PHYSICAL REVIEW E VOLUME 50, NUMBER 3 SEPTEMBER 1994

# Equilibrium properties of a polymer chain in an Euler fluid

Michael Schulz
*Abteilung Theoretische Physik, Universität Ulm, 89069 Ulm, Germany*

Klaus Handrich
*Fachbereich Physik, Technische Universität Ilmenau, D-7300 Ilmenau, Germany*

(Received 1 November 1993; revised manuscript received 9 June 1994)

A field theoretical formulation for the motion of a polymer chain in an Euler Fluid was analyzed. Using a projection formalism an exact representation of the effective chain action was obtained. The mean field approximation gives an effective equation of motion for the polymer chain in the Euler fluid. As a result of the interaction between chain and liquid, we get a general effective friction, stochastic forces, and an additional attractive contribution to the potential for the polymer chain. The influence of this contribution to the equilibrium end to end distance and diffusion properties of the polymer chain are discussed.

PACS number(s): 61.25.Hq, 05.70.Ln, 05.40.+j

## I. INTRODUCTION

The determination of the microscopical motion for a polymer chain in a thermodynamical bath is a complicated multiple-body problem. In principal, there exist two general possibilities for the determination or for analysis of the equations of motion of such a many-body system $\Sigma$ in a thermodynamical bath. On the other hand, one can use, in the frame of an analytical description, the complete or effective equations of motion of $\Sigma$ in the phase space or (in the limit of vanishing inertia, the Brownian limit) in the configuration space or one can start from the evolution equation of the probability distribution function of the system $\Sigma$. Both ways are closely connected because one obtains an effective Hamiltonian from the evolution equation of the probability distribution function by solving the inverse dynamical problem [1,2] and obtaining the evolution equation for the distribution function of the relevant general coordinates of $\Sigma$ by a projection formalism [3]. Therefore analytical investigations in the microscopical motion of a polymer chain are in the usual Brownian limit bases, in most cases on a Langevin equation [4,5], Fokker-Planck equations [6], or projection formalism [7,8], from which an effective description of the environment dynamics results (for example, by stochastic forces, diffusion coefficients, or frictional forces).

On the other hand, the motion of a polymer chain in a thermodynamical bath can be analyzed by using well known numerical methods (molecular dynamics [9], Monte Carlo simulations [10–12], or Brownian dynamics [13]). Generally, there exist two reasonable ways for a numerical solution of this problem. The first possible numerical realization was based on the investigation of the detailed microscopic dynamics of the polymer chain and the thermodynamical environment (which can be other polymer chains [14], liquids, or surfaces [15]). Clearly, because of the restricted computation time and the computation memory, such simulations are only possible for short chains and small volumes. In the second case one uses effective external forces and friction coefficients, which describe the interaction with the thermodynamical bath (see, for example, [16]).

In most numerical and analytical studies of a polymer chain in a simple liquid it is reasonable to use one constant friction coefficient $\eta$ for the description of the Brownian behavior of each monomer. The microscopic interactions between chain and liquid (hydrodynamic interaction, Oseen tensor) are reduced to this one free parameter $\eta$ (a second parameter is the strength of the thermodynamic noise, but this value is connected with the friction coefficient by the fluctuation-dissipation theorem).

Unfortunately, an analytical formulation of an equation of motion for a polymer chain in a frictionless liquid (called an Euler fluid) is not possible by using the typical above- mentioned standard procedures (because $\eta \to 0$ follows a vanishing interaction between chain and liquid). On the other hand, because of the numerical restrictions, it is reasonable to obtain an effective equation (e.g., an equation which contains only the relevant polymer chain coordinates) for such a polymer chain. Therefore, we need at first a realistic analytical description for this problem on a microscopic level.

## II. MODEL

### A. Hamiltonian for the liquid

We start our investigation with a description of the liquid. We get, for the simplest case ($N$ identical molecules with radial symmetry, only two-body interactions), the Hamiltonian

$$H_L = \sum_i^N \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}\sum_{i,j} v(\mathbf{r}_i - \mathbf{r}_j) \ . \qquad (1)$$

For the following considerations we use the mass density

©1994 The American Physical Society

$$\rho(\mathbf{r}) = \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \tag{2}$$

and the local current density

$$\mathbf{j}(\mathbf{r}) = \sum_{i}^{N} \frac{\mathbf{p}_i}{m} \delta(\mathbf{r} - \mathbf{r}_i) \ , \tag{3}$$

which is connected with the local velocity $\mathbf{v}$ by the relation $\mathbf{j} = \rho \mathbf{v}$. Introducing the hydrodynamic potential $\phi$ with $\mathbf{v} = \nabla \phi$, we get the Hamiltonian

$$H_L = \frac{1}{2} \int d^d r \rho(\mathbf{r}) \nabla \phi(\mathbf{r})^2 + \int \int d^d r d^d r' \rho(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') \tag{4}$$

in the special case for liquid without turbulence and friction. It is simple to prove that the field $\phi$ corresponds to the field momentum $\rho$ [17].

The general representation of (4) can be obtained from the Lagrangian [18,19]

$$L = -\rho \left( \lambda \dot{\Psi} - \dot{\Phi} + \frac{\mathbf{v}^2}{2} \right) - u[\rho] \tag{5}$$

with the potentials $\Psi$, $\Phi$ and $\lambda$, the local density $\rho$, the density dependent intrinsic energy $u[\rho]$ [determined by the functional $\int d^d r d^d r' \rho(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}')$], and the general local velocity $\mathbf{v} = \lambda \nabla \Psi - \nabla \Phi$. This Lagrangian guarantees the continuous equation $\dot{\rho} + \nabla(\rho \mathbf{v}) = 0$ and the full frictionless Navier-Stokes equation (Euler equation)

$$\dot{\mathbf{v}} + \frac{1}{2} \nabla \mathbf{v}^2 + \nabla \frac{\partial u(\rho)}{\partial \rho} = 0$$

under consideration of the boundary conditions $\lambda + \mathbf{v} \cdot \nabla \lambda = 0$ and $\dot{\Psi} + \mathbf{v} \cdot \nabla \Psi = 0$. From (5) the Hamiltonian follows

$$H_L = \int d^d r \left[ \frac{1}{2} \frac{\mathbf{j}(\mathbf{r})^2}{\rho(\mathbf{r})} + u[\rho, \mathbf{r}] \right] \ . \tag{6}$$

