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Numerical determination of relaxation times by static equilibrium values☆

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Abstract

The numerical determination of relaxation times or other characteristic dynamical variables is often connected with intrinsic computational problems and consequently can be legitimately criticized. We present here for finding dynamical variables a general numerical method, which allows one to avoid these problems, and which is based exclusively on numerical equilibrium values: 02.70**, 05.20**, 64.10**. © 2001 Elsevier Science Ltd. All rights reserved.

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The characterization of thermodynamic processes is based mostly on statements about relaxation processes whose theoretical treatment by analytical methods is possible only in simple or very special cases. Numerical simulation methods are usually used for more complex problems, but in the majority of cases essential difficulties arise as a result of the properties of the numerical approaches. We consider in this paper the numerical simulation of a physical system Σ made up of a sufficient large bath Σ_b and the subsystem Σ_0 of the objects. Molecular dynamics methods are based on the integration of the exact or effective equations of motion for the underlying thermodynamical systems and thus these methods can lead to a realistic determination of relaxation times. The difficulty of these methods is given by the numerical algorithm: it is necessary to realize a large number of very time expensive numerical integration steps and unfortunately, each step realizes in general only a small change of the thermodynamic state of the system. Hence, one can investigate only small time intervals (less than 10^{-8} s), despite the cost of these computation methods.

Decreasing the integration time by a reduction of the number or thermodynamical observables leads to new problems. In the usual Brownian dynamics method [1], the thermodynamic environment (thermodynamic bath) is replaced by introducing microscopical friction coefficients and external stochastic forces [2–4]. The disadvantage of this method is, that one needs information about the dynamics of the bath, which are reflected in the memory terms (friction coefficients) and the correlation functions of the stochastic forces. In the simplest case (simple friction coefficients and white noise for the stochastic forces) there exists one free parameter and the unsolved problem is the way the effective (temperature dependent interactions are changed in comparison to the original (mechanical) interactions. This is general problem of all molecular dynamics methods, if they are used for the determination of dynamical values, e.g. constrained dynamics methods [5,6] (with a permanent redefining of the friction coefficient), Gibbsian dynamics methods [7,8] (solution of generalized Newtonian equations of motion with additional degrees of freedom) or direct renormalization [9] (with a conservation of the total kinetic energy). All these numerical methods yield the exact equilibrium distribution in the configuration (coordinate) space, in particular both the momentum and configuration space, but the additional constraints or degrees of freedom lead to uncertain deviations of the dynamical values from reality [10]. Pure Monte Carlo simulations [11,12] and combined Monte Carlo — Molecular Dynamics methods [13,14] can also used with the same restrictions for dynamical investigations [14–16], but here we have the additional problem of the unknown ratio between a Monte Carlo step and a real time step.

Still a large number of numerical data must be processed (in practice, one must determine a sufficiently large number

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of time dependent functions $f(t)$ for the computation of one average $\bar{f}(t)$). Only short real time intervals can be investigated in most cases, i.e. only short relaxation times can be observed with high accuracy by such methods. The aim of this paper is the presentation of a method, which allows the determination of dynamical values (especially relaxation times) by using only equilibrium values (which can be determined with a high accuracy by numerical methods mentioned above). Our specific interest is to justify the *linear* relaxation behavior we have employed to study the melt and intrinsic viscosity of Rouse chain models and the melt viscosity of normal alkanes using the Kramers potential method [17–20]. This method provided these viscosities directly from available Monte Carlo data on the equilibrium radius of gyration of these chains and thus connects our work to polymer theory.

We consider a system Σ_0 in a $2N$-dimensional general phase space, with N coordinates x_i (configuration space) and N canonical conjugated momenta p_i (momentum space), i.e. with $2N$ general coordinates Z_i

$$\mathbf{Z} = \begin{pmatrix} x \\ p \end{pmatrix}, \qquad x = (x_1, \ldots, x_N), \;\; p = (p_1, \ldots, p_N)$$

which is in contact with a thermodynamic bath Σ_b. Formally, the equations of motion for this thermodynamic system can be determined by using the projection operator formalism [3]

$$\wp_\beta(t) = \Omega_{\beta\gamma}\, \wp_\gamma(t) - \int_0^t \mathrm{d}t' \mathbf{Y}_{\beta\gamma}(t')\, \wp_\gamma(t - t') + \zeta_\beta. \tag{1}$$

