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Statistical Mechanics of Viscoelasticity

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A unified treatment of viscoelasticity is developed in the framework of nonequilibrium classical statistical mechanics. An exact correspondence between Mori's continued-fractions formalism and rheological circuits is shown.

KEY WORDS: Viscoelasticity; nonequilibrium statistical mechanics; continued fractions; rheological circuits.

1. INTRODUCTION

In two preceding publications[3,4] we began a statistical mechanical investigation of equilibrium elasticity: "bulk" and "wall" expressions for the static elastic moduli were derived in the framework of equilibrium classical statistical mechanics and sufficient conditions for the vanishing of the shear modulus were found. In this paper, we continue this study by handling viscoelasticity by means of nonequilibrium statistical mechanics.

Viscoelasticity deals with the mechanical response of a material to an externally imposed, time-dependent deformation. Its basic objects are the static modulus and the relaxation function (we limit ourselves to the linear theory, involving only small, homogeneous deformations; plasticity is ignored); it would then be highly desirable to characterize them microscopically by means of statistical mechanics. On the other hand, the question arises of whether the simple mechanical models widely used in viscoelasticity have a firm physical basis or, on the contrary, are just convenient tools to fit the experimental data.

Although the first part of this program has been largely developed by many authors (see references in the text), the resulting treatment contains

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unsatisfactory points: at the theoretical level, no unified description exists; the exact correspondence between the theory of viscoelasticity and non-equilibrium statistical mechanics has not been systematically investigated; moreover, the recovery of equilibrium elasticity remains unclear, especially since there exists some confusion in the literature about the different definitions of the static moduli. Concerning the second point, which has not been studied yet to our knowledge, we shall show that there is an exact correspondence between Mori's continued-fraction formalism and a certain ladder circuit representation.

This paper is organized as follows: in Section 2, we recall the phenomenology of viscoelasticity and the representation in terms of mechanical circuits. Section 3 contains the statistical derivation of the relaxation function and the static modulus by means of linear response theory. Section 4 deals with the circuit representation of the response function, illustrated with the linear chain of oscillators in Section 5.

Finally, let us remark that the correspondence between the electric and viscoelastic circuits allows us to apply the results of Section 4 to electrodynamics.

2. THEORY OF LINEAR VISCOELASTICITY

In this section, we shall define the main quantities of interest characterizing the viscoelastic behavior of a body subjected to a given deformation. General references are provided in textbooks on the subject.[9,15,16,23,24]

In a relaxation experiment, constant strain $u^0_{\alpha\beta}$ is applied at $t=0$; the resulting increase of stress $\Delta\tau_{\alpha\beta}(t)$ is given by

$$\Delta\tau_{\alpha\beta}(t) = [B_{\alpha\beta\gamma\delta} + K_{\alpha\beta\gamma\delta}(t)]\, u^0_{\gamma\delta} \tag{2.1}$$

(the Einstein summation convention over repeated Greek indices is assumed; in what follows we shall omit them). Here B is the static elastic modulus. $K(t)$, monotonically decreasing with $K(\infty)=0$, is the relaxation function. $B+K(0)$ is the instantaneous elastic modulus. One speaks of a viscoelastic fluid if $B=0$ and of a viscoelastic solid if $B\neq 0$. The Boltzmann superposition principle, cornerstone of the theory, lies in the assumption that during a viscoelastic deformation in which the applied strain is varied, the resulting stress can be determined from the sum of the strain increases. For a deformation such that $u(-\infty)=0$, (2.1) and the superposition principle lead to

$$\Delta\tau(t) = Bu(t) + \int_{-\infty}^{t} du(\tau)\, K(t-\tau) \tag{2.2}$$

If we put $K(t) \equiv 0$ in (2.2), we find the Hookean solid, described by

$$\Delta\tau(t) = Eu(t) \tag{2.3}$$

Putting $B = 0$ and $K(t) = \gamma\,\delta(t)$ leads to the Newtonian fluid:

$$\Delta\tau(t) = \gamma\dot{u}(t) \tag{2.4}$$

where γ is the coefficient of viscosity. Although viscoelastic fluids (i.e., those for which $B = 0$) are generally non-Newtonian, it is possible to define a static viscosity coefficient η by the application of a constant strain rate $\dot{u} = \text{const}$: we get indeed from (2.2)

$$\Delta\tau(t) = \eta\dot{u} \tag{2.5}$$

with

$$\eta = \int_0^\infty d\tau\, K(\tau) \tag{2.6}$$

In many experimental situations, the viscoelastic body is subjected to a harmonic strain of the form

$$u(t) = u_0 \cos \omega t \tag{2.7}$$

The resulting stress increment is, from (2.2),

$$\Delta\tau(t) = \{[B + E_1(\omega)] \cos \omega t - E_2(\omega) \sin \omega t\}\, u_0 \tag{2.8}$$

where $E_1(\omega)$, the dynamic or storage modulus, and $E_2(\omega)$, the dynamic friction or loss modulus, are given by the one-sided Fourier transforms

$$\begin{aligned} E_1(\omega) &= \omega \int_0^\infty d\tau\, K(\tau) \sin \omega\tau \\ E_2(\omega) &= \omega \int_0^\infty d\tau\, K(\tau) \cos \omega\tau \end{aligned} \tag{2.9}$$

The dynamic friction is related to the mean power dissipated during a cycle $T = 2\pi/\omega$ by

$$P(\omega) = \frac{1}{T}\int_0^T du(t) = \frac{1}{2}\,\omega E_2(\omega)\, u_0^2 \tag{2.10}$$

$\tilde{B}(\omega) := B + E_1(\omega)$ can be interpreted as the frequency-dependent elastic modulus, restoring the static and the instantaneous elastic modulus, in the

low- and high-frequency limits, respectively (see, e.g., Ref. 9 for the derivation):

$$\begin{aligned} \lim_{\omega \to 0} \tilde{B}(\omega) &= B \\ \lim_{\omega \to \infty} \tilde{B}(\omega) &= B + K(0) \end{aligned} \tag{2.11}$$

In the same way, the dynamic viscosity $\eta(\omega)$ is defined by

$$\eta(\omega) := E_2(\omega)/\omega \tag{2.12}$$

with the limits

$$\begin{aligned} \lim_{\omega \to 0} \eta(\omega) &= \eta \\ \lim_{\omega \to \infty} \eta(\omega) &= 0 \end{aligned} \tag{2.13}$$

The low-frequency limit then restores the static viscosity coefficient η given by (2.6). The vanishing of $\eta(\omega)$ at high frequency constitutes the analytical statement of the intuitively obvious fact that under these circumstances, the material is behaving as an elastic solid.

