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Some formal properties of the MTGLE representation of generalized Brownian motion theory

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The molecular time scale generalized Langevin equation (MTGLE) representation of generalized Brownian motion theory [S. A. Adelman, Adv. Chem. Phys. **44**, 143 (1980)] is reformulated to yield a more rigorous and general theory. Key results include: (i) The theory is extended so as to be valid for an arbitrary real scalar process $\dot{r}_0(t)$ whose dynamics are governed by an arbitrary Hermitian Liouville operator L and whose statistics are governed by an arbitrary inner product $\langle\ \rangle$; (ii) a rigorous development of the equivalent harmonic chain representation of $\dot{r}_0(t)$ is presented; (iii) the dynamical and statistical properties of the equivalent chain are rigorously shown to be formally identical to the dynamical and statistical properties of physical harmonic chains obeying classical Boltzmann statistics; (iv) the concept of clamping of equivalent chain atoms is developed for both dynamics and statistics in a rigorous manner. The clamping concept plays a role in the MTGLE theory somewhat analogous to the role played by successive projection operations in the Mori theory; (v) the MTGLE random forces $\dot{R}_p(t)$ are shown to be nonstationary processes if the inner product is $\langle\ \rangle$. A new inner product $\langle\ \rangle_{r_0,r_1,\ldots,r_{p-1}}$ is developed which renders the random forces stationary; (vi) the normal modes of the equivalent chain are shown to be simply related to the eigenfunctions of L; (vii) the MTGLE fluctuation–dissipation theorems are shown to be direct consequences of the orthonormality of the eigenfunctions of L; (viii) the connection between the MTGLE and Mori representations is made.

I. INTRODUCTION

Recently[1] a new formulation of generalized Brownian motion theory[2–4] has been developed. This formulation, which we call the molecular time scale generalized Langevin equation (MTGLE) theory, provides an exact reduced description of condensed phase dynamics which is particularly convenient for describing molecular motion on ultrashort (subpicosecond) time scales, e.g., the time scales associated with chemically effective molecular collisions. The MTGLE theory was, in fact, originally developed to provide methods for the theoretical description and numerical simulation of condensed phase chemical reactions.

Our purpose here is to reformulate the MTGLE theory so as to make it more rigorous and general and also to present a number of new results. These are two reasons for the present reformulation.

(i) Certain aspects of the theory, in particular the concept of chain atom clamping, were previously discussed intuitively rather than rigorously. The intuitive elements are eliminated in this paper and a purely mathematical formulation is presented.

(ii) The present formulation further clarifies the physical and mathematical basis for the existence of generalized Langevin equation representations. A key new result along these lines is that the fluctuation–dissipation theorems (which carry the essential content of the theory) are shown to be simple consequences of the orthonormality of the eigenfunctions of the system Liouville operator L.[5]

The main developments in this paper are as follows: (i) The MTGLE theory is formulated for an arbitrary real stationary scalar process $\dot{r}_0(t)$ whose dynamics is generated by an arbitrary Hermitian Liouville operator L, and whose statistics is governed by an arbitrary inner product $\langle\ \rangle$ (Secs. II and III and Appendix A). (ii) The MTGLE hierarchy is formulated in a rigorous manner for response functions and dynamical variables (Secs. IV and VI and Appendix B). (iii) The MTGLE equivalent harmonic chain representation is developed for both response functions and dynamical variables (Secs. V and VII). (iv) The normal modes of the equivalent chain are studied (Secs. V and VIII). (v) The abstract statistics of the equivalent chain atoms and modes are rigorously shown to be formally identical to the classical Boltzmann statistics of real harmonic chains (Secs. IX and XII and Appendix D). (vi) The MTGLE fluctuation–dissipation and orthogonality theorems are proven in three different ways (Sec. X and Appendices C and F). (vii) The MTGLE theory is shown to provide an explicit algorithm for construction of eigenfunctions of the Liouville operator L. Moreover, the normal modes of the equivalent chain are shown to be directly related to the eigenfunctions of L (Sec. XI). (viii) The MTGLE random forces are shown to be nonstationary processes if the inner product is chosen to be $\langle\ \rangle$. A new inner product $\langle\ \rangle_{r_0,r_1,\ldots,r_{p-1}}$ is developed which renders the random forces stationary (Sec. XII and Appendix E). (ix) The concept of chain atom clamping is rigorously developed for both dynamics and statistics. Clamping plays a role in the MTGLE theory somewhat analogous to the role played by successive projection operations in the Mori theory (Secs. V, VIII, and XII). (x) The connection between the MTGLE and Mori[2] representations is made (Appendix F).

II. BASIC ASSUMPTIONS

We present in this section the mathematical assumptions upon which the theory in this paper is based. We consider a pair of real dynamical variables $r_0(t)$ and $\dot{r}_0(t) = (d/dt)\, r_0(t)$. We will, for convenience, refer to to these variables as the coordinate $[r_0(t)]$ and velocity $[\dot{r}_0(t)]$ of an atom of mass m. The quantity $r_0(t)$ may also be regarded as an arbitrary real dynamical variable.