Here the local current density $\mathbf{j} = \rho \mathbf{v}$ must be expressed by the field components $\Psi$,$\Phi$,$\lambda$ and the field momenta $\delta L / \delta \dot{\Phi} = \rho$ and $\delta L / \delta \dot{\Psi} = -\lambda \rho = \xi$ (Note that $\delta L / \delta \dot{\lambda} = 0$.) For the following calculations it is sufficient enough to use the harmonic representation of the Hamiltonian (6). We get

$$H_L = \frac{1}{2} \int d^d r \left[ \bar{\rho} (\nabla \Phi)^2 - 2 (\nabla \Psi) \cdot (\nabla \Phi) + \frac{\bar{\xi}^2}{\bar{\rho}} (\nabla \Psi)^2 \right] + \frac{1}{2} \int \int d^d r d^d r' \delta \rho(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \delta \rho(\mathbf{r}') \tag{7}$$

with the deviations from the averaged values $\delta \xi = \xi - \bar{\xi}$ and $\delta \rho = \rho - \bar{\rho}$ (Note that from the mass conservation it follows that $\int \delta \rho d^d r = 0$.) The equation of motion for $\Psi$ is given in this harmonic representation by $\dot{\Psi} = 0$, e.g., $\Psi$ is a time-invariant function. Therefore with the transformation $\phi = \Phi - \Psi \bar{\xi} \bar{\rho}^{-1}$ Eq. (7) becomes

$$H_l = \frac{1}{2} \int d^d r \bar{\rho} (\nabla \phi)^2 + \frac{1}{2} \int \int d^d r d^d r' \delta \rho(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \delta \rho(\mathbf{r}') \ . \tag{8}$$

Clearly, (4) is equivalent to the harmonic representation (8) of the full hydrodynamic field system [defined by (5)], because all "turbulence" contributions to the full hydrodynamic equations (determined by the fields $\Psi$ and $\xi$) are of higher order.

### B. Hamiltonian of the polymer chain

The Hamiltonian of the chain (length $N$, radial symmetric monomer structure) is determined by

$$H_C = \sum_{i}^{N} \frac{\mathbf{p}_i^2}{2M} + V[\mathbf{R}] \tag{9}$$

($\mathbf{p}_i$ momentum of the $i$th monomer, $\mathbf{R}_i$ the coordinate of the $i$th monomer, and $M$ the mass of monomers). The potential $V[\mathbf{R}]$ contains the contribution of the interaction between consecutive monomers along the chain and all other intramolecular interaction terms (for example, excluded volume effects). It should be remarked that $H_C$ contains only the coordinates of the center of mass of the effective monomers. The contributions of all other degrees of freedom (bond length and bond angle fluctuations, rotations of side groups) are neglected for the calculations following in Secs. IV and V.

### C. Interaction part

The main contributions of the interaction between chain monomers and liquid molecules are based on a sum of two body potentials $w(\mathbf{r})$

$$H_I = \sum_{i=1}^{N} \sum_{j} w(\mathbf{R}_i - \mathbf{r}_j) \ . \tag{10}$$

Using the definition of the density (2), the interaction can be written as

$$H_I = \frac{1}{m} \sum_{i=1}^{N} \int d^d r \rho(\mathbf{r}) w(\mathbf{R}_i - \mathbf{r}) \ . \tag{11}$$

As a result of these considerations we get the full Hamiltonian of the liquid- polymer chain system

$$H = H_C + \frac{1}{m} \sum_{i=1}^{N} \int d^d r \delta \rho(\mathbf{r}) w(\mathbf{R}_i - \mathbf{r}) + \frac{1}{2} \int d^d r \bar{\rho} (\nabla \phi)^2 + \frac{1}{2} \int \int d^d r d^d r' \delta \rho(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \delta \rho(\mathbf{r}') \ . \tag{12}$$

(Irrelevant constant contributions are neglected.) After a simple Fourier transformation, (12) becomes

$$H = H_C + \frac{1}{m\sqrt{V}} \sum_{\mathbf{k}} \delta\rho_{\mathbf{k}} w(k) g_{-\mathbf{k}} + \frac{\bar{\rho}}{2} k^2 \mid \phi_{\mathbf{k}} \mid^2 + \frac{v(k)}{2} \mid \delta\rho_{\mathbf{k}} \mid^2 \tag{13}$$

with

$$\phi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \phi_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{14}$$

$$\delta\rho(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \delta\rho_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} , \tag{15}$$

and

$$v(r) = \frac{1}{V} \sum_{\mathbf{k}} v(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}} , \tag{16}$$

$$w(r) = \frac{1}{V} \sum_{\mathbf{k}} w(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}} . \tag{17}$$

The value

$$g_{\mathbf{k}} = \sum_{i}^{N} \exp\{i\mathbf{k} \cdot \mathbf{R}_i\} \tag{18}$$

is the Fourier transformed density of the polymer chain. Note that the observables $\delta\rho_{\mathbf{k}}$, $\phi_{\mathbf{k}}$, and $g_{\mathbf{k}}$ are invariant against a complex conjugation and a simultaneous change $\mathbf{k} \rightarrow -\mathbf{k}$. From this it follows that the values of one-half of the $\mathbf{k}$ space are dependent on the values of the opposite half, e.g., the observables of one-half of the space are sufficient for the description of the Hamiltonian. On the other hand, the real part and the imaginary part of $\delta\rho_{\mathbf{k}}$, $\phi_{\mathbf{k}}$, and $g_{\mathbf{k}}$ are independent values. Therefore, it is reasonable to separate this observables in the real and the imaginary part, from which each part occupies one-half of the full $\mathbf{k}$ space (for example $\sqrt{2}\mathrm{Re}\phi_{\mathbf{k}} \rightarrow \phi_{\mathbf{k}}$ occupies one-half of the $\mathbf{k}$ space and $\sqrt{2}\mathrm{Im}\phi_{\mathbf{k}} \rightarrow \phi_{\mathbf{k}}$ occupies the opposite half of the $\mathbf{k}$ space). The Hamiltonian (13) is invariant against this definition, e.g., it is possible to use (13) with the new meaning of the variables $\delta\rho_{\mathbf{k}}$, $\phi_{\mathbf{k}}$, and $g_{\mathbf{k}}$.