Here

$$\wp_\beta(t) = \mathrm{e}^{\mathrm{i}Lt}\wp_\beta,$$

(L is the Liouville operator) are the relevant time dependent observables of the system Σ_0 (The total set of $\wp_\alpha$ contains all linear independent functions of the $2N$ generalized coordinates Z_i and spans the subspace $\mathscr{R}_\parallel$) The complete Liouville space $\mathscr{R}$ is formed by $\mathscr{R}_\parallel$ and the space $\mathscr{R}_\perp$ of all other (irrelevant) observables which are connected with the bath Σ_b (1) contains the memory matrix $\mathbf{Y}_{\beta\gamma}(t)$, the frequency matrix $\mathbf{\Omega}_{\beta\gamma}$ and the residual forces $\zeta_\beta(t)$ which remain always in the space $\mathscr{R}_\perp$. These residual forces are mainly determined by the dynamics of the bath and have for the relevant observables the meaning of stochastic forces. Under the reasonable assumption if all correlations of the bath are characterized by sufficiently short times, it is possible to use the Markovian approximation and replace the memory matrix by a simple effective friction matrix $\mathbf{\lambda}_{\beta\gamma} = \int_0^\infty \mathbf{Y}_{\beta\gamma}(t)\,\mathrm{d}t$ whereas the residual forces behave as white noise. Because of the property $(AB)(t) = \mathrm{e}^{\mathrm{i}Lt}(AB) = A(t)B(t)$ of the Liouville operator, all time dependent relevant observables $\wp_\beta$ can be replaced by functions of the time dependent general coordinates $\mathbf{Z}(t)$ and the equations of motion for these coordinates have now the general characteristic structure

$$\dot{Z}_i = \Phi_i(Z(t)) + \zeta_i. \tag{2}$$

Clearly, the effective forces Φ are determined by the friction and frequency matrix (and are therefore temperature dependent) and consequently, unfortunately, it is impossible to determine Φ_i for most cases of physical interest. If the thermodynamic fluctuations (the deviations $\xi_i = Z_i - \bar{Z}_i$ of the general coordinates Z_i from the thermodynamic average $\bar{Z}_i$ are sufficiently small (in absence of critical behavior due, e.g. to a phase transition), it is reasonable to realize a linear formulation of these equations by a Taylor expansion of the potential around the minimum $\mathbf{Z}^0$. On neglecting all higher correlations $\bar{Z}_i = \mathrm{Z}_i^0$, i.e. the equilibrium state is determined by

$$\Phi(Z^0) = \begin{pmatrix} \Phi^x(x^0, p^0) \\ \Phi^p(x^0, p^0) \end{pmatrix} = 0$$

and the linearized equations of motion becomes

$$\dot{\xi}_i = -\Gamma_{ij}\xi_j + f_i \tag{3}$$

with

$$\mathbf{\Gamma} = \begin{pmatrix} \Gamma^{xx} & \Gamma^{xp} \\ \Gamma^{px} & \Gamma^{pp} \end{pmatrix} = -\begin{pmatrix} \dfrac{\partial \Phi^x}{\partial x} & \dfrac{\partial \Phi^x}{\partial p} \\ \dfrac{\partial \Phi^p}{\partial x} & \dfrac{\partial \Phi^p}{\partial p} \end{pmatrix}.$$

Formally, the relaxation time spectrum is now completely determined, because the homogeneous solution $\exp\{-\Gamma t\}$) of Eq. (3) determines the time behavior of the autocorrelation functions of the thermodynamic observables ξ_i. These correlation functions are represented by a linear combination of exponential functions

$$\langle \xi_i(t)\, \xi_j(0)\rangle = \sum_{m=1,N} C_{ij}^m \exp\left(-\frac{t}{\tau_m}\right)$$

in which the τ_m^{-1} are the eigenvalues of $\mathbf{\Gamma}$. In this sense, it is reasonable to speak about relaxation times τ_m and a relaxation time spectrum, respectively. Unfortunately, whereas the determination of the relaxation times from $\mathbf{\Gamma}$ is always possible (perhaps by using numerical standard procedures), the determination of the correct matrix elements Γ_{ij} becomes very difficult or impossible for complex system and one is forced to use numerical simulations methods (with the above discussed problems) for the investigation of the real dynamics of the system $\Sigma = \Sigma_0 + \Sigma_\mathrm{b}$.