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We assume that: (i) The time development of an arbitrary dynamical variable $A(t)$ is generated by a Liouville operator L via

$$\dot{A}(t) = iLA(t) \tag{2.1a}$$

or [here and below $A(t=0) \equiv A$ for all dynamical variables $A(t)$]

$$A(t) = e^{iLt}A \ . \tag{2.1b}$$

(ii) An abstract inner product exists[6] with the standard properties

$$\langle AB^* \rangle = \langle BA^* \rangle^* \ , \tag{2.2a}$$

$$0 \le \langle AA^* \rangle \ , \tag{2.2b}$$

$$\left\langle A \sum_a c_a C_a^* \right\rangle = \sum_a c_a \langle AC_a^* \rangle \ . \tag{2.2c}$$

We will choose the inner product so that the velocity autocorrelation function (vaf) $\langle \dot{r}_0(t)\dot{r}_0 \rangle$ is real. (iii) The Liouville operator L is Hermitian if the inner product is $\langle\ \rangle$, i.e.,

$$\langle (LA)B \rangle = \langle A(LB)^* \rangle \ . \tag{2.3}$$

(iv) The dynamics are smooth in the sense that the derivatives

$$\dot{r}_0^{(p)}(t) \equiv (d^p/dt^p)\, r_0(t), \quad p = 1, 2, \ldots \ . \tag{2.4}$$

exist at all times t for every allowed trajectory $r_0(t)$.

All subsequent results follow as exact consequences of the above assumptions and the additional assumption that all Fourier and Laplace transforms and moments defined below exist.

III. BASIC PROPERTIES OF THE VELOCITY AUTOCORRELATION FUNCTION

We first briefly review those basic properties of the velocity autocorrelation function (vaf) which will be required to construct the theory in this paper. We define the normalized vaf $\dot{\chi}(t)$ by

$$\dot{\chi}(t) = \frac{\langle \dot{r}_0(t)\dot{r}_0 \rangle}{\langle \dot{r}_0^2 \rangle} = \frac{\langle \dot{r}_0(t+\tau)\dot{r}_0(\tau) \rangle}{\langle \dot{r}_0^2 \rangle} \ . \tag{3.1}$$

The stationary property, i.e., the validity of the second equality in Eq. (3.1) for all times τ, follows from the Hermitian property of L.

Setting $\tau = -t$ in Eq. (3.1) shows that $\dot{\chi}(t)$ is even. Thus $\dot{\chi}(t)$ has the basic properties

$$\dot{\chi}(-t) = \dot{\chi}(t) \ , \quad \dot{\chi}(0) = 1, \quad \chi(0) = 0 \ . \tag{3.2}$$

The Hermitian property of L, or equivalently the stationary property of the vaf, additionally yields

$$\langle \dot{r}_0^{(p+1)}(t+\tau)\dot{r}_0^{(q)}(\tau) \rangle = -\langle \dot{r}_0^{(p)}(t+\tau)\dot{r}_0^{(q+1)}(\tau) \rangle \ . \tag{3.3}$$

Since $\dot{\chi}(t)$ is even, its Fourier transform $\rho(\omega)$ may be written as

$$\rho(\omega) = \frac{2}{\pi}\int_0^\infty \cos\omega t\, \dot{\chi}(t)\, dt$$

$$\equiv \frac{2}{\pi}\,\mathrm{Re}\left\{\lim_{\epsilon \to 0}\int_0^\infty \exp[-(i\omega+\epsilon)t]\,\dot{\chi}(t)\, dt\right\} \tag{3.4a}$$

or

$$\dot{\chi}(t) = \int_0^\infty \cos\omega t\, \rho(\omega)\, d\omega \ . \tag{3.4b}$$

Since $\rho(-\omega) = \rho(\omega)$ by Eq. (3.4a), the odd moments of $\rho(\omega)$ vanish. We define the even moments of $\rho(\omega)$, $\overline{\omega^{2p}}$, $p = 0, 1, 2, \ldots$ by

$$\overline{\omega^{2p}} = \int_0^\infty \omega^{2p}\rho(\omega)\, d\omega \ . \tag{3.5}$$

Using Eqs. (3.1), (3.3), and (3.4) these moments may be expressed as

$$\omega^{2p} = (-)^p \frac{d^{2p}}{dt^{2p}}\dot{\chi}(t)\Big|_{t=0} = (-)^p\langle \dot{r}_0^{(2p)}\dot{r}_0 \rangle = \langle \dot{r}_0^{(p)}\dot{r}_0^{(p)} \rangle \ge 0 \ . \tag{3.6}$$

Equation (3.6) shows that $\omega^{2p} \ge 0$ for all p. This suggests that $\rho(\omega) \ge 0$ and that it is thus a non-negative spectral density. This may be proven as follows. Consider the eigenvalue problem

$$L\phi_\lambda = \omega_\lambda \phi_\lambda \ . \tag{3.7}$$

Since L is Hermitian its eigenfunctions form an orthonormal set which we assume is complete and its eigenvalues ω_λ are real. These properties permit us to express $\rho(\omega)$ as [for $\omega \ge 0$]

$$\rho(\omega) = \frac{2}{\langle \dot{r}_0^2 \rangle}\sum_\lambda |\langle \phi_\lambda \dot{r}_0 \rangle|^2\, \delta(\omega - \omega_\lambda) \ . \tag{3.8}$$

Equation (3.8) is derived in Appendix A.

