \varphi_1} \frac{\partial}{\partial \varphi_2} \tag{12}$$

and can now fully determine how the Smoluchowski operator acts on the unperturbed eigenfunction:

$$-\hat{L}_S Y_{m_1}^{l_1} Y_{m_2}^{l_2} = \{D_{11}^\perp [l_1(l_1+1) + l_2(l_2+1)] + \Delta D_{11}(m_1^2 + m_2^2) + 2D_{12}^\parallel m_1 m_2\} Y_{m_1}^{l_1} Y_{m_2}^{l_2}$$
$$+ D_{12}^\perp (c_{l_1 m_1}^+ c_{l_2 m_2}^- Y_{m_1+1}^{l_1} Y_{m_2-1}^{l_2} + c_{l_1 m_1}^- c_{l_2 m_2}^+ Y_{m_1-1}^{l_1} Y_{m_2+1}^{l_2}) \tag{13}$$

where we used $D_{12}^\parallel = D_{12}^\perp + \Delta D_{12}$ and the coefficients $c_{lm}^\pm$ are defined in equation (10).

3. Time correlation functions and observables

We are interested in quantities that can be measured in experiments. We therefore define the most general time correlation function

$$\Gamma\binom{l_1 l_2 m_1 m_2}{l_1' l_2' m_1' m_2'}|t) = \langle Y_{m_1}^{l_1*}[\hat{\nu}_1(t)] Y_{m_2}^{l_2*}[\hat{\nu}_2(t)] Y_{m_1'}^{l_1'}[\hat{\nu}_1(0)] Y_{m_2'}^{l_2'}[\hat{\nu}_2(0)]\rangle \tag{14}$$

which can be related to useful observables. Formally, Γ is calculated using the propagator $P(\hat{\nu}_1, \hat{\nu}_2, t|\hat{\nu}_1', \hat{\nu}_2', 0)$ that gives the probability of finding the two particles with orientations $\hat{\nu}_1$ and $\hat{\nu}_2$ at time t when they had with certainty the orientations $\hat{\nu}_1'$ and $\hat{\nu}_2'$ at time $t = 0$:

$$\Gamma\binom{l_1 l_2 m_1 m_2}{l_1' l_2' m_1' m_2'}|t) = \int \int Y_{m_1}^{l_1*}(\hat{\nu}_1) Y_{m_2}^{l_2*}(\hat{\nu}_2) P(\hat{\nu}_1, \hat{\nu}_2, t|\hat{\nu}_1', \hat{\nu}_2', 0)$$
$$\times W(\hat{\nu}_1', \hat{\nu}_2', t = 0) Y_{m_1'}^{l_1'}(\hat{\nu}_1') Y_{m_2'}^{l_2'}(\hat{\nu}_2') \, d\hat{\nu}_1 \, d\hat{\nu}_2 \, d\hat{\nu}_1' \, d\hat{\nu}_2' \tag{15}$$

where $W(\hat{\nu}_1', \hat{\nu}_2', t = 0)$ is the probability distribution for $\hat{\nu}_1'$ and $\hat{\nu}_2'$ at $t = 0$. In the following, we will use an isotropic distribution $W = 1/(4\pi)^2$ since the interaction potential of the particles does not depend on their orientations. However, one could also think of a situation where one first 'aligns' the particles and then lets them evolve with time t. In such a case, W would be given by a product of delta functions. The time evolution of the correlation function is calculated from a master equation that we derive by taking the time derivative of equation (15), then using the Smoluchowski equation (6) for the propagator and finally letting $\hat{L}_S = \hat{L}_S^+$ act on the spherical harmonics at time t:

$$\frac{\partial}{\partial t} \Gamma\binom{l_1 l_2 m_1 m_2}{l_1' l_2' m_1' m_2'}|t) = \int \int [\hat{L}_S Y_{m_1}^{l_1*}(\hat{\nu}_1) Y_{m_2}^{l_2*}(\hat{\nu}_2)] P(\hat{\nu}_1, \hat{\nu}_2, t|\hat{\nu}_1', \hat{\nu}_2', 0)$$
$$\times W(\hat{\nu}_1', \hat{\nu}_2', t = 0) Y_{m_1'}^{l_1'}(\hat{\nu}_1') Y_{m_2'}^{l_2'}(\hat{\nu}_2') \, d\hat{\nu}_1 \, d\hat{\nu}_2 \, d\hat{\nu}_1' \, d\hat{\nu}_2'. \tag{16}$$