## III. PROJECTION FORMALISM

The Hamiltonian (13) determines the behavior of the general liquid-polymer chain system. On the other hand, the liquid plays the role of a thermodynamic bath for the motion of the polymer chain. Therefore, the knowledge of the motion is irrelevant, e.g., it is possible to average over the degrees of freedom for the liquid. We expect a change of the chain potential $V[\mathbf{R}]$ and the introduction of an effective friction and stochastic forces in the equation of motion of the relevant coordinates $\mathbf{R}$ as a result of the interaction between bath and polymer chain.

The usual formalism for the determination of an effective equation of motion for the relevant coordinates (coordinates of the polymer chain) is based on a path integral representation [20] and is similar to the projection formalism in Liouville space [7,21,3]. Here we show briefly the main point of this idea. Starting from the statistical density operator $\hat{\rho}(t)$, we get

$$\hat{\rho}(t) = \exp\{-i\hbar^{-1}Ht\}\hat{\rho}(0)\exp\{i\hbar^{-1}Ht\} \tag{19}$$

or

$$\langle \phi, \mathbf{R} \mid \hat{\rho}(t) \mid \mathbf{R}', \phi' \rangle = \int\int d\phi'' dR'' d\phi''' dR''' \times \wp(\phi, \mathbf{R}, t; \phi'', \mathbf{R}'', 0)\wp(\phi'', \mathbf{R}'', i\hbar\beta; \phi''', \mathbf{R}''', 0)\wp(\phi''', \mathbf{R}''', 0; \phi', \mathbf{R}', t) , \tag{20}$$

with $\beta = 1/kT$ and the evolution matrix

$$\wp(\phi, \mathbf{R}, t; \phi'', \mathbf{R}, 0) = \int D[\phi]D[\mathbf{R}] \exp\left\{ i\frac{S[\phi, \mathbf{R}]}{\hbar} \right\} . \tag{21}$$

Note, that the path in (21) satisfies the boundary conditions $\phi(t) = \phi$, $\mathbf{R}(t) = \mathbf{R}$, $\phi(0) = \phi'$, and $\mathbf{R}(0) = \mathbf{R}'$. The action $S(\phi, \mathbf{R})$ is given by the usual definition

$$S[\phi, \mathbf{R}] = \int_0^t L(\dot{\phi}, \phi, \dot{\mathbf{R}}, \mathbf{R}) dt'$$

[the Lagrangian $L$ follows from the Hamiltonian (13) by the typical Legendre transformation]. The imaginary part ($0 \rightarrow i\hbar\beta$) of the path integral in (20) is a result of the statistical weight $\hat{\rho}(0) \sim \exp(-\beta H)$. From (20) it is reasonable to collect the different parts of $\langle \phi, \mathbf{R} \mid \hat{\rho}(t) \mid \mathbf{R}', \phi' \rangle$ to one common path integral with an integration curvature in a complex time space ($t \rightarrow 0 \rightarrow i\hbar\beta \rightarrow t + i\hbar\beta$).

The effective equation of motion for the polymer chain follows from the total time evolution of the density matrix $\langle \phi, \mathbf{R} \mid \hat{\rho}(t) \mid \mathbf{R}', \phi' \rangle$ by the projection of the relevant observables (e.g., the calculation of the trace for the irrelevant fields $\phi$)

$$\langle \mathbf{R} \mid \hat{\rho}(t) \mid \mathbf{R}' \rangle = \mathrm{tr}_{\phi} \langle \phi, \mathbf{R} \mid \hat{\rho}(t) \mid \mathbf{R}', \phi' \rangle .$$

The determination of this trace is a standard procedure and follows straightforwardly [because of the harmonic (Gaussian) character of the $\phi$ part of the Hamiltonian (13) and therefore the Lagrangian $L$, an exact determination of this trace, is possible]. We get

$$\langle \mathbf{R} \mid \hat{\rho}(t) \mid \mathbf{R}' \rangle = \int D[R] \exp\left\{ i \frac{S_e(\mathbf{R})}{\hbar} \right\} \tag{22}$$

The effective action $S_e(\mathbf{R})$ is given by the sum of the action of the free polymer chain $S_c$, corresponding to (9) and additional parts $\mu_{\mathbf{k}}$, which results from the interaction between the bath (Euler fluid) and the polymer chain. We get the representation