Equation (3.8) shows $\rho(\omega) \ge 0$. Moreover, from either Eqs. (3.2) and (3.4b) or Eq. (3.8) and the completeness property, it follows that

$$\int_0^\infty \rho(\omega)\, d\omega = 1 \ .$$

Thus the spectral density $\rho(\omega)$ has the following basic properties

$$\rho(\omega) \ge 0 \ , \tag{3.9a}$$

$$\rho(-\omega) = \rho(\omega) \ , \tag{3.9b}$$

$$\int_0^\infty \rho(\omega)\, d\omega = 1 \ . \tag{3.9c}$$

IV. MTGLE HIERARCHY FOR RESPONSE FUNCTIONS

The mathematical structure of the MTGLE theory is based on a hierarchy of effective equations of motion for response functions $\hat{\theta}_1(t)$, $\hat{\theta}_2(t), \ldots$, and associated coordinate variables $R_1(t)$, $R_2(t), \ldots$, which characterize an infinite sequence of abstract heat baths. We develop in this section the hierarchy for response functions.

A. Definition of $\hat{\theta}_1(z)$

We begin by introducing the Einstein frequency ω_{e_0} of the atom and the coupling constant $\omega_{c_1}^2$ which couples the atom to the first abstract heat bath. These are defined in terms of the moments $\overline{\omega^2}$ and $\overline{\omega^4}$ by

$$\omega_{e_0}^2 = \overline{\omega^2} = \int_0^\infty \omega^2\rho(\omega)\, d\omega \ge 0 \ , \tag{4.1a}$$

$$\omega_{c_1}^4 = \overline{\omega^4} - (\overline{\omega^2})^2 = \int_0^\infty (\omega^2 - \omega_{e_0}^2)^2\rho(\omega)\, d\omega \ge 0 \ . \tag{4.1b}$$

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Next, notice that for very short times the time series expansion

$$\dot{\chi}(t) = 1 - (\omega_{e_0}^2/2!)t^2 + \cdots$$

may be written as

$$\dot{\chi}(t) = \cos\omega_{e_0} t \ , \quad \text{short times} \ . \tag{4.2}$$

The short time limit of $\dot{\chi}(t)$, Eq. (4.2), is identical to the normalized vaf of an isolated or Einstein harmonic oscillator. This is why we call ω_{e_0} the Einstein frequency.

Except for the special case $\omega_{c_1}^2 = 0$ [or equivalently $\rho(\omega) = \delta(\omega - \omega_{e_0})$], the Einstein limit Eq. (4.2) breaks down as t increases. The Einstein limit must, however, be properly built into a full theory of $\dot{\chi}(t)$. We thus seek an exact representation of $\dot{\chi}(t)$ which explicitly displays the Einstein limit, Eq. (4.2).

This representation, written in the Laplace transform domain, is

$$\hat{\chi}(z) = [z^2 + \omega_{e_0}^2 - \omega_{c_1}^4 \hat{\theta}_1(z)]^{-1} \ , \tag{4.3}$$

where $\hat{\chi}(z) = \mathcal{L}\chi(t)$ and $\hat{\theta}_1(z) = \mathcal{L}\dot{\theta}_1(t)$ and where $\mathcal{L}$ denotes a Laplace transform.[7]

Equation (4.3) reduces to the Einstein limit if $\omega_{c_1}^2 = 0$. The breakdown of the Einstein limit is rigorously accounted for by the heat bath response function $\hat{\theta}_1(z)$. Equation (4.3) *defines* $\hat{\theta}_1(z)$.

We next show that $\dot{\theta}_1(t) = \mathcal{L}^{-1}[z\hat{\theta}_1(z)]$ has formal properties identical to those of $\dot{\chi}(t)$, Eqs. (3.2) and (3.9). We present two different arguments to establish this point since it is necessary for the existence of the MTGLE hierarchy. One argument is presented in Sec. IV B; the other is given in Appendix B. The argument in Appendix B is based on simple analytic function theory and was suggested by similar arguments presented by Kadanoff and Martin.[8]

B. Formal properties of $\dot{\theta}_1(t)$

We take the inverse Laplace transform of Eq. (4.3) using Eq. (3.2). This yields the following effective equation of motion for $\dot{\chi}(t)$:

$$\ddot{\chi}(t) = -\omega_{e_0}^2 \chi(t) + \omega_{c_1}^4 \int_0^t \chi(t-\tau)\,\theta_1(\tau)\,d\tau \ . \tag{4.4}$$

Since $\dot{\chi}(-t) = \dot{\chi}(t)$, Eq. (4.4) implies that $\dot{\theta}_1(-t) = \dot{\theta}_1(t)$. This may be proven, for example, as follows. Differentiating Eq. (4.4) twice and using Eq. (3.2) yields

$$\dddot{\chi}(t) = -\omega_{e_0}^2 \dot{\chi}(t) + \omega_{c_1}^4 \int_0^t \dot{\chi}(t-\tau)\,\theta_1(\tau)\,d\tau + \omega_{c_1}^4 \theta_1(t). \tag{4.5}$$

Evaluating Eq. (4.5) at $t = 0$ and using Eq. (3.2) shows that $\theta_1(0) = 0$. Continuing this differentiation process, one may show that all even derivatives of $\theta_1(t)$ vanish at $t = 0$. Thus, $\theta_1(-t) = -\theta_1(t)$ or $\dot{\theta}_1(-t) = \dot{\theta}_1(t)$.