With the help of equation (13) and the definition (15), the master equation assumes the form

$$-\frac{\partial}{\partial t} \Gamma\binom{l_1 l_2 m_1 m_2}{l_1' l_2' m_1' m_2'}|t) = \{D_{11}^\perp [l_1(l_1+1) + l_2(l_2+1)] + \Delta D_{11}(m_1^2 + m_2^2)$$
$$+ 2D_{12}^\parallel m_1 m_2\} \Gamma\binom{l_1 l_2 m_1 m_2}{l_1' l_2' m_1' m_2'}|t)$$
$$+ D_{12}^\perp [c_{l_1 m_1}^+ c_{l_2 m_2}^- \Gamma\binom{l_1 l_2 m_1+1 m_2-1}{l_1' l_2' m_1' m_2'}|t) + c_{l_1 m_1}^- c_{l_2 m_2}^+ \Gamma\binom{l_1 l_2 m_1-1 m_2+1}{l_1' l_2' m_1' m_2'}|t)]. \tag{17}$$

The time evolution of various observables can now be calculated with the help of this equation. We illustrate two cases which should be measurable in experiments.
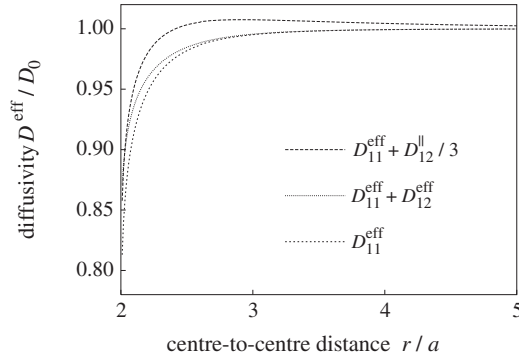
Figure 2. The effective rotational diffusion constants D_{11}^{eff}, $D_{11}^{\text{eff}} + D_{12}^{\parallel}/3$ and $D_{11}^{\text{eff}} + D_{12}^{\text{eff}}$ in units of D_0 as a function of the reduced particle separation r/a.

3.1. One-particle diffusion

Let us investigate the time correlation function for the orientation of particle 1:

$$\langle \hat{\boldsymbol{\nu}}_1(t) \cdot \hat{\boldsymbol{\nu}}_1(0) \rangle = \frac{4\pi}{3} \sum_{m=-1}^{1} \langle Y_m^{1*}[\hat{\boldsymbol{\nu}}_1(t)] Y_m^1[\hat{\boldsymbol{\nu}}_1(0)] \rangle = \frac{(4\pi)^2}{3} \Gamma\binom{10m0}{10m0}|t). \tag{18}$$

The first equality is just the addition theorem for spherical harmonics [15] and the second equality used $l_2 = l_2' = m_2 = m_2' = 0$, i.e., $Y_0^0 = 1/\sqrt{4\pi}$ for the second particle in the definition (14) of $\Gamma(\ldots|t)$. Since $c_{00}^{+/-} = 0$, $\Gamma\binom{10m0}{10m0}|t)$ does not couple to other Γs. The evolution equation is therefore simple and gives

$$\Gamma\binom{10m0}{10m0}|t) = \Gamma\binom{10m0}{10m0}|0) e^{-(2D_{11}^{\perp} + \Delta D_{11} m^2)t}. \tag{19}$$

Compared to the single-particle result of equation (3) ($l = 1$), the decay rate of the correlation function now also depends on the azimuthal quantum number m due to presence of the second particle. With $\Gamma\binom{10m0}{10m0}|0) = 1/(4\pi)^2$ (isotropic distribution of $\hat{\boldsymbol{\nu}}_1(0)$), the correlation function (18) becomes

$$\langle \hat{\boldsymbol{\nu}}_1(t) \cdot \hat{\boldsymbol{\nu}}_1(0) \rangle = \tfrac{1}{3} e^{-2D_{11}^{\perp} t}(1 + 2e^{-\Delta D_{11} t}). \tag{20}$$

Finally, the mean square angular displacement of $\hat{\boldsymbol{\nu}}_1(t)$ is calculated from $\langle |\hat{\boldsymbol{\nu}}_1(t) - \hat{\boldsymbol{\nu}}_1(0)|^2 \rangle = 2(1 - \langle \hat{\boldsymbol{\nu}}_1(t) \cdot \hat{\boldsymbol{\nu}}_1(0) \rangle)$ and for small times it reads

$$\langle |\hat{\boldsymbol{\nu}}_1(t) - \hat{\boldsymbol{\nu}}_1(0)|^2 \rangle \approx 4 D_{11}^{\text{eff}} t \qquad \text{with } D_{11}^{\text{eff}} = \frac{2D_{11}^{\perp} + D_{11}^{\parallel}}{3}. \tag{21}$$

So D_0 in the analogous single-particle equation (4) is replaced by the average of the self-diffusion constants $D_{11}^{\perp}$ and $D_{11}^{\parallel}$ that encode the presence of the second particle. The effective diffusion constant D_{11}^{eff} in units of D_0 is plotted in figure 2 as a function of the reduced particle separation r/a.