$$S_e(\mathbf{R}) = S_c(\mathbf{R}) + i \sum_{\mathbf{k}} \mu_k \tag{23}$$

with

$$\begin{aligned}
\mu_{\mathbf{k}} = {} & \int_0^{\hbar\beta} d\tau \int_0^{\hbar\beta} d\tau' \frac{k w(k)^2 \sqrt{\bar{\rho}}}{2m^2 V \sqrt{v(k)}} \chi_{\mathbf{k}}(\tau - \tau') g_{\mathbf{k}}(i\tau) g_{\mathbf{k}}(i\tau') \\
& -i \int_0^{\hbar\beta} d\tau \int_0^{\infty} dt' \frac{k w(k)^2 \sqrt{\bar{\rho}}}{2m^2 V \sqrt{v(k)}} \frac{\cosh(\sqrt{v(k)\bar{\rho}}\frac{\hbar\beta}{2} k + it' - \tau)}{\sinh(\sqrt{v(k)\bar{\rho}}\frac{\hbar\beta}{2} k)} g_{\mathbf{k}}(i\tau)[g_{\mathbf{k}}(t') - g_{\mathbf{k}}(t' + i\hbar\beta)] \\
& + \int_0^{\infty} dt' \int_0^{t'} dt'' \frac{k w(k)^2 \sqrt{\bar{\rho}}}{2m^2 V \sqrt{v(k)}} \coth\left( \sqrt{v(k)\bar{\rho}} \frac{\hbar\beta}{2} k \right) \cos[\sqrt{v(k)\bar{\rho}} k (t' - t'')] \\
& \times [g_{\mathbf{k}}(t'') - g_{\mathbf{k}}(t'' + i\hbar\beta)][g_{\mathbf{k}}(t') - g_{\mathbf{k}}(t' + i\hbar\beta)] \\
& + i \int_0^{\infty} dt' \int_0^{t'} dt'' \frac{k w(k)^2}{2m^2 V k v(k)} \cos[\sqrt{v(k)\bar{\rho}} k (t' - t'')][g_{\mathbf{k}}(t'') - g_{\mathbf{k}}(t'' + i\hbar\beta)][\dot{g}_{\mathbf{k}}(t') + \dot{g}_{\mathbf{k}}(t' + i\hbar\beta)] \\
& + i \frac{k w(k)^2}{2m^2 V k v(k)} [g_{\mathbf{k}}(0) + g_{\mathbf{k}}(i\hbar\beta)] \int_0^{\infty} dt' \cos[\sqrt{v(k)\bar{\rho}} k t'][g_{\mathbf{k}}(t') - g_{\mathbf{k}}(t' + i\hbar\beta)] \\
& - i \int_0^{\infty} dt' \frac{k w(k)^2}{2m^2 V k v(k)} [g_{\mathbf{k}}(t')^2 - g_{\mathbf{k}}(t' + i\hbar\beta)^2] - \int_0^{\hbar\beta} d\tau \frac{k w(k)^2}{2m^2 V k v(k)} g_{\mathbf{k}}(i\tau)^2 \ .
\end{aligned} \tag{24}$$

The function $\chi_{\mathbf{k}}(t)$ is defined by

$$\chi_{\mathbf{k}}(\tau) = \frac{\cosh\left( \sqrt{v(k)\bar{\rho}}\frac{\hbar\beta}{2} k - \tau \right)}{\sinh\left( \sqrt{v(k)\bar{\rho}}\frac{\hbar\beta}{2} k \right)} - \frac{2}{\sqrt{v(k)\bar{\rho}} k} \delta(\tau) \ .$$

This general equation implies also quantum mechanic effects. The last three terms correspond to the correction of the potential $V(\mathbf{R})$, for which we can write

$$\Delta V = -\frac{1}{2m^2 V} \sum_{\mathbf{k}} \frac{w(k)^2}{v(k)} g_{\mathbf{k}}^2 \ . \tag{25}$$

Using the definition

$$u(k) = \frac{1}{2m^2} \ , \frac{w(k)^2}{v(k)} \ , \tag{26}$$

we get an additional two-body (radial symmetric) interaction between the monomers of the polymer chain

$$\Delta V = -\frac{1}{V} \sum_{\mathbf{k}} u(k) g_{\mathbf{k}}^2 = -\sum_{i,j} u(\mid \mathbf{R}_i - \mathbf{R}_j \mid) \ . \tag{27}$$

This potential part of (24) can collect in the potential of the polymer chain [given by the action $S_c$ in Eq. 23]. For example, for the preceding calculations that means that $V(\mathbf{R})$ is the sum of the bare potential and the correction $\Delta V$, i.e., the potential of the free Hamiltonian gets a correction term (27), which has a negative sign, e.g., as a result of the interaction between the liquid and the polymer chain which follows an additional attractive potential. (Note that $u(k)$ is always positive because a negative $u(k)$ and therefore a negative $v(k)$ [see Eq. (26)] correspond to an instable liquid.) If all topological and molecular details of the monomers and liquid molecules become irrelevant (which is the case if only large scale effects are of interest), it is possible to reduce the interaction potentials to $\delta$-like functions, i.e., $v(r) \simeq v_0 \delta(r)$, $w(r) \simeq w_0 \delta(r)$, and $u(r) \simeq u_0 \delta(r)$. From Eq. (27) an additional effective attraction of the monomers follows and therefore a decrease of the excluded volume potential $V_{eff} = V_{ex\ vol} - u_0$ follows as a result of the interaction between chain and the liquid.

From the effective action (23) and (24) we get the mean- field approximation for the equation of motion by using the saddle-point method. For large temperatures ($\hbar\beta$ is sufficiently small), it is reasonable to neglect the contributions to the effective action along the imaginary axis (from 0 to $i\hbar\beta$) and use the new coordinates $\mathbf{R} = \mathbf{Y} + \mathbf{y}$ and $\mathbf{R} = \mathbf{Y} - \mathbf{y}$ for the two parts of the path parallel to the real axis of the complex time plane. Hence we get, for the effective action in the second order of the expansion in powers of the small difference value $\mathbf{y}$,

$$S_e = \sum_{i=1}^{N}\int_0^\infty \left(2M\dot{Y}_i^\alpha(t')\dot{y}_i(t')^\alpha - 2\frac{\partial V(\mathbf{Y})}{\partial Y_i^\alpha}y_i^\alpha(t')\right)$$
$$+i\sum_{i,j}\int_0^\infty dt'\int_0^\infty dt''\sum_{\mathbf{k}}\alpha_{\mathbf{k}}(t'-t'')\left.\frac{\partial g_{\mathbf{k}}(t')}{\partial Y_i^\alpha}\right|_{\mathbf{y}=0}\left.\frac{\partial g_{\mathbf{k}}(t'')}{\partial Y_j^\beta}\right|_{\mathbf{y}=0} y_i^\alpha(t')y_j^\beta(t'')$$
$$-\sum_{i,j}\int_0^\infty dt'\int_0^\infty dt''\sum_{\mathbf{k}}\kappa_{\mathbf{k}}(t'-t'')\left.\frac{\partial g_{\mathbf{k}}(t')}{\partial Y_i^\alpha}\right|_{\mathbf{y}=0} y_i^\alpha(t')\left.\frac{\partial g_{\mathbf{k}}(t'')}{\partial Y_j^\beta}\right|_{\mathbf{y}=0}\dot{Y}_j^\beta(t'') \tag{28}$$