We next show $\dot{\theta}_1(0) = 1$. This follows by differentiating Eq. (4.5) and evaluating at $t = 0$ to yield

$$\omega_{c_1}^4 \dot{\theta}_1(0) = \dddot{\chi}(0) + \omega_{e_0}^2 \dot{\chi}(0) = \omega_{c_1}^4 \ . \tag{4.6}$$

The final equality in Eq. (4.6) follows from Eqs. (3.4b) and (4.1). Equation (4.6) proves $\dot{\theta}_1(0) = 1$. These results show $\dot{\theta}_1(t)$ has basic properties identical to those of $\dot{\chi}(t)$, i.e., [cf. Eq. (3.2)]

$$\dot{\theta}_1(-t) = \dot{\theta}_1(t) \ , \quad \dot{\theta}_1(0) = 1 \ , \quad \theta_1(0) = 0 \ . \tag{4.7}$$

Since $\dot{\theta}_1(t)$ is even, we may define its Fourier transform $\sigma_1(\omega)$ by [cf. Eqs. (3.4)]

$$\sigma_1(\omega) = \frac{2}{\pi} \int_0^\infty \cos\omega t\, \dot{\theta}_1(t)\, dt$$

$$\equiv \frac{2}{\pi} \operatorname{Re} \lim_{\epsilon \to 0} \int_0^\infty \exp[-(i\omega + \epsilon)t]\, \dot{\theta}_1(t)\, dt \ , \tag{4.8a}$$

and

$$\dot{\theta}_1(t) = \int_0^\infty \cos\omega t\, \sigma_1(\omega)\, d\omega \ . \tag{4.8b}$$

We next show that $\sigma_1(\omega) \geq 0$. Integrating Eq. (3.4a) by parts yields the following expression for $\rho(\omega)$,[7]

$$\rho(\omega) = -(2\omega/\pi)\, \mathrm{Im}[\lim_{\epsilon \to 0} \hat{\chi}(i\omega + \epsilon)] \ . \tag{4.9a}$$

Equation (4.8a) analogously yields for $\sigma_1(\omega)$,

$$\sigma_1(\omega) = -(2\omega/\pi)\, \mathrm{Im}[\lim_{\epsilon \to 0} \hat{\theta}_1(i\omega + \epsilon)] \ . \tag{4.9b}$$

Equation (4.3), however, may be rewritten as

$$\tilde{\chi}^{-1}(i\omega + \epsilon) = \omega_{e_0}^2 - (\omega - i\epsilon)^2 - \omega_{c_1}^4 \hat{\theta}_1(i\omega + \epsilon) \ .$$

Combining this result with Eqs. (4.9) then yields

$$\omega_{c_1}^4 \sigma_1(\omega) = \lim_{\epsilon \to 0} \frac{\rho(\omega)}{|\hat{\chi}(i\omega + \epsilon)|^2} \ . \tag{4.10}$$

Since $\omega_{c_1}^4 \geq 0$ and $\rho(\omega) \geq 0$, according to Eq. (4.10) $\sigma_1(\omega) \geq 0$. Thus, $\sigma_1(\omega)$ is the non-negative spectral density of $\dot{\theta}_1(t)$. Equation (4.7), (4.8), and (4.10), moreover, show that $\sigma_1(\omega)$ has formal properties identical to those of $\rho(\omega)$, Eqs. (3.9), i.e.,

$$\sigma_1(\omega) \geq 0 \ , \tag{4.11a}$$

$$\sigma_1(-\omega) = \sigma_1(\omega) \ , \tag{4.11b}$$

$$\int_0^\infty \sigma_1(\omega)\, d\omega = 1 \ . \tag{4.11c}$$

Finally we define the Einstein frequency ω_{e_1} of the first heat bath and the coupling constant $\omega_{c_2}^2$ linking the first and second heat baths by [cf. Eqs. (4.1)]

$$\omega_{e_1}^2 = \int_0^\infty \sigma_1(\omega)\, \omega^2 d\omega \geq 0 \ , \tag{4.12a}$$

$$\omega_{c_1}^4 = \int_0^\infty \sigma_1(\omega)\, [\omega^2 - \omega_{e_1}^2]^2 d\omega \geq 0 \ . \tag{4.12b}$$