In the foregoing, we considered the deformation starting at $t = -\infty$, which eliminated transient effects; the frequency-dependent moduli previously defined therefore characterized steady-state conditions. However, it is useful also to consider a deformation $u(t) = 0$ begining at $t = 0$ with a possible jump $u(0)$.

Then (2.2) gives

$$\Delta\tau(t) = Bu(t) + K(t)\, u(0) + \int_{0^+}^{t} du(\tau)\, K(t-\tau) \tag{2.14}$$

$$= [B + K(0)]\, u(t) + \int_{0^+}^{t} dK(\tau)\, u(t-\tau) \tag{2.15}$$

The Laplace transform of (2.14) or (2.15) reads

$$\overline{\Delta\tau}(s) = H(s)\, \bar{u}(s) \tag{2.16}$$

where $H(s)$, the response function, is given by

$$H(s) = B + s\bar{K}(s) \tag{2.17}$$

The following limits hold:

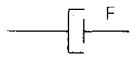
$$\lim_{s \to 0} H(s) = B$$

$$\lim_{s \to \infty} H(s) = B + K(0) \tag{2.18}$$

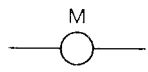
$$\lim_{s \to 0} (1/s)[H(s) - B] = \eta$$

The Laplace transform representation of the response function constitutes the most convenient way to introduce simple mechanical models reproducing the stress–strain constitutive relations: the Hookean solid, for which $H(s) = E$, is represented by a spring of constant E:

In the same way, the Newtonian fluid, for which $H(s) = Fs$, is represented by a dashpot of constant F:



Let us also introduce the mass, represented by



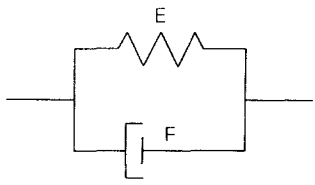
and corresponding to the constitutive relation

$$\Delta\tau(s) = Ms^2\bar{u}(s) \tag{2.19}$$

Arbitrary connections of a finite number of these three basic elements, in series or in parallel, lead to a response function of the form

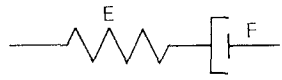
$$H(s) = Q(s)/P(s) \tag{2.20}$$

where $Q(s)$ and $P(s)$ are polynomials in s, with $\deg Q(s) \geqslant \deg P(s)$. The simplest examples are



(2.21)

with $H(s) = E + Fs$ (Kelvin solid), and



(2.22)

with $H(s) = (E + Fs)^{-1} EFs$ (Maxwell fluid).

3. STATISTICAL FORMULATION

Let $\mathscr{H}(\mathbf{x}, \mathbf{p}, t)$, the Hamiltonian of the N-particle system, be of the form

$$\mathscr{H}(\mathbf{x}, \mathbf{p}, t) = H(\mathbf{x}, \mathbf{p}) + h_{\Lambda(t)}(\mathbf{x}) \tag{3.1}$$

where $h_{\Lambda(t)}(\mathbf{x})$ is the wall potential keeping the system confined to the bounded region $\Lambda(t) \subset \mathbb{R}^{\nu}$, and

$$H(\mathbf{x}, \mathbf{p}) = \sum_{i=1}^{N} \frac{p_i^{\alpha} p_i^{\alpha}}{2m} + V(\mathbf{x}) \tag{3.2}$$

where $V(\mathbf{x})$ contains all the remaining interactions, left unspecified. We define $F_i^{\alpha} := -\partial V(\mathbf{x})/\partial x_i^{\alpha}$.

The time-dependent stress tensor is

$$\tau_{\alpha\beta}(t) = \frac{1}{|\Lambda(t)|} \int d\mathbf{x}\, d\mathbf{p}\, f(\mathbf{x}, \mathbf{p}, t)\, T_{\alpha\beta}(\mathbf{x}, \mathbf{p}) \tag{3.3}$$

where

$$T_{\alpha\beta}(\mathbf{x}, \mathbf{p}) = -\sum_{i=1}^{N} \frac{p_i^{\alpha} p_i^{\beta}}{m} - \sum_{i=1}^{N} F_i^{\alpha} x_i^{\beta} \tag{3.4}$$

and $f(\mathbf{x}, \mathbf{p}, t)$ is the N-particle distribution function, which obeys the Liouville equation

$$\begin{aligned} \frac{\partial}{\partial t} f(\mathbf{x}, \mathbf{p}, t) &= -\sum_{i=1}^{N} \left(\frac{\partial \mathscr{H}}{\partial p_i^{\alpha}} \frac{\partial f}{\partial x_i^{\alpha}} - \frac{\partial \mathscr{H}}{\partial x_i^{\alpha}} \frac{\partial f}{\partial p_i^{\alpha}} \right) \\ &=: -\{\mathscr{H}(\mathbf{x}, \mathbf{p}, t), f(\mathbf{x}, \mathbf{p}, t)\} =: -iLf(\mathbf{x}, \mathbf{p}, t) \end{aligned} \tag{3.5}$$

We consider a homogeneous time-dependent deformation starting at $t = 0$:

$$x'^{\alpha} = [\delta_{\alpha\beta} + u_{\alpha\beta}(t)]\, x^{\beta} =: D_{\alpha\beta}(t)\, x^{\beta} \tag{3.6}$$