(greek indices correspond to space coordinates) with

$$\alpha_{\mathbf{k}}(t'-t'') = \frac{2u(k)k\sqrt{\bar{\rho}}v(k)}{V}\coth\left(\sqrt{v(k)\bar{\rho}}\frac{\hbar\beta}{2}k\right)\cos[\sqrt{v(k)\bar{\rho}}k(t'-t'')] \tag{29}$$

and

$$\kappa_{\mathbf{k}}(t'-t'') = \frac{2u(k)}{V}\cos[\sqrt{v(k)\bar{\rho}}k(t'-t'')]\ . \tag{30}$$

The equation of motion for **Y** follows from the variation of the action (28)

$$\frac{\delta S_e}{\delta y_i^\alpha} = -\left(2M\ddot{Y}_i^\alpha(t) + 2\frac{\partial V(\mathbf{Y})}{\partial Y_i^\alpha}\right) + 4i\sum_j\int_0^t dt'\sum_{\mathbf{k}}\alpha_{\mathbf{k}}(t-t')\left.\frac{\partial g_{\mathbf{k}}(t)}{\partial Y_i^\alpha}\right|_{\mathbf{y}=0}\left.\frac{\partial g_{\mathbf{k}}(t')}{\partial Y_j^\beta}\right|_{\mathbf{y}=0} y_j^\beta(t')$$
$$-2\sum_j\int_0^t dt'\sum_{\mathbf{k}}\kappa_{\mathbf{k}}(t-t')\left.\frac{\partial g_{\mathbf{k}}(t)}{\partial Y_i^\alpha}\right|_{\mathbf{y}=0}\left.\frac{\partial g_{\mathbf{k}}(t')}{\partial Y_j^\beta}\right|_{\mathbf{y}=0}\dot{Y}_j^\beta(t')\ . \tag{31}$$

The equation of motion of $\mathbf{y}(t)$ is an homogeneous integral- differential equation, e.g., the influence of **Y** on the motion of $\mathbf{y}(t)$ is given by a multiplicative coupling. The motion of these variable is determined by some nonlinearities (e.g., the behavior of this variable shows a deterministic chaos) and it is reasonable to interpret the inhomogeneous part of (31) as an external noise or stochastic force, from which the evolution of $\mathbf{Y}(t)$ was driven. Using (28) and (31) it is simple to show that the correlation function of the stochastic force **f**

$$f_i(t) = 2i\sum_j\int_0^t dt'\alpha_{\mathbf{k}}(t-t')\frac{\partial g_{\mathbf{k}}(t)}{\partial Y_i}\frac{\partial g_{\mathbf{k}}(t')}{\partial Y_j}y_j(t') \tag{32}$$

is determined by

$$\langle f_i(t)f_j(t')\rangle = \frac{\hbar}{2}\sum_{\mathbf{k}}\alpha_{\mathbf{k}}(t-t')\frac{\partial g_{\mathbf{k}}(t)}{\partial Y_i}\frac{\partial g_{\mathbf{k}}(t')}{\partial Y_j}\ , \tag{33}$$

which corresponds to the fluctuation-dissipation theorem.

## IV. CLASSICAL EQUATION OF MOTION

For the most applications it is sufficient enough to use the classical relations, e.g., we set $\hbar \to 0$ (and therefore $\mathbf{Y} \to \mathbf{R}$). With

$$\kappa^{\alpha\beta}(\mathbf{R}_i(t) - \mathbf{R}_j(t'), t-t') = \sum_{\mathbf{k}}\kappa_{\mathbf{k}}(t-t')k^\alpha k^\beta e^{\mathbf{k}(\mathbf{R}_i-\mathbf{R}_j)} \tag{34}$$

and (18) the equation of motion for the polymer chain in an Euler fluid follows

$$M\ddot{R}_i^\alpha(t) + \frac{\partial V(\mathbf{R})}{\partial R_i^\alpha} + \sum_j\int_0^t dt'\kappa(\mathbf{R}_i(t) - \mathbf{R}_j(t'), t-t')^{\alpha\beta}\dot{R}_j^\beta(t') = f_i(t) \tag{35}$$

The stochastic force is determined by the correlation function

$$\langle f_i(t)f_j(t')\rangle = \frac{\hbar}{2}\alpha(\mathbf{R}(t) - \mathbf{R}(t'), t-t') = kT\kappa(\mathbf{R}(t) - \mathbf{R}(t'), t-t')\ . \tag{36}$$

The equation of motion is determined by an external stochastic noise **f** with a correlation function $\kappa$, which is dependent on the time difference and the history of the polymer chain [defined by the difference $\mathbf{R}(t) - \mathbf{R}(t')$]. The relaxation function determines an effective friction as a result of the interaction of liquid-polymer chain. This friction is connected to the noise by the well known fluctuation-dissipation theorem [see Eq. (36)]. The structure of (35) is equivalent to a Langevin equation with external stochastic forces and a memory (or relaxation) function, which is dependent on the time and the history of the chain configuration. The cause for this relaxation term is the interaction with the liquid. Each motion of a monomer $R_j(t')$ generates phononlike excitations at time $t'$. The interaction of these liquid phonons with a monomer at a time $t > t'$ in $R_i$ determines the functional structure of the memory, i.e., we have a dependence of the time difference $t - t'$ and of the distance between the creation point $R_i(t')$ of a phonon and the interaction of this phonon with another monomer in $R_i(t)$. Note that Eq. (35) does not contain the contributions of the fast modes of the internal degrees of freedom of the monomers (discussed in Sec. II B). The consideration of these terms with very short time scales leads, in the course of projection formalism, to an additional simple friction term $\zeta_0\dot{\mathbf{R}}_j(t)$ and a second stochastic force $\phi_i(t)$ with a correlation function

$$\langle \phi_i^\alpha(t)\phi_j^\beta(t')\rangle = kT\zeta_0\delta(t-t')\delta^{\alpha\beta}\delta_{ij} \tag{37}$$

and Eq. (35) now becomes the generalized form

$$M\ddot{R}_i^\alpha(t) + \zeta_0\dot{R}_i^\alpha(t) + \frac{\partial V(\mathbf{R})}{\partial R_i^\alpha} + \sum_j \int_0^t dt' \kappa(\mathbf{R}_i(t) - \mathbf{R}_j(t'), t-t')^{\alpha\beta}\dot{R}_j^\beta(t') = f_i(t) + \phi_i(t) = F_i(t)\ . \tag{38}$$