3.2. Two-particle diffusion

To access the diffusion constant $D_{12}^{\parallel}$, we consider the correlation function

$$\langle \hat{\boldsymbol{\nu}}_1(t) \cdot \hat{\boldsymbol{\nu}}_2(t) \hat{\boldsymbol{\nu}}_1(0) \cdot \hat{\boldsymbol{\nu}}_2(0) \rangle = \left(\frac{4\pi}{3} \right)^2 \sum_{m_1=-1}^{1} \sum_{m_2=-1}^{1} \Gamma\binom{11m_1m_1}{11m_2m_2}|t). \tag{22}$$

The correlation functions $\Gamma(^{11\pm1\pm1}_{11m_2m_2}|t)$ do not couple to other Γs and therefore relax with a rate $2(D^\perp_{11} + D^\parallel_{11} + D^\parallel_{12})$ as determined from the first two lines of equation (17). The quantity $\Gamma(^{1100}_{11m_2m_2}|t)$ couples to $\Gamma(^{111-1}_{11m_2m_2}|t)$ and $\Gamma(^{11-11}_{11m_2m_2}|t)$ but can be determined straightforwardly from the three coupled evolution equations. So, ultimately the correlation function (22) appears as a sum of three exponentials. Since we are mainly interested in the short time limit of equation (22), we present a shortcut towards the result. With the Taylor expansion

$$\Gamma(^{11m_1m_1}_{11m_2m_2}|t) = \frac{1}{(4\pi)^2}\delta_{m_1m_2} - a_{m_1}t, \tag{23}$$

where the coefficients a_{m_1} are directly determined from the master equation (17) using $\Gamma(^{111-1}_{11m_2m_2}|0) = \Gamma(^{11-11}_{11m_2m_2}|0) = 0$, we immediately arrive at

$$\langle\hat{\boldsymbol{\nu}}_1(t) \cdot \hat{\boldsymbol{\nu}}_2(t)\hat{\boldsymbol{\nu}}_1(0) \cdot \hat{\boldsymbol{\nu}}_2(0)\rangle \approx \tfrac{1}{3}[1 - 4(D^{\text{eff}}_{11} + D^\parallel_{12}/3)t]. \tag{24}$$

Note that D^{eff}_{11}, familiar from the one-particle diffusion (see equation (21)), is modified here by $D^\parallel_{12}/3$. Figure 2 illustrates $D^{\text{eff}}_{11} + D^\parallel_{12}/3$ as a function of particle separation.

In the same manner, we can also determine the short time limit of

$$\langle\hat{\boldsymbol{\nu}}_1(t) \cdot \hat{\boldsymbol{\nu}}_2(0)\hat{\boldsymbol{\nu}}_2(t) \cdot \hat{\boldsymbol{\nu}}_1(0)\rangle = \left(\frac{4\pi}{3}\right)^2 \sum_{m_1=-1}^{1} \sum_{m_2=-1}^{1} \Gamma(^{11m_1m_2}_{11m_2m_1}|t) \tag{25}$$

and obtain

$$\langle\hat{\boldsymbol{\nu}}_1(t) \cdot \hat{\boldsymbol{\nu}}_2(0)\hat{\boldsymbol{\nu}}_2(t) \cdot \hat{\boldsymbol{\nu}}_1(0)\rangle \approx \tfrac{1}{3}[1 - 4(D^{\text{eff}}_{11} + D^{\text{eff}}_{12})t] \tag{26}$$

with

$$D^{\text{eff}}_{12} = \frac{2D^\perp_{12} + D^\parallel_{12}}{3}. \tag{27}$$

We again plot $D^{\text{eff}}_{11} + D^{\text{eff}}_{12}$ in figure 2. A comparison of all three effective diffusion constants in figure 2 only reveals small differences that pose a challenge for measurements in an experiment. Nevertheless, for small particle distances, the effect of hydrodynamic interactions calculated on the basis of lubrication theory should be measurable.

A natural extension of the theory presented here is a chain of more than two particles. However, the mobilities or diffusion tensors in such a system can no longer be described by the two-particle system; when a particle is situated between two other colloids, three-body effects become important, certainly for small separations. So experiments could be used to measure deviations from the effective diffusion constants presented in this article. Furthermore, the coupling to positional fluctuations of the particles has to be incorporated.

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