The standard response theory applies to mechanical perturbations,[25] i.e., to perturbations that represent the action of external fields added to the unperturbed Hamiltonian; the deformation of a system does not belong to this class[49,50]: one speaks in this case of thermal perturbation. However, and this constitutes the main point of this derivation, it is possible to generalize Green's dilatation method[19] by a canonical transformation, by which the deformation appears explicitely in the Hamiltonian $H(\mathbf{x}, \mathbf{p})$ and therefore transforms the thermal perturbation into a mechanical one; we define

$$\tilde{x}_i := D^{-1}(t)\, x_i, \qquad \tilde{p}_i := D^{\mathrm{tr}}(t)\, p_i \tag{3.7}$$

The canonical character of (3.7) is easily checked.[12] We also define

$$g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, t) := f(D\tilde{\mathbf{x}}, D^{-1\mathrm{tr}}\tilde{\mathbf{p}}, t) = f(\mathbf{x}, \mathbf{p}, t) \tag{3.8}$$

This satisfies

$$\frac{\partial}{\partial t} g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, t) = -\{\mathscr{H}(D\tilde{\mathbf{x}}, D^{-1\mathrm{tr}}\tilde{\mathbf{p}}, t), g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, t)\} \tag{3.9}$$

where we used the invariance of Poisson brackets with respect to a canonical transformation.

We get

$$h_{\Lambda(t)}(D\tilde{\mathbf{x}}) = h_{\Lambda}(\tilde{\mathbf{x}}) \tag{3.10}$$

where $\Lambda := \Lambda(0)$ is the undeformed domain, and

$$H(D\tilde{\mathbf{x}}, D^{-1\mathrm{tr}}\tilde{\mathbf{p}}) = H(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) + T_{\gamma\delta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})\, u_{\gamma\delta}(t) + O(u^2) \tag{3.11}$$

$H(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) + h_{\Lambda}(\tilde{\mathbf{x}})$ is then the unperturbed Hamiltonian for $g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, t)$, and $T_{\gamma\delta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})\, u_{\gamma\delta}(t)$ is the linear part of the perturbation. Application of the standard linear response theory[1,10] leads to

$$g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, t) = g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, 0) - \int_0^t d\tau\, u_{\gamma\delta}(t-\tau)\, e^{-iL\tau} \times \{T_{\gamma\delta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}), g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, 0)\} + O(u^2) \tag{3.12}$$

where the Liouville operator L acting on the dynamical variable $A(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})$ is defined as

$$iLA(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) = \{H(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) + h_{\Lambda}(\tilde{\mathbf{x}}), A(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})\} \tag{3.13}$$

Since the system is unperturbed at $t = 0$, we have

$$g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, 0) = f_{\mathrm{eq}}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) \tag{3.14}$$

We shall work in the canonical ensemble, where f_{eq} is given by the Boltzmann factor; we get then

$$\{T_{\gamma\delta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}), f_{eq}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})\} = \beta f_{eq}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})\, iLT_{\gamma\delta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) \tag{3.15}$$

and

$$g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, t) = f_{eq}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) - \beta \int_0^t d\tau\, u_{\gamma\delta}(t-\tau) \times f_{eq}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})\, e^{-iL\tau} \dot{T}_{\gamma\delta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) + O(u^2) \tag{3.16}$$

where we used the invariance of $f_{eq}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})$ with respect to the unperturbed time evolution.

We are now in a position to come back to our starting point, Eq. (3.3). The invariance of the phase space element leads to

$$\tau_{\alpha\beta}(t) = \frac{1}{|\Lambda(t)|} \int d\tilde{\mathbf{x}}\, d\tilde{\mathbf{p}}\, g(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, t)\, T_{\alpha\beta}(D\tilde{\mathbf{x}}, D^{-1\mathrm{tr}}\tilde{\mathbf{p}}) \tag{3.17}$$

But

$$\frac{1}{|\Lambda(t)|} = \frac{1}{|\Lambda| \det D(t)} = \frac{1}{|\Lambda|} [1 - \delta_{\gamma\delta} u_{\gamma\delta}(t)] + O(u^2) \tag{3.18}$$

and

$$T_{\alpha\beta}(D\tilde{\mathbf{x}}, D^{-1\mathrm{tr}}\tilde{\mathbf{p}}) = T_{\alpha\beta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) + [W_{\alpha\beta\gamma\delta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) + \delta_{\beta\gamma} T_{\alpha\delta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})]\, u_{\gamma\delta}(t) + O(u^2) \tag{3.19}$$

where

$$W_{\alpha\beta\gamma\delta}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) = \sum_{i=1}^{N} \frac{1}{m} (\delta_{\alpha\delta} \tilde{p}_i^{\gamma} \tilde{p}_i^{\beta} + \delta_{\beta\delta} \tilde{p}_i^{\alpha} \tilde{p}_i^{\gamma} + \delta_{\beta\gamma} \tilde{p}_i^{\alpha} \tilde{p}_i^{\delta}) - \sum_{i,j=1}^{N} \tilde{x}_i^{\beta} \tilde{x}_i^{\delta} \frac{\partial F_i^{\alpha}(\tilde{\mathbf{x}})}{\partial \tilde{x}_j^{\gamma}} \tag{3.20}$$

Replacing in (3.17) $\tilde{g}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, t)$ by the expression (3.16), we have, up to linear terms in $u_{\alpha\beta}(t)$,

$$\tau_{\alpha\beta}(t) = \tau_{\alpha\beta}(0) + \frac{1}{|\Lambda|} \langle W_{\alpha\beta\gamma\delta} + \delta_{\beta\gamma} T_{\alpha\delta} - \delta_{\gamma\delta} T_{\alpha\beta} \rangle\, u_{\gamma\delta}(t) - \frac{\beta}{|\Lambda|} \int_0^t d\tau\, u_{\gamma\delta}(t-\tau) \langle T_{\alpha\beta}(\tau)\, \dot{T}_{\gamma\delta}(0) \rangle \tag{3.21}$$

where we used the unitarity of the evolution operator, and defined

$$\langle A \rangle := \int d\tilde{\mathbf{x}}\, d\tilde{\mathbf{p}}\, A(\tilde{\mathbf{x}}, \tilde{\mathbf{p}})\, f_{\text{eq}}(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}) \tag{3.22}$$