## V. DISCUSSION OF THE RESULTS

### A. Mean end to end distance

For the determination of the mean end to end distance we use the typical mean-field approach, starting from the effective free energy of the polymer chain

$$F = \frac{R^2}{N} + \bar{V}_{eff}\frac{N^2}{R^3}\ . \tag{39}$$

Here $\bar{V}_{eff} \sim V_{eff} = V_{ex\ vol} - u_0$ is a value for the effective interaction between two arbitrary monomers. The mean end to end distance (determined by the minimum of $F$, $\partial F/\partial R = 0$) becomes, in the mean field approximation,

$$R \sim \bar{V}_{eff}^{\frac{1}{5}} N^{\frac{3}{5}}\ , \tag{40}$$

or by using (26)

$$\frac{R^5}{N^3} = a_0 - a_1X^2 \tag{41}$$

with the polymer specific constants $a_0$ and $a_1$ and the value

$$X = \frac{w_0\sqrt{\bar\rho}}{c_0 m}$$

($c_0 = \sqrt{v_0\bar\rho}$ is the sound velocity of the liquid), which is determined by the properties of the liquid and the interaction between the polymer and the liquid.

### B. Dynamical behavior

For the determination of the dynamic properties, we use the customary approximation $M = 0$ and neglect the (effective) excluded volume potential. For the potential between consecutive monomers it is reasonable to use a simple harmonic form, i.e.,

$$\frac{\partial V(\mathbf{R})}{\partial R_i^\alpha} = -\mu_0[R_{i+1}^\alpha + R_{i-1}^\alpha - 2R_i^\alpha] \tag{42}$$

with the elastic constant $\mu_0 = 2k_BT/l_0^2$ ($k_B$ is the Boltzmann constant) Hence, by using the Fourier representation

$$\mathbf{R}_n = \xi_0 + 2\sum_{p=1}\xi_p\cos(\omega_p n) \tag{43}$$

($\omega_p = 2\pi p/N$) we get, in the continuous representation [$\mathbf{R}_n \to \mathbf{R}(s)$, $n$ (discrete) $\to s$ (continuous variable)],

$$\zeta_0\dot{\xi}_p^\alpha(t) + \omega_p^2\mu_0\xi_p^\alpha(t) + \frac{1}{N}\int_0^t dt' \int_0^N\int_0^N ds ds' \cos(\omega_p s) \times \sum_{\mathbf{k}} \kappa_{\mathbf{k}}(t-t')k^\alpha k^\beta \exp\{i\mathbf{k}[\mathbf{R}(s,t) - \mathbf{R}(s',t')]\} \times \left(\dot{\xi}_0^\beta(t') + 2\sum_{q=1}\dot{\xi}_q^\beta(t')\cos(\omega_q s')\right) = F_p^\alpha(t)\ . \tag{44}$$

The evolution equation for the correlation function $\langle \xi_p^\alpha(t)\xi_{p'}^\beta(t')\rangle = \chi_p(t-t')\delta_{pp'}\delta^{\alpha\beta}$ follows from (44) and under consideration of the exact relation $\langle \xi_p^\alpha(t)F_{p'}(t)^\beta\rangle = 0$,

$$\zeta_0\dot{\chi}_p(t) + \omega_p^2\mu_0\chi_p(t) + \frac{1}{3N}\int_0^t dt' \int_0^N\int_0^N ds ds' \cos(\omega_p s) \times \sum_{\mathbf{k}} \kappa_{\mathbf{k}}(t-t')\mathbf{k}^2 \langle \exp\{i\mathbf{k}[\mathbf{R}(s,t) - \mathbf{R}(s',t')]\} \left(\dot{\xi}_0(t') + 2\sum_{q=1}\dot{\xi}_q(t')\cos(\omega_q s')\right)\xi_p(0)\rangle \approx \zeta_0\dot{\chi}_p(t) + \omega_p^2\mu_0\chi_p(t) + \frac{1}{3N}\int_0^t dt' \sum_{\mathbf{k}} \kappa_{\mathbf{k}}(t-t')k^2\Omega(\mathbf{k},p,t-t')\chi_p(t') = 0. \tag{45}$$

$\Omega(\mathbf{k},p,t)$ is the Fourier transformed dynamic structure factor $\Omega(\mathbf{k},s-s',t-t')$ for two monomers in the distance $\Delta s = s - s'$ along the polymer chain. For the determination of $\chi_q(t)$, we use a perturbation theory in terms of $u_0$. Therefore, we substitute in the first order of the perturbation theory (linear in $u_0$) the dynamic structure factor by

$$\Omega(\mathbf{k},p,t) \to \Omega(\mathbf{k},p,t)\mid_{u_0=0} \ .$$

This value can be determined straightforwardly by the simple Rouse theory with the friction coefficient $\zeta_0$ and the elastic coefficient $\mu_0$, i.e., by the solution of the evolution equation for the unperturbed correlation function. We get [see Appendix A, Eq. (A12)]

$$\Omega(\mathbf{k},p,t) = \Omega(\mathbf{k},p)e^{-k^2(D_1 t+D_2\sqrt{t})} \tag{46}$$

with the static structure factor $\Omega(\mathbf{k},p)$ [see Eq. A5]. The diffusion coefficient $D_1$ is determined by (A11) and the anomalous diffusion coefficient $D_2$ by (A9). With the value

$$Y_p(t) = \chi_p(0) - \chi_p(t) \ ,$$

it follows, for the Laplace transformed solution of (45), that

$$Y_p(z) = \frac{k_B T N^{-1}}{z[z\zeta_0 + \mu_0\omega_p^2 + M(p,z)]}, \tag{47}$$

in which the "self energy" term is given by

$$M(p,z) = \frac{Nzu_0}{3\pi^2}\int_0^\infty dk\Bigg(k^4\Omega(k,p) \times \int_0^\infty dt e^{-zt}\cos(c_0 kt)e^{-k^2(D_1 t+D_2\sqrt{t})}\Bigg) \ . \tag{48}$$