To avoid this situation we add an infinitesimal small external harmonic contribution

$$\delta V(\mathbf{Z}, \eta) = \mathbf{Z}\eta\mathbf{Z} = \begin{pmatrix} x \\ p \end{pmatrix}\begin{pmatrix} \eta^{xx} & \eta^{xp} \\ \eta^{px} & \eta^{pp} \end{pmatrix}\begin{pmatrix} x \\ p \end{pmatrix}$$

to the Hamiltonian. This leads to a small additional contribution δL to the Liouville operator. It is simple to see, that δL always maps a relevant observable to another element of

$\mathscr{R}_{\|}$.Therefore, δL does not change the memory matrix (and therefore the friction coefficients), whereas all contributions to the frequency matrix change Eq. (2) to

$$\dot{Z}_i = \Phi(\mathbf{Z}) - \sigma\eta\mathbf{Z} + \zeta_i$$

with

$$\sigma = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}.$$

Note that the contributions of δV to the generalized effective forces Φ are equal to the contributions without the thermodynamic bath. Therefore, it is possible to add this contribution directly to the effective equations of motion (2) and the present method is also valid for numerical simulations of systems, in which the bath is reduced to the action of some few parameters (Brownian dynamics, Monte Carlo Simulations). Now, the equilibrium state is determined by

$$\Phi(Z^0) - \sigma\eta Z^0 = 0. \tag{4}$$

As a result of this additional potential one get a new equilibrium state $Z^0(\eta)$, which can be represented for sufficient small values η by a first order Taylor expansion

$$Z_i^0(\eta) = Z_i^0(0) + \frac{\partial Z_i^0(\eta)}{\partial \eta_{mn}}|_{\eta=0}\eta_{mn}. \tag{5}$$

Using Eq. (4), we get

$$\Gamma_{ij}\frac{\partial Z_j^0}{\partial \eta_{mn}} = -\sigma_{im}Z_n^0.$$

Therefore Eq. (5) becomes

$$Z_k^0(\eta) = Z_k^0(0) - \tau_{kl}\sigma_{lm}\eta_{mn}Z_n^0(0) \tag{6}$$

with $\tau = \mathbf{\Gamma}^{-1}$ (The eigenvalues of τ are the relaxation times of system). Now we have the possibility of determining the relaxation time directly from static equilibrium values (which are obtained with sufficiently high accuracy from the usual numerical solutions.) The changing of the thermodynamic average $\bar{\mathbf{Z}}$ of the general coordinates as a result of an arbitrary infinitesimal small additional harmonic contribution $\delta V = \eta_{ij}Z_iZ_j$ allows the determination of the relaxation time spectrum straightforwardly by using Eq. (6).

The present representation is based on equilibrium values of the generalized coordinates of both the configuration space and the momentum space. Thus Eq. (6) is suitable for Molecular Dynamics methods, which determine simultaneously the exact equilibrium distribution in the $2N$ dimensional phase space. Moreover, Eq. (6) assumes, that the thermodynamical averages of the momenta are not equal to 0, because in this case only a part of the τ-matrix can be determined. Such cases (especially for all Monte Carlo simulations, which act only in configuration space) make possible the determination of the submatrix

$$\tau^{xp} = [\Gamma^{px} - \Gamma^{pp}(\Gamma^{xp})^{-1}\Gamma^{xx}]^{-1}.$$

However, in the case of strong damping (or its equivalent vanishing inertia) the knowledge of τ^{xp} is often sufficient for the determination of reasonable results. This situation is typical for the determination of the relaxation times of a macromolecular objects, for which analytical investigations are only possible for some special types of topology [21,22] and molecular interactions. Here, numerical simulations [23,24] are a reasonable alternative for solving the majority of physical questions. Because, in the physically interesting time intervals each monomer behaves as a Brownian particle it is not necessary to consider the inertia term in the equation of motion. At first, one reduces Eq. (3) (elimination of the generalized momenta) to a N dimensional system of second order differential equations for the coordinates of the configuration space

$$\ddot{x} = [\Gamma^{xp}\Gamma^{px} - \Gamma^{xp}\Gamma^{pp}(\Gamma^{xp})^{-1}\Gamma^{xx}]x + [\Gamma^{xp}\Gamma^{pp}(\Gamma^{xp})^{-1} + \Gamma^{xx}]\dot{x}. \tag{7}$$