Making use of the stationarity of the equilibrium distribution

$$\langle T_{\alpha\beta}(\tau)\, \dot{T}_{\gamma\delta}(0) \rangle = -\langle \dot{T}_{\alpha\beta}(\tau)\, T_{\gamma\delta}(0) \rangle \tag{3.23}$$

and comparing (3.21) with (2.15), we get

$$K_{\alpha\beta\gamma\delta}(\tau) = \frac{\beta}{|A|} \left[\langle T_{\alpha\beta}(\tau)\, T_{\gamma\delta}(0) \rangle - \lim_{\tau \to \infty} \langle T_{\alpha\beta}(\tau)\, T_{\gamma\delta}(0) \rangle \right] \tag{3.24}$$

where the second term on the right-hand side has been added in order to ensure, as required by definition, the vanishing of the relaxation function at infinity. We assume that the system possesses the mixing property,[11] i.e.,

$$\lim_{\tau \to \infty} \langle T_{\alpha\beta}(\tau)\, T_{\gamma\delta}(0) \rangle = \langle T_{\alpha\beta} \rangle \langle T_{\gamma\delta} \rangle \tag{3.25}$$

Defining $\langle A; B \rangle := \langle AB \rangle - \langle A \rangle \langle B \rangle$, we get finally

$$K_{\alpha\beta\gamma\delta}(\tau) = (\beta/|A|) \langle T_{\alpha\beta}(\tau);\, T_{\gamma\delta}(0) \rangle \tag{3.26}$$

Equation (3.26) makes the link between the theory of viscoelasticity and statistical mechanics. It remains to obtain an expression for the static elastic modulus; again, comparison of (3.21) with (2.15) leads to

$$B_{\alpha\beta\gamma\delta} = \frac{1}{|A|} \left[\langle W_{\alpha\beta\gamma\delta} \rangle + \delta_{\beta\gamma} \langle T_{\alpha\delta} \rangle - \delta_{\gamma\delta} \langle T_{\alpha\beta} \rangle - \beta \langle T_{\alpha\beta};\, T_{\gamma\delta} \rangle \right] \tag{3.27}$$

which is (as it must be) the same expression as formula (2.13) of Ref. 3, obtained in the equilibrium framework.

The frequency-dependent elastic moduli and dynamic viscosity tensors are then, respectively,

$$\tilde{B}_{\alpha\beta\gamma\delta}(\omega) = B_{\alpha\beta\gamma\delta} + \frac{\beta\omega}{|A|} \int_0^\infty d\tau \sin \omega\tau\, \langle T_{\alpha\beta}(\tau);\, T_{\gamma\delta}(0) \rangle \tag{3.28}$$

$$\eta_{\alpha\beta\gamma\delta}(\omega) = \frac{\beta}{|A|} \int_0^\infty d\tau \cos \omega\tau \langle T_{\alpha\beta}(\tau);\, T_{\gamma\delta}(0) \rangle \tag{3.29}$$

When the system is isotropic, it is possible to define the bulk modulus $\lambda(\omega)$ and the shear modulus $\mu(\omega)$ by

$$\tilde{B}_{\alpha\beta\gamma\delta}(\omega) =: \delta_{\alpha\beta}\delta_{\gamma\delta}\lambda(\omega) + (\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\, \mu(\omega) \tag{3.30}$$

and a frequency-dependent compressibility

$$1/\chi(\omega) = \lambda(\omega) + (2/v)\,\mu(\omega) \tag{3.31}$$

where v is the dimension of the system; the isothermal compressibility is recovered by the low-frequency limit

$$\lim_{\omega \to 0} \frac{1}{\chi(\omega)} = \frac{1}{\chi_T} = -|\Lambda| \frac{\partial p(\Lambda)}{\partial |\Lambda|} \tag{3.32}$$

Let us remark that, although the dynamic viscosity always possesses an interpretation in terms of dissipated power,

$$P(\omega) = \tfrac{1}{2}\,\omega^2 \eta_{\alpha\beta\gamma\delta}(\omega)\, u_{\alpha\beta} u_{\gamma\delta} \tag{3.33}$$

its components have the mechanical interpretation (2.5) only if the corresponding component of the static elastic moduli tensor vanishes, i.e., if the system is behaving like a viscoelastic fluid for this component. This is of course the case for ordinary fluids with $\mu(0) = \tilde{B}_{1212}(0) = 0$. The shear viscosity

$$\eta_S := \eta_{1212}(0) = \frac{\beta}{|\Lambda|} \int_0^\infty d\tau \, \langle T_{12}(\tau)\, T_{12}(0) \rangle \tag{3.34}$$

(recall that $\langle T_{12} \rangle = 0$ for fluids) can then be directly determined in a transverse constant strain rate experiment, by

$$\Lambda \tau_{12}(\tau) = \eta_S \dot{u}_{12}(\tau) \tag{3.35}$$

Concerning the infinite-frequency (or adiabatic) elastic moduli

$$\tilde{B}_{\alpha\beta\gamma\delta}(\infty) = \frac{1}{|\Lambda|} \left[\langle W_{\alpha\beta\gamma\delta} \rangle + \delta_{\beta\gamma} \langle T_{\alpha\delta} \rangle - \delta_{\gamma\delta} \langle T_{\alpha\beta} \rangle \right] \tag{3.36}$$

we remark that they do not contain the stress–stress fluctuation and are therefore, from a theoretical point of view, easier to handle than the static ones. (Let us recall that the relationship between the adiabatic moduli and the energy is the same as that between the static moduli and the free energy.) If the interaction potential contains two-body terms only, direct evaluation of (3.36) and (3.27) requires the knowledge of the two-point correlation function and the four-point correlation functions, respectively (see, however, Ref. 4, where the use of the "wall theorem" leads to substan-

tial simplifications). For an isotropic system interacting through two-body central interactions, we get from (3.36)

$$\mu(\infty) = \tilde{B}_{1212}(\infty) = \rho kT + \frac{S(v)}{2v(v+2)} \int_0^\infty dr\, n_2(r) \frac{d}{dr}\left[r^{v+1} \frac{dV(r)}{dr} \right] \tag{3.37}$$

$$\lambda(\infty) = \tilde{B}_{1122}(\infty) = \rho kT + \frac{S(v)}{2v(v+2)} \int_0^\infty dr\, r^{2v+4} n_2(r) \frac{d}{dr}\left[r^{-v-3} \frac{dV(r)}{dr} \right] \tag{3.38}$$

where $n_2(r)$ is the two-point distribution function in the thermodynamic limit, supposed to depend only on the distance between the particles (we assume that the integrand converges sufficiently rapidly to this thermodynamic limit in order to take this limit under the integral; such hypotheses are discussed in Ref. 3). Here $S(v)$ is the surface of the unit v-dimensional sphere [$S(1) = 2$, $S(2) = 2\pi$, $S(3) = 4\pi$, etc.].