For the relaxation modes (this means $zl_0c_0^{-1} \ll 1$, i.e, the velocity of the liquid phonons is very high in comparison to the effective diffusionlike motion of the monomers) we get, by using the approximations in Appendix (B),

$$Y_p(z) \approx \frac{k_B T N^{-1}}{z[z\zeta_{eff} + \mu_0\omega_p^2 + C\omega_p^{1/2}z^2]} \tag{49}$$

with an effective friction coefficient

$$\zeta_{eff} = \zeta_0 + \frac{11}{36\pi^{3/2}}\Gamma\left(\frac{1}{6}\right)\frac{u_0 c_0^{2/3}}{l_0^3 D_2^{4/3}} \tag{50}$$

and

$$C = \frac{\sqrt{6}}{4\pi^{3/2}}\frac{u_0}{l_0^4 c_0}. \tag{51}$$

Straightforwardly, (49) leads to an effective diffusion coefficient

$$D_{eff} = \frac{k_B T}{N\zeta_{eff}} \tag{52}$$

of the polymer chain (or the center of mass of the polymer chain) in the Euler fluid.

In principle, the $N$ dependence of the diffusion coefficient is the same as in the simple Rouse case, but the fast phononlike modes in the Euler fluid realizes a change of the temperature behavior. For large temperatures $T$ or large pure friction coefficients $\zeta_0$ (note that $\zeta_0$ results only from the internal degrees of freedom of the polymer chain), it follows that $\zeta_{eff} \approx \zeta_0$ and therefore $D_{eff} \sim T\zeta_0^{-1}/N$. In the opposite case (low temperatures or low bare friction coefficient $\zeta_0$), we get $\zeta_{eff} \approx \zeta_0^{2/3}T^{-2/3}$ and therefore $D_{eff} \sim T^{5/3}\zeta_0^{-2/3}$, i.e., a second (anomalous) temperature behavior of the diffusion coefficient.

### C. Conclusions

We have shown that the behavior of a free chain in a frictionless (Euler) fluid is strongly determined by mechanical properties of this liquid (sound velocity, and density). Particularly, the characteristic mesoscopical parameters of a chain in the equilibrium state — the mean square radius of gyration or the end to end distance— shows an additional negative part. In the case of a sufficiently large interaction energy $w_0$ between monomers and liquid molecules or sufficiently low sound velocity, this additional term becomes strong enough to compensate for the excluded volume potential (i.e., the monomer-monomer interaction) and the polymer chain shows a collapse. It should be remarked that this effect is well known, but this important property now has an explicit representation.

A similar situation follows for the determination of dynamical properties of the polymer chain in a frictionless liquid. Equations (49)– (51) are an explicit representation of the frequency spectra and the effective friction coefficient, which depends on the temperature and the microscopical parameters of the polymer chain, the liquid, and the interaction between both. As expected, we get the well known classical temperature behavior and dependence on the chain length of the diffusion coefficient for high temperatures, whereas an anomalous temperature behavior occurs in the low-temperature regime.

## APPENDIX A

### Approximation of the dynamic structure factor

Using $Y_p(t) = \chi_p(0) - \chi_p(t)$, we get, for $u_0 = 0$, the typical Rouse equation

$$\zeta_0\dot{Y}_p^{(0)} + \mu_0\omega_p^2 Y_p^{(0)} = \frac{k_B T}{N} \tag{A1}$$

with the well known solution

$$Y_p^{(0)}(t) = \frac{l_0^2 N}{2\pi^2}\frac{1 - e^{\frac{tp^2}{\tau_R}}}{p^2} \tag{A2}$$

and the Rouse time

$$\tau_R = \frac{l_0^2 N^2 \zeta_0}{2\pi^2 k_B T}. \tag{A3}$$

For the dynamic structure factor of two monomers in $s$ and $s'$ it is reasonable to use the approximation

$$\begin{aligned}\Omega(\mathbf{k}, s, s', t) &= \langle \exp\{i\mathbf{k} \cdot [\mathbf{R}(s,t) - \mathbf{R}(s',0)]\}\rangle \\ &\approx \exp\left\{ -\frac{\mathbf{k}^2}{6} \langle [\mathbf{R}(s,t) - \mathbf{R}(s',0)]^2 \rangle \right\} \\ &\approx \Omega(\mathbf{k}, s - s') \exp\{-\mathbf{k}^2 Y_0^{(0)}(t)\} \\ &\quad \times \exp\{-2\mathbf{k}^2 \Phi(s, s', t)\}\end{aligned} \tag{A4}$$

Here $\Omega(\mathbf{k}, s - s')$ is the well known static structure factor

$$\Omega(\mathbf{k}, s - s') = \exp\left\{ -\frac{\mathbf{k}^2}{6} \mid s - s' \mid l_0^2 \right\} \tag{A5}$$

with the Fourier transformed form for sufficiently large $N$

$$\Omega(\mathbf{k}, p) \approx \frac{1}{N} \int_0^N ds \Omega(\mathbf{k}, s) = \frac{1}{N} \frac{\frac{k^2 l_0^2}{6}}{\left(\frac{k^2 l_0^2}{6}\right)^2 + \omega_p^2} \tag{A6}$$

and

$$\Phi(s, s', t) = \sum_{p=1}^{\infty} \cos(\omega_p s) \cos(\omega_p s') Y_p^{(0)}(t) \ . \tag{A7}$$

From (A5) follows that the main contributions to the dynamic structure factor are expected for $s \approx s'$, i.e., it is reasonable to approximate $\Phi(s, s', t)$ by $\Phi(s, s, t)$. We get

$$\begin{aligned}\Phi(s, s, t) &= \sum_{p=1}^{\infty} \cos(\omega_p s)^2 Y_p^{(0)}(t) \\ &\approx \frac{1}{2} \int_0^{\infty} dp Y_p^{(0)}(t) \\ &= \frac{1}{2} D_2 \sqrt{t}\end{aligned} \tag{A8}$$

with

$$D_2 = \sqrt{\frac{k_B T l_0^2}{2\pi \zeta_0}} \ . \tag{A9}$$

On the other hand, we get

$$Y_0^{(0)}(t) = D_1 t \tag{A10}$$

with the bare diffusion coefficient

$$D_1 = \frac{k_B T}{N \zeta_0} \ . \tag{A11}$$

In summary, the approximation for the dynamic structure factor is determined by

$$\Omega(\mathbf{k}, p, t) = \Omega(\mathbf{k}, p) e^{-k^2 (D_1 t + D_2 \sqrt{t})} \ . \tag{A12}$$