C. Response function hierarchy

Equations (4.7) and (4.11) show that $\dot{\theta}_1(t)$ has formal properties identical to those of $\dot{\chi}(t)$, Eqs. (3.2) and (3.9). This indicates that one may recursively continue the procedure of Sec. IV B (and also Appendix B). This process defines an infinite sequence of response functions $\dot{\theta}_2(t)$, $\dot{\theta}_3(t)$, ... All response functions have formal properties identical to those of $\dot{\chi}(t)$. All satisfy effective equations of motion identical in form to Eq. (4.4) [see Eq. (4.18) below]. The general pth response function has the basic properties [cf. Eq. (3.2)]

$$\dot{\theta}_p(-t) = \dot{\theta}_p(t) \ , \quad \dot{\theta}_p(0) = 1 \ , \quad \dot{\theta}_p(0) = 0 \ . \tag{4.13}$$

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The spectral density of $\dot{\theta}_p(t)$, $\sigma_p(\omega)$, is defined by

$$\sigma_p(\omega) = \frac{2}{\pi}\int_0^\infty \cos\omega t\, \dot{\theta}_p(t)\, dt \ , \tag{4.14a}$$

$$\dot{\theta}_p(t) = \int_0^\infty \cos\omega t\, \sigma_p(\omega)\, d\omega \ . \tag{4.14b}$$

The spectral density $\sigma_p(\omega)$ has the following properties [cf. Eqs. (3.9)]:

$$\sigma_p(\omega) \geq 0 \ , \tag{4.15a}$$

$$\sigma_p(-\omega) = \sigma_p(\omega) \ , \tag{4.15b}$$

$$\int_0^\infty \sigma_p(\omega)\, d\omega = 1 \ . \tag{4.15c}$$

The Einstein frequency ω_{ep} of the pth heat bath and the coupling constant linking the pth and $(p+1)$th heat baths are defined by [cf. Eqs. (4.1)]:

$$\omega_{ep}^2 = \int_0^\infty \omega^2 \sigma_p(\omega)\, d\omega \geq 0 \ , \tag{4.16a}$$

and

$$\omega_{cp+1}^4 = \int_0^\infty [\omega^2 - \omega_{ep}^2]^2 \sigma_p(\omega)\, d\omega \geq 0 \ . \tag{4.16b}$$

The quantities $(\omega_{ep}^2, \omega_{cp+1}^2)$ may all be computed in terms of the moments of $\rho(\omega)$ via an algorithm presented elsewhere.[9] Finally, the hierarchy is continued by the Laplace space[7] definition of the response function $\dot{\theta}_{p+1}(t)$ of the $(p+1)$th heat bath. This is [cf. Eq. (4.3)]:

$$\hat{\theta}_p(z) = [z^2 + \omega_{ep}^2 - \omega_{cp+1}^4 \hat{\theta}_{p+1}(z)]^{-1} \ . \tag{4.17}$$

Notice that for $p=1$, Eq. (4.17) defines $\hat{\theta}_2(z)$; for $p=2$, Eq. (4.17) defines $\hat{\theta}_3(z)$, etc. The time domain form of Eq. (4.17) is [cf. Eq. (4.4)]

$$\ddot{\theta}_p(t) = -\omega_{ep}^2 \theta_p(t) + \omega_{cp+1}^4 \int_0^t \theta_p(t-\tau)\, \theta_{p+1}(\tau)\, d\tau \ . \tag{4.18}$$

D. Continued fraction representations

Continued fraction representations for $\hat{\chi}(z)$, $\hat{\theta}_1(z), \ldots$, may be immediately derived from Eqs. (4.3) and (4.17). The continued fraction representation of $\hat{\chi}(z)$ is

$$\hat{\chi}(z) = \cfrac{1}{z^2 + \omega_{e0}^2 - \cfrac{\omega_{c1}^4}{z^2 + \omega_{e1}^2 - \cfrac{\omega_{c2}^4}{z^2 + \omega_{e2}^2 - \cfrac{\omega_{c3}^4}{\cdots}}}} \tag{4.19}$$

The corresponding representation of $\hat{\theta}_p(z)$ for $p=1, 2, 3, \ldots$, is

$$\hat{\theta}_p(z) = \cfrac{1}{z^2 + \omega_{ep}^2 - \cfrac{\omega_{cp+1}^4}{z^2 + \omega_{ep+1}^2 - \cfrac{\omega_{cp+2}^4}{z^2 + \omega_{ep+2}^2 - \cfrac{\omega_{cp+3}^4}{\cdots}}}} \ . \tag{4.20}$$

V. EQUIVALENT HARMONIC CHAIN REPRESENTATION FOR RESPONSE FUNCTIONS

A central feature of the MTGLE formalism is that the temporal development of the response functions $\chi(t)$, $b_1(t), \ldots$, and associated dynamical variables $r_0(t)$, $R_1(t), \ldots$, may be rigorously represented by trajectories of fictitious atoms belonging to abstract harmonic chains. The chain parameters are the set of Einstein frequencies ω_{ep}^2 and coupling constants ω_{cp+1}^2 defined recursively in Sec. IV. The chain representations are, in essence, time domain representations of the Laplace domain continued fractions presented in Sec. IV D.