The virial expression for the pressure

$$P = \lim_{|\Lambda| \to \infty} -\tau_{11}(\Lambda) = \rho kT + \frac{S(v)}{2v} \int_0^\infty dr\, r^v n_2(r) \frac{dV(r)}{dr} \tag{3.39}$$

is linearly dependent with the adiabatic Lamé coefficients; the following holds:

$$\lambda(\infty) - \mu(\infty) = 2(P - \rho kT) \tag{3.40}$$

which constitutes the generalized Cauchy identity [$\lambda(\infty) = \mu(\infty)$ was stated in 1828 by Cauchy[8,30]].

Equation (3.40) was derived by Zwanzig and Mountain[51] for $v = 3$.

Remarks

1. In (3.27) and (3.36), the terms linear with respect to the stress tensor will be referred to as pressure corrections. In a general way, they have often been omitted in the literature[26,44,48] (see, however, Refs. 2 and 37 for a correct treatment of these corrections; see also Ref. 47, keeping in mind that the so-called Lagrangian strain tensor does not constitute in general a convenient expansion parameter[3]).

The source of this confusion lies in the fact that the elastic moduli tensor (static or adiabatic), which is the derivative of the stress tensor with

respect to the displacements gradients, is not the second derivative of the thermodynamic potential (the free energy; respectively, the energy), pressure corrections making precisely the difference.

2. The expression (3.34) was first obtained in 1953 by Green,[21] who identified the transport coefficients appearing in experimentally known transport laws with those derived from a Fokker–Planck equation that the set of "gross variables" are postulated to obey.

The use of a local grand canonical equilibrium ensemble led Mori[34] in 1958 to the same expression, which was obtained also by Montroll[33] in 1959 by a simple derivation in the spirit of the Kubo formalism. Equation (3.34) was found again by McLennan[31] in 1960 by explicit consideration of local generalized forces which bring the system about a deviation from equilibrium. These different methods are discussed in an excellent review by Zwanzig.[50]

The bulk viscosity $\eta_b := \eta_{1122}(0)$ obtained from (3.29) differs from the expressions given by Mori[35] and De Vault and McLennan[13,32] by the fact that these authors consider the autocorrelation of the stress tensor corrected by derivatives of the pressure with respect to the number of particles and the energy. It is generally admitted[13,50] that the first correction is conditionned by the use of the grand canonical ensemble (see Refs. 3 and 41, where similar corrections arise already at the equilibrium level when passing from one ensemble to another). The second correction seems to arise from an incorrect treatment of the hydrodynamic equations used both by Mori and McLennan: the momentum conservation equation should contain the hard-wall forces exerted by the container on the system. Omission of this term leads, via the virial theorem,[4,28] to a vanishing pressure. On the other hand, the isothermal character of the coefficients obtained is uncertain because in Ref. 13 this second correction arises from the time derivative of the local temperature. Moreover, the use of phenomenological equations, such as the Navier–Stokes equation, which are ill-adapted to discuss the pressure corrections, and the fact that the bulk viscosity does not possesses the mechanical interpretation (2.5) constitute supplementary sources of difficulty.

3. In 1952, Green[20] derived (3.37) (without the kinetic part) by expanding the virial pressure (3.39) in the deformed state in terms of displacement gradients. Indeed, such a procedure leads to the adiabatic moduli and generates in a straightforward way the pressure corrections. Equations (3.37) and (3.38) were also obtained by Zwanzig and Mountain,[51] but their derivation would be incorrect if $\mu(0) \neq 0$, whereas (3.38) holds in the general case; moreover, they reduced the four-body expression $\langle T_{12} T_{12} \rangle$ in a two-body form by their equation (32), where the

boundary term is missing (putting $A = R_j^a$ would lead, by use of the virial theorem,[4] to a vanishing pressure!).

4. The form (3.26) for the relaxation function ensures that the dissipated power (3.33) is positive. Let us define

$$f(t) := \frac{\beta}{|\Lambda|} \langle T_{\alpha\beta}(t); T_{\gamma\delta}(0) \rangle u_{\alpha\beta} u_{\gamma\delta} \tag{3.41}$$

where $u_{\alpha\beta}$ is an unspecified real matrix; for arbitrary $t_i \in \mathbb{R}$ and $z_i \in \mathbb{C}$

$$\sum_{i,j=1}^{N} f(t_i - t_j) z_i z_j^* = \frac{\beta}{|\Lambda|} < \left| \sum_{i=1}^{N} [T_{\alpha\beta}(t_i) - \langle T_{\alpha\beta} \rangle] u_{\alpha\beta} z_i \right|^2 \geqslant 0 \tag{3.42}$$

i.e., $f(t)$ is a positive-definite function, as was pointed out in Ref. 13 (we used the stationarity property of the equilibrium time evolution). By Bochner's theorem[39] and due to the fact that $f(t)$ is an even function, it follows that

$$\int_0^\infty dt \cos \omega t \, f(t) \geqslant 0 \tag{3.43}$$

which leads, via (3.29), to the positiveness of the dissipated power. The fact that $f(t)$ is of positive type implies in particular that $|f(t)| \leqslant f(0)$, but $f(t)$ need not be monotonic and nor indeed even positive for all values of its argument.[13] (In Section 5, we meet an example where $f(t)$ is the Bessel function of order zero.) The customary assumption about the monotonicity of the relaxation function should then be weakened. The concept of fading memory materials[10] constitutes precisely such an extension (which, however, does not tell anything about the positive-definiteness of the relaxation function).