## APPENDIX B: DETERMINATION OF THE SELF-ENERGY PART $M(P, Z)$

From (48) and (A5), we get

$$M(p, z) = \frac{2 N z u_0}{\pi^2 l_0^5} m(p, z) \tag{B1}$$

with the integral

$$\begin{aligned}m(p, z) = &\int_0^{\infty} dy \frac{y^6}{y^4 + 36\omega_p^2} \\ &\times \int_0^{\infty} dt \cos(y\tau) e^{-z\tau_0 \tau} e^{-y^2 \left(\frac{\tau}{\tau_1} + \sqrt{\frac{\tau}{\tau_1}}\right)}.\end{aligned} \tag{B2}$$

Here we have introduced the elementary time

$$\tau_0 = \frac{l_0}{c_0}$$

and the dimensionless values

$$\tau_1 = \frac{l_0 c_0}{D_1}, \quad \tau_2 = \frac{l_0^3 c_0}{D_2^2},$$

which characterized the ratio between the sound velocity and the diffusion velocity of the monomers ($\tau_2$) and the center of mass of the polymer chain ($\tau_1$), respectively. Therefore, we get the relation

$$1 \ll \tau_2 \ll \tau_1 \ . \tag{B3}$$

Splitting the integration over $y$ into (B2) into two regions $(0, \sqrt{6\omega_p})$ and $(\sqrt{6\omega_p}, \infty)$ and using the typical cutoff representation

$$\int_0^a dy \cdots \to \int_0^{\infty} e^{-(\frac{y}{a})^2} dy,$$

we get approximately ($x = z\tau_0$)

$$\begin{aligned}m(p, x) \approx &\int_0^{\sqrt{6\omega_p}} dy \frac{y^6}{36\omega_p^2} \int_0^{\infty} dt \cos(y\tau) e^{-x\tau} e^{-y^2 (\frac{\tau}{\tau_1} + \sqrt{\frac{\tau}{\tau_1}})} \\ &+ \int_{\sqrt{6\omega_p}}^{\infty} dy \left( y^2 \int_0^{\infty} dt \cos(y\tau) e^{-x\tau} e^{-y^2 (\frac{\tau}{\tau_1} + \sqrt{\frac{\tau}{\tau_1}})} \right) \\ \approx &\int_0^{\infty} dy \left( \frac{y^6}{36\omega_p^2} \int_0^{\infty} dt \cos(y\tau) e^{-x\tau} e^{-y^2 (\frac{\tau}{\tau_1} + \sqrt{\frac{\tau}{\tau_1}} + \frac{1}{6\omega_p})} \right) \\ &+ \int_0^{\infty} dy \left( y^2 \int_0^{\infty} dt \cos(y\tau) e^{-x\tau} e^{-y^2 (\frac{\tau}{\tau_1} + \sqrt{\frac{\tau}{\tau_1}}) a} \right) \\ &- \int_0^{\infty} dy \left( y^2 \int_0^{\infty} dt \cos(y\tau) e^{-x\tau} e^{-y^2 (\frac{\tau}{\tau_1} + \sqrt{\frac{\tau}{\tau_1}} + \frac{1}{6\omega_p})} \right) = I_1 + I_2 + I_3 \ .\end{aligned} \tag{B4}$$

Now we get the following approximations for the region of the relaxation modes ($x \ll 1$):

$$I_1 \approx \frac{3}{8}\sqrt{\pi}x(6\omega_p)^{1/2}, \quad I_2 \approx \frac{11}{72}\sqrt{\pi}\Gamma(\frac{1}{6})\tau_2^{2/3}, \quad I_3 \approx \frac{1}{2}\sqrt{\pi}x(6\omega_p)^{1/2}$$

and therefore Eq. (49) for $Y_p(z)$.

[1] H.L. Frisch, G. Forgacs, and S.T. Chui, Phys. Rev. A **20**, 561 (1979).

[2] H.L. Frisch and P. Rujan, Phys. Rev. A **25**, 1815 (1982).

[3] S. Nakajima, Prog. Theor. Phys. **20**, 948, (1958).

[4] M. Muthukumar and K. Freed, Macromolecules **11**, 843 (1978).

[5] S. F. Edwards and K. F. Freed, J. Chem. Phys. **61**, 1189 (1974).

[6] M. Schulz and I. Alig, J. Chem. Phys. **87**, 5631 (1992).

[7] R. Zwanzig, Adv. Chem. Phys. **15**, 325 (1969).

[8] K. S. Schweizer, J. Chem. Phys. **91**, 5802 (1989).

[9] M. Bishop, M. H. Kalos, and H. L. Frisch, J. Chem. Phys. **70**, 1299 (1979).

[10] A. Baumgärtner, Ann. Rev. Phys. Chem. **35**, 419 (1984).

[11] K. Kremer and K. Binder, J. Chem. Phys. **81**, 6381 (1984).

[12] C. C. Crabb and J. Kovas, Macromolecules **13**, 602 (1980).

[13] D. Ceperly, M. H. Kalos, and J. L. Lebowitz, Phys. Rev. Lett. **41**, 313 (1978).

[14] K. Kremer, G. S. Grest, I. Carmesin, Phys. Rev. Lett. **61**, 566 (1988).

[15] K. F. Mansfield and D. N. Theodorou, Macromolecules, **22**, 3143 (1989).

[16] M. Fixman, J. Chem. Phys. **69**, 1527 (1978).

[17] L. D. Landau, J. Phys. (USSR) **5**, 71 (1941).

[18] A. Clebsch, J. Reine Angew. Math. **54**, 293 (1957).

[19] A. Clebsch, J. Reine Angew. Math. **56** (1959).

[20] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).

[21] H. Mori, Prog. Theor. Phys. **34**, 399 (1965).