A. Chain representation for $\dot{\chi}(t)$

We first derive the chain representation for $\dot{\chi}(t)$. We define the coordinates of chain "atom" 0, $\rho_0(t)$, and chain atom 1, $\rho_1(t)$, by

$$\rho_0(t) = \chi(t) \ , \tag{5.1}$$

$$\rho_1(t) = \omega_{c1}^2 \int_0^t \chi(t-\tau)\theta_1(\tau)d\tau = \omega_{c1}^2 \int_0^t \theta_1(t-\tau)\, \rho_0(\tau)\, d\tau \ . \tag{5.2}$$

With these definitions, Eq. (4.4) becomes

$$\ddot{\rho}_0(t) = -\omega_{e0}^2 \rho_0(t) + \omega_{c1}^2 \rho_1(t) \ . \tag{5.3a}$$

An equation of motion for $\rho_1(t)$ follows from Eq. (4.18) (with $p=1$) and Eq. (5.2). It is

$$\ddot{\rho}_1(t) = -\omega_{e1}^2 \rho_1(t) + \omega_{c1}^2 \rho_0(t) + \omega_{c1}^4 \int_0^t \theta_2(t-\tau)\, \rho_1(\tau)\, d\tau \ . \tag{5.3b}$$

$\chi(t)$ is the particular trajectory $\rho_0(t)$, which satisfies the initial conditions $\dot{\rho}_0 = 1$, $\rho_0 = \rho_1 = \dot{\rho}_1 = 0$. These initial conditions follow from Eqs. (5.1) and (5.2), since $\chi(0) = 0$, $\dot{\chi}(0) = 1$. That is,

$$\dot{\chi}(t) = \dot{\rho}_0(t) \ ,$$

if

$$\rho_0 = 0, \ \dot{\rho}_0 = 1 \ , \quad \rho_1 = 0, \ \dot{\rho}_1 = 0 \ . \tag{5.4}$$

Equations (5.3) constitute the two-atom chain equations.

The general $(N+1)$-atom chain equations, $N = 1, 2, \ldots$, may be developed by continuing the procedure just described. The $(N+1)$-atom chain equations are found to be

$$\ddot{\rho}_0(t) = -\omega_{e0}^2 \rho_0(t) + \omega_{c1}^2 \rho_1(t) \ ,$$

$$\ddot{\rho}_1(t) = -\omega_{e1}^2 \rho_1(t) + \omega_{c1}^2 \rho_0(t) + \omega_{c2}^2 \rho_2(t) \ ,$$

$$\vdots$$

$$\ddot{\rho}_N(t) = -\omega_{eN}^2 \rho_N(t) + \omega_{cN}^2 \rho_{N-1}(t) + \omega_{cN+1}^4 \int_0^t \theta_{N+1}(t-\tau)\, \rho_N(\tau)\, d\tau \ . \tag{5.5}$$

The $\rho_q(t)$ are defined recursively in terms of $\rho_0(t)$ by [cf. Eq. (5.2)]:

$$\rho_q(t) = \omega_{cq}^2 \int_0^t \theta_q(t-\tau)\, \rho_{q-1}(\tau)\, d\tau \ , \quad q \geq 1 \ . \tag{5.6}$$

Equation (5.2) and (5.6) show $\rho_q = \dot{\rho}_q = 0$, $q \geq 1$. Thus,

$$\dot{\chi}(t) = \dot{\rho}_0(t) \ ,$$

if

$$\rho_0 = 0, \ \dot{\rho}_0 = 1 \ , \quad \rho_q = \dot{\rho}_q = 0 \ , \quad q \geq 1 \ . \tag{5.7}$$

We next pass to the limit of an infinite $(N \to \infty)$ chain. For this case, Eqs. (5.5) may be written as

$$\ddot{\rho}(t) = -\omega^2 \rho(t) \ , \tag{5.8}$$

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where

$$\rho(t) = \begin{pmatrix} \rho_0(t) \\ \rho_1(t) \\ \vdots \end{pmatrix} \tag{5.9}$$

is an infinite vector and where ω^2 is the following infinite symmetric matrix

$$\omega^2 = \begin{bmatrix} \omega_{e0}^2 & \omega_{c1}^2 & 0 & 0 & 0 & . & . & . \\ \omega_{c1}^2 & \omega_{e1}^2 & \omega_{c2}^2 & 0 & 0 & . & . & . \\ 0 & \omega_{c2}^2 & \omega_{e2}^2 & \omega_{c3}^2 & 0 & . & . & . \\ \vdots & \vdots & \vdots & \vdots & \vdots & & & \end{bmatrix} . \tag{5.10}$$

The vaf $\dot{\chi}(t)$ is the velocity of chain atom 0, $\dot{\rho}_0(t)$, given the following initial conditions [cf. Eq. (5.7)]

$$\rho = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}, \quad \dot{\rho} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}. \tag{5.11}$$

Moreover, for arbitrary initial conditions the velocity of the pth atom $\rho_p(t)$ is found by solving Eq. (5.8) to be

$$\dot{\rho}_p(t) = \sum_{q=1}^{\infty} \{[\cos\omega t]_{pq}\dot{\rho}_q - [\omega \sin\omega t]_{pq}\rho_q\} .$$