5. The method of dilatation is particularly useful in the sense that it does not imply knowledge of the form of the "wall potential." In fact, the question about the nature of this potential is more subtle that can appear at first sight: an arbitrary external potential, sufficiently high outside the system, cannot do the job, contrarly to widespread opinion: this arbitrariness would be reflected on the force acting on the particles, i.e., on the pressure. On the other hand, it appears straightforward that the elastic collision of a particle with the wall implies a generalized force proportional to the square of the particle velocity.[6]

Let us emphasize again that the method used is of course limited by its initial framework: linear response theory, canonical ensemble, and homogeneous deformation; it excludes the large amplitude of deformation, in particular the shock waves, as well as the consideration of local depen-

dent viscoelastic properties, such as like sound propagation. Moreover, the interesting molecular dynamics studies at constant stress of Andersen,[52] Parrinello and Rahman,[53] Ray and Rahman,[54] and Hoover *et al.*[55] are beyond the scope of this article. Finally, the absence of interaction terms between the system and the thermostat during the perturbation constitutes a failure inherent to any application of the linear response theory; see, however, Ref. 49, p. 145, for some arguments justifying such a procedure.

4. LADDER NETWORK REPRESENTATION

Let $A(\mathbf{x}, \mathbf{p})$ be a dynamical variable (whose invariant part is set to be zero for convenience) obeying to the Liouville equation

$$\frac{d}{dt} A(\mathbf{x}, \mathbf{p}) = iLA(\mathbf{x}, \mathbf{p}) \tag{4.1}$$

Mori's formalism,[36] which consists in representing the Laplace transform of the autocorrelation of A by means of a continued fraction, is obtained by a Gram–Schmidt orghogonalization of the sequence of the initial time derivatives of A, relative to the inner product

$$(A, B) := \langle \bar{A} B \rangle \tag{4.2}$$

[the brackets are defined in (3.22)]. Let us briefly recall Mori's result. Setting

$$P_k \cdots := \frac{(f_k, \ldots)}{(f_k, f_k)} f_k \tag{4.3}$$

$$f_k := iL_k f_{k-1} \tag{4.4}$$

$$L_k \cdots := (\mathbb{1} - P_{k-1}) L_{k-1} \cdots \tag{4.5}$$

with

$$f_0 := A(0), \qquad L_0 := L \tag{4.6}$$

and

$$f_k(t) := \exp(iL_k t) f_k \tag{4.7}$$

It can be shown that the Laplace transforms of

$$\Xi_j(t) := \frac{(f_j, f_j(t))}{(f_j, f_j)} \tag{4.8}$$

obey the recurrence relations

$$\bar{\Xi}_j(s) = \frac{1}{s - i\omega_j + \Delta_{j+1}\bar{\Xi}_{j+1}(s)} \tag{4.9}$$

where

$$\omega_j := \frac{(f_j, L_j f_j)}{(f_j, f_j)} \tag{4.10}$$

$$\Delta_j := \frac{(f_j, f_j)}{(f_{j-1}, f_{j-1})} \tag{4.11}$$

Mori's original work did not fully exploit the autoadjontness of the Liouville operator with respect to the inner product (4.2). Indeed, it can be shown that

$$\omega_j = 0 \tag{4.12}$$

when A is a Hermitian variable,[14] and that (4.4) reduces to[29]

$$f_k = iL_{f_{k-1}} + \Delta_{k-1} f_{k-2} \tag{4.13}$$

The iteration of (4.9) leads to the announced continued fraction. This formalism possesses a conceptual interpretation (hierarchy of generalized Langevin equations[7,36]), and provides a theoretical tool for numerical calculations.[22,45] What is new, to our knowledge, is the interpretation of (4.9) in terms of a mechanical circuit, which we shall develop now. Taking as observable

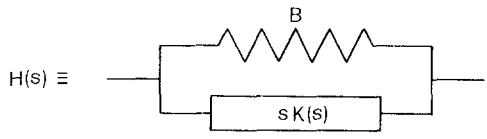
$$A_{\alpha\beta}(\mathbf{x}, \mathbf{p}) := T_{\alpha\beta}(\mathbf{x}, \mathbf{p}) - \langle T_{\alpha\beta}(\mathbf{x}, \mathbf{p}) \rangle \tag{4.14}$$

we write the relaxation function (3.16) as

$$K(t) = \frac{\beta}{|A|} \langle A(t)\, A(0) \rangle = \frac{\beta}{|A|} \langle A^2 \rangle\, \Xi_0(t) \tag{4.15}$$

We suppose here that we are concerned with a single variable A, and therefore we did not write the indices in (4.15) (when, on the contrary, we consider, e.g., $K_{1222}(t)$, which involves the time correlations of two different observables, the previous formalism must first be generalized to include matrix correlation functions, which does not offer difficulties[7]).

The following circuit corresponds to the response function (2.17):



(4.16)

Applying (4.9) twice leads to

$$\frac{1}{s\bar{\Xi}_{2j}(s)} = 1 + \frac{\Delta_{2j+1}}{s^2 + \Delta_{2j+2} s\bar{\Xi}_{j+2}(s)} \tag{4.17}$$

Defining

$$h_j(s) := \frac{\beta}{|\Lambda|} \langle A^2 \rangle \frac{\Delta_2 \Delta_4 \cdots \Delta_{2j}}{\Delta_1 \Delta_3 \cdots \Delta_{2j-1}} s\bar{\Xi}_{2j}(s) \tag{4.18}$$

$$M_j := \frac{\beta}{|\Lambda|} \langle A^2 \rangle \frac{\Delta_2 \Delta_4 \cdots \Delta_{2j}}{\Delta_1 \Delta_3 \cdots \Delta_{2j+1}} \tag{4.19}$$

$$E_j := \frac{\beta}{|\Lambda|} \langle A^2 \rangle \frac{\Delta_2 \Delta_4 \cdots \Delta_{2j}}{\Delta_1 \Delta_3 \cdots \Delta_{2j-1}} \tag{4.20}$$