In general, it is $\Gamma^{xp} \sim 1/m$, i.e. after multiplication with $(\Gamma^{xp})^{-1}$ and the realization and $m \to 0$ (under consideration of the definition $\Gamma^{pp}(\Gamma^{xp})^{-1} = \mathbf{\Lambda} = \text{const.}$) it follows that

$$\dot{x} = -\mathbf{\Lambda}^{-1}(\tau^{xp})^{-1}x. \tag{8}$$

In a large number of cases (e.g. if the coordinates corresponds to equivalent particles, such as the monomers in a macromolecule) one can assume, that the matrix $\mathbf{\Lambda}$ can be replaced by an unitary matrix with a constant prefactor. Therefore, the relaxation times are complete determined by Eq. (8) from equilibrium values with a high accuracy, except for the prefactor [25].

We demonstrate the effectiveness of this method on a simple example and determine the relaxation time for the Schlögl model [26], because all results are well known [27,28]. (For more realistic applications on complicated systems see Ref. [25,29]) This model has only one relevant coordinate (particle number X) and is described by the kinetic equations

$$B + X \to C \qquad A + X \to 2X \qquad C \to B + X$$
$$2X \to A + X \tag{9}$$

with the reaction constants k_i ($i = 1,\ldots,4$) and corresponds in the positive Poisson representation [28] to a general stochastic differential equation (equivalent to Eq. (2))

$$\dot{\alpha} = g(\alpha) + h(\alpha)\,\xi(t) \tag{10}$$

with

$$g(\alpha) = k_3C + (k_2A - k_1B)\alpha - k_4\alpha^2 \tag{11}$$

and

$$h(\alpha) = \sqrt{2(k_2A\alpha - k_4\alpha^2)}.$$

The relaxation time is given by

$$\tau_R = \frac{1}{\sqrt{(k_2A - k_1B)^2 + 4k_3k_4C}}. \tag{12}$$

Table 1
Comparison of the relaxation times ($\tau_{R,num}$: numerical simulation, $\tau_{R,theo}$ Predictions from (19)) for different values C, $A = 50$, $B = 5$, $k_i = 1\ \forall i$

C/10000	$\tau_{R,num}$	$\tau_{R,theo}$
0.1	0.01272 ± 0.0001	0.01288
1.0	0.00479 ± 0.0001	0.00488
2.0	0.00348 ± 0.0001	0.00349
3.0	0.00280 ± 0.0001	0.00286
4.0	0.00248 ± 0.0001	0.00248
5.0	0.00221 ± 0.0001	0.00222

Here, the variable α is the coordinate and corresponds to the average number of particles $\bar{X} = \langle\alpha\rangle$. To determine the relaxation time of Eq. (10) by using Eq. (6) it is necessary for an additional contribution $\eta\alpha$ to the general force $g(\alpha)$, i.e. we introduce a new additional reaction.

$$X + \eta \rightarrow D$$

to the reaction scheme (9) and determine for this general system the function $\bar{x}(\eta) = \langle\alpha\rangle_n$ by numerical simulations. By the way, this is also a reasonable alternative for the determination of relaxation times of chemical reactions. Table 1 shows the numerical relaxation time (determined from Eq. (6) and a very simple program with a total CPU time of approximately 3 min on an IBM RISC 3200 workstation) in comparison with the values of Eq. (12) for different concentrations C. It should be mentioned, that for situations with a very small average particle number $\bar{X}$, the difference between the numerical and theoretical results is large because the fluctuations of X have the same (or higher) order of magnitude as the average $\bar{X}$.