Using the initial conditions of Eqs. (5.11), the above expression simplifies to

$$\dot{\rho}_p(t) = [\cos\omega t]_{p0} . \tag{5.12}$$

Thus, the vaf is given by

$$\dot{\chi}(t) = \dot{\rho}_0(t) = [\cos\omega t]_{00} . \tag{5.13}$$

We next note that since ω^2 is a symmetric matrix, it may be diagonalized to yield a diagonal matrix ω_D^2, i.e.,

$$\omega_D^2 = \mathbf{U}^T \omega^2 \mathbf{U} , \tag{5.14}$$

where the orthogonal matrix $\mathbf{U}$ satisifes

$$\mathbf{U}^T\mathbf{U} = \mathbf{U}\mathbf{U}^T = 1 , \tag{5.15}$$

and where

$$\omega_D^2 = \begin{bmatrix} \omega_0^2 & 0 & 0 & . & . & . \\ 0 & \omega_1^2 & 0 & . & . & . \\ 0 & 0 & \omega_2^2 & . & . & . \\ \vdots & \vdots & \vdots & & & \end{bmatrix} \tag{5.16}$$

is the diagonal matrix of (squared) normal mode frequencies ω_λ. These frequencies will now be shown to be the eigenvalues of the Liouville operator L defined in Eq. (3.7).

Using Eqs. (5.14) and (5.15) one may represent $\cos\omega_D t$ as

$$\cos\omega t = \mathbf{U}\cos\omega_D t\,\mathbf{U}^T .$$

Comparing the above equation with Eq. (5.13) yields the following representation for $\dot{\chi}(t)$

$$\dot{\chi}(t) = \sum_{\lambda=0}^{\infty} U_{0\lambda}U_{0\lambda}\cos\omega_\lambda t . \tag{5.17}$$

Comparing Eqs. (3.4b) and (5.17) gives the following representation for $\rho(\omega)$

$$\rho(\omega) = \sum_{\lambda=0}^{\infty} U_{0\lambda}U_{0\lambda}\,\delta(\omega - \omega_\lambda) . \tag{5.18}$$

A comparison of Eqs. (3.8) and (5.18) proves that the normal mode frequencies are identical to the eigenvalues ω_λ of L belonging to eigenfunctions ϕ_λ with nonvanishing projections $\langle\phi_\lambda \dot{r}_0\rangle$ onto $\dot{r}_0$.

B. Chain representation for $\dot{\theta}_p(t)$

To derive a chain representation for $\dot{\theta}_p(t)$, we define a set of chain atom coordinates $\rho_q^{(p)}(t)$, $q = p, p+1, \ldots$, recursively by [cf. Eqs. (5.1) and (5.6)]

$$\rho_p^{(p)}(t) = \theta_p(t) , \tag{5.19a}$$

$$\rho_q^{(p)}(t) = \omega_{cq}^2 \int_0^t \theta_q(t-\tau)\,\rho_{q-1}^{(p)}(\tau)\,d\tau , \quad q \geq p+1 . \tag{5.19b}$$

Note that $\rho_q^{(0)}(t) \equiv \rho_q(t)$. The $(N+1)$-atom chain equations are found using these definitions and Eq. (4.18) to be [cf. Eq. (5.5)]:

$$\begin{aligned} \ddot{\rho}_p^{(p)}(t) &= -\omega_{ep}^2\rho_p^{(p)}(t) + \omega_{cp+1}^2\rho_{p+1}^{(p)}(t) \\ \ddot{\rho}_{p+1}^{(p)}(t) &= -\omega_{ep+1}^2\rho_{p+1}^{(p)}(t) + \omega_{cp+1}^2\rho_p^{(p)}(t) + \omega_{cp+2}^2\rho_{p+1}^{(p)}(t) \\ &\vdots \\ \ddot{\rho}_{p+N}^{(p)}(t) &= -\omega_{ep+N}^2\rho_{p+N}^{(p)}(t) + \omega_{cp+N}^2\rho_{p+N-1}^{(p)}(t) \\ &\quad + \omega_{cp+N+1}^4 \int_0^t \theta_{p+N+1}(t-\tau)\,\rho_{p+N}^{(p)}(\tau)\,d\tau . \end{aligned} \tag{5.20}$$

The response function $\dot{\theta}_p(t)$ is determined from Eqs. (5.20) via the prescription

$$\dot{\theta}_p(t) = \dot{\rho}_p(t) ,$$

if

$$\rho_p^{(p)} = 0, \quad \dot{\rho}_p^{(p)} = 1 , \quad \rho_q^{(p)} = \dot{\rho}_q^{(p)} = 0 , \quad q \geq p+1 . \tag{5.21}$$

Passing to the $N \to \infty$ limit, Eqs. (5.20) may be written as

$$\ddot{\rho}^{(p)}(t) = -[\omega^{(p)}]^2\rho^{(p)}(t) , \tag{5.22}$$

where the infinite vector is

$$\rho^{(p)}(t) = \begin{pmatrix} \rho_p^{(p)}(t) \\ \rho_{p+1}^{(p)}(t) \\ \vdots \end{pmatrix} , \tag{5.23}$$

and where the infinite symmetric matrix $[\omega^{(p)}]^2$ is defined by

$$[\omega^{(p)}]^2 = \begin{bmatrix} \omega_{ep}^2 & \omega_{cp+1}^2 & & 0 & 0 & . & . & . \\ \omega_{cp+1}^2 & \omega_{ep+1}^2 & \omega_{cp+2}^2 & 0 & 0 & . & . & . \\ 0 & \omega_{cp+2}^2 & \omega_{ep+2}^2 & \omega_{cp+3}^2 & 0 & . & . & . \\ \vdots & \vdots & \vdots & \vdots & & & & \end{bmatrix} . \tag{5.24}$$