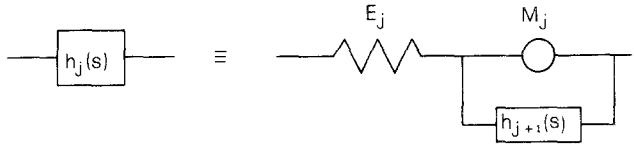
for $j = 0, 1, 2, \ldots$, we can write (4.15) as

$$\frac{1}{h_j(s)} = \frac{1}{E_j} + \frac{1}{M_j s^2 + h_{j+1}(s)} \tag{4.21}$$

By (4.15) and (4.18), we have

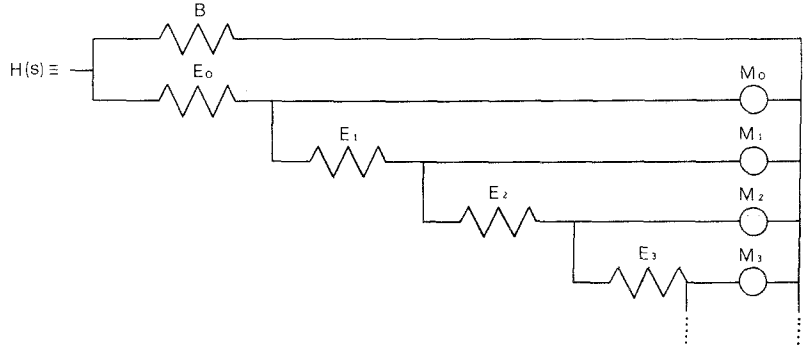
$$s\bar{K}(s) = h_0(s) \tag{4.22}$$

The main point lies in the fact that (4.21) corresponds to the following circuit representation:



(4.23)

We are then led to the following infinite ladder network representation for the response function:



(4.24)

Let us remark that

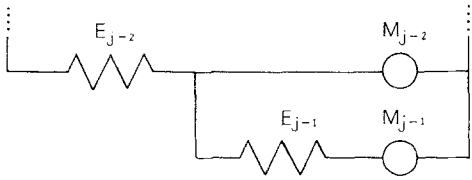
$$M_j = \frac{\beta}{|A|} \frac{|f_2|^4 |f_4|^4 \cdots |f_{2j}|^4}{|f_1|^4 |f_3|^4 \cdots |f_{2j-1}|^4 |f_{2j+1}|^2} \tag{4.25}$$

$$E_j = \frac{\beta}{|A|} \frac{|f_2|^4 |f_4|^4 \cdots |f_{2j-2}|^4}{|f_1|^4 |f_3|^4 \cdots |f_{2j-1}|^4} |f_{2j}|^2 \tag{4.26}$$

with

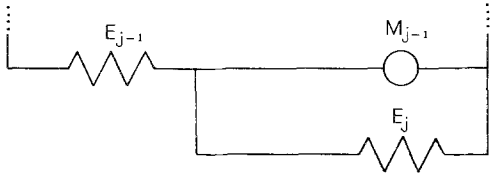
$$|f_j|^2 := (f_j, f_j) \tag{4.27}$$

Let J be the first index for which $|f_J| = 0$. If $J = 2j$, (case a), then $E_j = 0$ and the circuit (4.24) ends with



(4.28)

If $J = 2j + 1$ (case b), then $M_j = \infty$ and (4.24) ends with



(4.29)

In both cases we have

$$K(0) = \lim_{s \to \infty} s\bar{K}(s) = E_0 \tag{4.30}$$

In case (a) we get

$$\lim_{s \to 0} s\bar{K}(s) = 0 \tag{4.31}$$

$$\eta = \lim_{s \to 0} \bar{K}(s) = 0 \tag{4.32}$$

The absence of dashpot elements in (4.23) is a consequence of the conservative nature of the Hamiltonian systems considered here; let us stress the fact that the vanishing viscosity of the finite circuit does not involve the

same for the infinite one: the representation (4.23) is generally not uniformly convergent for $s=0$ (see remark 1 below). Moreover, as will be explicitly shown in the example of Section 4, the limit $s \to 0$ and the thermodynamic limit do not generally commute.

In case b, the viscosity diverges! It is in fact conjectured that, due to the symplectic structure of Hamiltonian systems, the Hilbert space spanned by $f_0, f_1, \ldots$, is of even dimension, and so the case b never appears.

Remarks

1. What about the convergence of the representation (4.24) in the infinite case? Let us first remark that the series $H_n(s)$ and $H^n(s)$ constructed by setting, respectively, $E_n = 0$ and $M_n = \infty$ have the following properties:

$$H_{n+1}(s) \geqslant H_n(s) \tag{4.33}$$

$$H^{n+1}(s) \leqslant H^n(s) \tag{4.34}$$

$$H_n(s) \leqslant H(s) \leqslant H^n(s) \tag{4.35}$$

(these inequalities are immediate when one considers the stress needed to deform the related circuits). Since these two series are monotonic and bounded, they therefore converge, respectively, to $H_\infty(s)$ and $H^\infty(s)$. Moreover, the following result (which is a consequence of the theorem due to Stieljes[14,43,46]) holds: if one or both of the two series

$$\sum_{j=0}^{\infty} M_j, \qquad \sum_{j=0}^{\infty} \frac{1}{E_j} \tag{4.36}$$

diverges, then

$$H_\infty(s) = H^\infty(s) = H(s) \tag{4.37}$$

and (4.24) is uniformly convergent for $\mathrm{Re}\, s \neq 0$. If both of the series (4.36) converge, then

$$H_\infty(s) \neq H^\infty(s) \tag{4.38}$$

and (4.24) diverges by oscillation.