The real applications of the presented method consist in the determination of the relaxation spectrum in systems with large number of degrees of freedom [25]. For these cases it is often of sufficient interest to get an approximation for the average relaxation time Therefore, we use the norm

$$\|Z^0(\eta)\| = \langle Z^0(\eta)|\rho|Z^0(\eta)\rangle$$

with measure ρ. Using the Schwarz inequality on Eq. (6), we have

$$\|Z^0(\eta)\| = \|(Z^0 - \tau\sigma\eta Z^0(0)\| \tag{13}$$

$$\leq \|Z^0(0)\| + \|\tau\sigma\eta Z^0(0)\|$$

$$\leq \|Z^0(0)\| + \|\tau\|\|\eta\|\|Z^0(0)\|$$

and

$$\|Z^0(0)\| = \|Z^0(\eta) + \tau\sigma\eta Z^0(0)\| \tag{14}$$

$$\leq \|Z^0(\eta)\| + \|\tau\|\|\eta\|\|Z^0(0)\|,$$

i.e. the sum of these two inequalities leads to

$$\lim_{\|\eta\|\to 0} |\frac{\|Z^0(\eta)\| - \|Z^0(0)\|}{\|\eta\|\|Z^0(0)\|}| \leq \|\tau\|. \tag{15}$$

In the case of the simple (but mostly used) measure $\rho = 1$ it follows that the final approximation yields

$$\lim_{\|\eta\|\to 0} |\frac{|Z^0(\eta)|^2 - |Z^0(0)|^2}{\|\eta\|\|Z^0(0)|^2}| \approx \|\tau\| \approx \bar{\tau}^2.$$

Thus, only a few numerical simulations of static thermodynamic properties for different small values η are sufficient for reasonable approximations of the averaged relaxation times for complicated many particle systems. The numerical effectiveness of this method is shown in the accurate results, given by [25,29].

In summary this method allows a clever way to handle all problems, which are connected with a direct determination of the relaxation times by the usual numerical methods.

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References

[1] Hiwatari Y, Stoll E, Schneider T. J Chem Phys 1978;68:3401.
[2] Machlup S, Onsager L. Phys Rev 1953;91:1512.
[3] Fick E, Sauermann E. The Qunatum Statistics of Dynamic Processes. Berlin: Springer, 1990.
[4] Zwanzig R. Adv Chem Phys 1969;15:325.
[5] Hoover WG. Ann Rev Phys Chem 1983;34:103.
[6] Evans DJ. J Chem Phys 1983;78:3293.
[7] Nosé S. J Chem Phys 1984;81:511.
[8] Hoover WG, Ladd AJC, Moran B. Phys Rev Lett 1982;48:1818.
[9] Woodcock VL. Chem Phys Lett 1971;10:257.
[10] Winkler RG. Phys Rev A 1992;45:2250.
[11] Binder K. Application of the Monte Carlo Method in Statistical Physics. Berlin: Springer, 1987.
[12] Fincham D, Heyes DM. Adv Chem Phys 1985;LXIII.
[13] Anderson HC. J Chem Phys 1980;72:2384.
[14] Schulz M, Winker RG, Reineker P. Phys Rev 1993;48:581.
[15] Schulz M, Sommer JU. J Chem Phys 1992;96:7102.
[16] Paul W, Binder K, Heermann DW, Kremer K. J Chem Phys 1991;95:7726.
[17] Frisch HL, Pistoor N, Sariban A, Binder K, Fesjian S. J Chem Phys 1988;89:5194.
[18] Frisch HL, Schutz M, Sharma PRS. Comput Polym Sci 1994;4:13.
[19] Ohno K, Schulz M, Binder K, Friscg HL. J Chem Phys 1994;101:4452.
[20] Paul W, Frisch HL. Phys Rev E 1999;60:697.
[21] Rouse PE. J Chem Phys 1953;21:1272.
[22] Graessley WW. Macromolecules 1980;13:372.
[23] Kremer K, Binder K. Comp Phys Rep 1988;7:262.
[24] Kremer K, Grest GS, Carmesin I. Phys Rev Lett 1988;61:2819.
[25] Frisch HL, Pistoor N, Sariban A, Binder K, Fesjian S. J Chem Phys 1988;89:5194.
[26] Schlögl F. Z Phys 1972;253:147.
[27] Elderfield DJ. J Phys A: Math Gen 1985;18:2049.
[28] Gardiner CW. Handbook of Stochastic Methods. Berlin: Springer, 1983.
[29] Frisch HL, Schulz M. To be published.