2. In a work[5] on the viscoelasticity of the Pearson gas (which constitutes a dissipative system), we were led to a ladder representation of the response function similar to (4.24), with the difference that springs were replaced by dashpots and masses by springs. Moreover, we established[6]

that this representation is possible if and only if the relaxation function is the Laplace transform of a positive quantity, i.e., if the so-called relaxation spectrum $R(\tau) \geqslant 0$ defined by

$$K(t) = \int_0^\infty d\tau\, R(\tau) \exp(-t/\tau) \tag{4.39}$$

exists. For the Hamiltonian systems considered here, nothing ensures that the relaxation spectrum exists; i.e., that $K(t)$ would be the Laplace transform of a positive function. On the other hand, we have seen in a remark of Section 3 that $K(t)$ is the Fourier transform of a positive function. The similarity of these two situations leads us to conjecture finally that the representation (4.24) holds if and only if the relaxation function (independently of its possible Hamiltonian origin) is of positive type.[6]

5. AN EXAMPLE: THE LINEAR CHAIN OF COUPLED OSCILLATORS

As an illustration of the previous developments, we shall consider the linear chain of N identical classical oscillators of mass m with periodic boundary conditions, which is one of the few exactly solvable available models. The Hamiltonian is given by

$$H(\mathbf{p}, \mathbf{x}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i,j=1}^{N} \frac{1}{2} \phi_{ij} x_i x_j \tag{5.1}$$

(we shall not give detailed calculations, but refer to, e.g., Refs. 17 and 18, which deal with the velocity autocorrelation function). Introducing the normal coordinates, the stress tensor (3.4) reads

$$T = -\sum_{q=1}^{N} P_q P_q^* + \sum_{q=1}^{N} \Omega_q^2 Q_q Q_q^* \tag{5.2}$$

We get

$$\langle T \rangle = 0 \tag{5.3}$$

and

$$\langle T(t)\, T(0) \rangle = 4(kT)^2 \sum_{q=1}^{N} \cos(2\, \Omega_q t) \tag{5.4}$$

where the Ω_q^2 are the eigenvalues of the dynamical matrix. Equation (3.10) reads

$$W = 3 \sum_{q=1}^{N} P_q P_q^* + \sum_{q=1}^{N} \Omega_q^2 Q_q Q_q^* \tag{5.5}$$

and we have

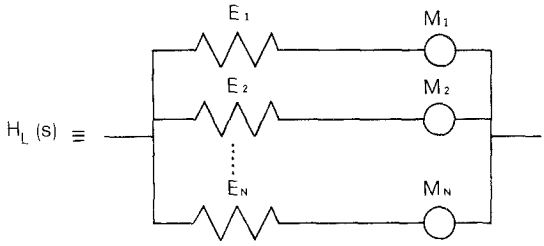
$$\langle W\rangle = \beta\langle T^2\rangle = 4NkT \tag{5.6}$$

The static elastic modulus B as defined by (3.17) is therefore vanishing. This fact is a direct consequence of the periodicity of the chain. (As a matter of fact, the wall theorem[4] enables us to express the elastic moduli tensor as an integral on the boundary of the system, missing in the case of the periodic chain.)

The response function (2.17) of the finite chain of length $|\Lambda| =: L$ is

$$H_L(s) = s\bar{K}_L(s) = s\frac{\beta}{L}\int_0^\infty dt\,\langle T(t)\,T\rangle = \frac{4kT}{L}\sum_{q=1}^{N}\frac{s^2}{s^2+4\Omega_q^2} \tag{5.7}$$

whose representation in terms of circuit is immediate:



(5.8)

with

$$E_q = 4kT/L, \qquad \pi_q = kT/L\Omega_q^2 \tag{5.9}$$

The viscosity

$$\eta_L = \lim_{s\to 0}\bar{K}_L(0) \tag{5.10}$$

is zero, and this representation is found to be inadequate when taking the thermodynamic limit $L\to\infty$: the values of the springs and masses tend to zero, while the number of elements grows to infinity! The alternative we shall develop now constitutes an illustration of the results obtained in Section 4. Restricting ourselves to nearest neighbor interactions of coupling values $m\omega^2$, we have

$$\Omega_q = 2\omega\sin(\pi q/N) \tag{5.11}$$

The thermodynamic limit of (5.4) is

$$K(t) = \lim_{L\to\infty}\frac{\beta}{L}\langle T(t)\,T(0)\rangle = \frac{4\rho kT}{\pi}\int_0^\pi dy\cos(4\omega t\sin y)$$
$$= 4\rho kTJ_0(4\omega t) \tag{5.12}$$

where ρ is the density of the linear chain. The Laplace transform of the relaxation function reads

$$\bar{K}(s) = 4\rho kT/(s^2 + 16\omega^2)^{1/2} \tag{5.13}$$

leading to a finite viscosity

$$\eta = \bar{K}(0) = \rho kT/\omega \tag{5.14}$$

It is then explicitly shown by this example that the limits $s \to 0$ and $L \to \infty$ do not generally commute. Taking the latter first, the Poincaré recurrence times grow to infinity[27] and dissipative behavior appears. Taking account of the result[38]

$$(1+4a)^{1/2} = 1 + \cfrac{2a}{1+\cfrac{a}{1+\cfrac{a}{1+\cfrac{a}{\ddots}}}} \tag{5.15}$$

we obtain

$$\bar{\Xi}_0(s) = \frac{1}{(16\omega^2 + s^2)^{1/2}} = \cfrac{1}{s+\cfrac{8\omega^2}{s+\cfrac{4\omega^2}{s+\cfrac{4\omega^2}{\ddots}}}} \tag{5.16}$$

Comparison of (5.16) with (4.9) leads to the identification

$$\Delta_1 = 8\omega^2, \qquad \Delta_j = 4\omega^2 \qquad \text{for} \quad j \geqslant 2 \tag{5.17}$$

(see Ref. 14 for a similar result in the case of the velocity autocorrelation function). The viscoelastic properties of the linear harmonic chain are therefore exactly given by the infinite circuit (4.24), with, by definitions (4.19) and (4.20),

$$\begin{aligned} B &= 0 \\ E_0 &= 4\rho kT \\ E_j &= 2\rho kT, \qquad j = 1, 2, 3,... \\ M_j &= \rho kT/2\omega^2, \qquad j = 0, 1, 2,... \end{aligned} \tag{5.18}$$

The series (4.36) diverge, so (4.24) is uniformly convergent for all s with a nonzero real part.

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