Notice that [cf. Eq. (5.13)]

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$$\dot{\theta}_p(t) = [\cos\omega^{(p)}t]_{pp} \ . \tag{5.25}$$

Since $[\omega^{(p)}]^2$ is a symmetric matrix, it may be diagonalized by an orthogonal matrix $\mathbf{U}^{(p)}$ to yield a diagonal matrix $[\omega_D^{(p)}]^2$, i.e.,

$$[\omega_D^{(p)}]^2 = \mathbf{U}^{(p)T}\,[\omega^{(p)}]^2\,\mathbf{U}^{(p)} \ , \tag{5.26}$$

where

$$\mathbf{U}^{(p)T}\,\mathbf{U}^{(p)} = \mathbf{U}^{(p)}\,\mathbf{U}^{(p)T} = \mathbf{1} \ , \tag{5.27}$$

and where

$$[\omega_D^{(p)}]^2 = \begin{bmatrix} [\omega_p^{(p)}]^2 & 0 & 0 & \cdot & \cdot & \cdot \\ 0 & [\omega_{p+1}^{(p)}]^2 & 0 & \cdot & \cdot & \cdot \\ 0 & 0 & [\omega_{p+2}^{(p)}]^2 & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \cdot & \cdot & \cdot \end{bmatrix} . \tag{5.28}$$

The above results yield a mode expansion for $\dot{\theta}_p(t)$ [cf. Eq. (5.17)]:

$$\dot{\theta}_p(t) = \sum_{\lambda=p}^{\infty} U_{p\lambda}^{(p)}\,U_{p\lambda}^{(p)}\cos\omega_\lambda^{(p)}t \tag{5.29}$$

and a spectral expansion for $\sigma_p(\omega)$ [cf. Eq. (5.18)]:

$$\sigma_p(\omega) = \sum_{\lambda=p}^{\infty} U_{p\lambda}^{(p)}\,U_{p\lambda}^{(p)}\,\delta(\omega-\omega_\lambda^{(p)}) \ . \tag{5.30}$$

C. Abstract clamping

We next introduce the concept of abstract clamping. This concept is a central feature of the mathematics of the MTGLE representation. It plays a role in the MTGLE theory which is somewhat analogous to the role played by the successive projection operations characteristic of the Mori theory.[2]

We first note that $[\omega^{(p)}]^2$, Eq. (5.24), may be obtained from ω^2, Eq. (5.10), by striking out the first p columns and rows of ω^2. We will refer to this mathematical process of striking out columns and rows as the abstract clamping of chain atoms 0, 1, ..., $p-1$ at their equilibrium positions. The reason for this is that for *physical* harmonic chains with frequency matrix ω^2, physical clamping of chain atoms 0, 1, ..., $p-1$ at their equilibrium positions gives a new dynamical system governed by the frequency matrix $[\omega^{(p)}]^2$.

We emphasize that for general systems clamping is a mathematical process which may not have a simple physical interpretation.

We have just discussed abstract clamping in the context of the MTGLE response function hierarchy. We will further develop the concept when we discuss the MTGLE dynamical variable hierarchy below.

VI. MOLECULAR TIME SCALE GENERALIZED LANGEVIN EQUATION

We now turn to the MTGLE hierarchy for $r_0(t)$, $R_1(t)$, $R_2(t)$, ..., where the $R_p(t)$ are abstract heat bath dynamical variables mentioned earlier.

A. MTGLE for $r_0(t)$

The MTGLE for $r_0(t)$ is

$$\ddot{r}_0(t) = -\omega_{e_0}^2 r_0(t) + \omega_{c_1}^4 \int_0^t \theta_1(t-\tau) r_0(\tau)\,d\tau + \omega_{c_1}^2 R_1(t). \tag{6.1}$$

We will refer to $R_1(t)$ in Eq. (6.1) as the abstract coordinate variable of the first heat bath and $\omega_{c_1}^2 R_1(t)$ as the first MTGLE random force.

Equation (6.1) is, so far, devoid of content. It is simply a defining relation for $R_1(t)$ in terms of the trajectory $r_0(t)$. The content of Eq. (6.1) arises because of the following two theorems:

$$\langle R_1(t)\,\dot{r}_0\rangle = 0 \ , \tag{6.2}$$

$$\frac{\langle \dot{R}_1(t)\,\dot{R}_1\rangle}{\langle \dot{r}_0^2\rangle} = \dot{\theta}_1(t) \ . \tag{6.3}$$

Equation (6.2) states that the MTGLE random force is always orthogonal to the initial velocity $\dot{r}_0$. Equation (6.3) is the MTGLE second fluctuation–dissipation theorem. These theorems may be proven directly from Eqs. (4.4) and (6.1). This direct proof is given in Appendix C.

B. MTGLE for $R_p(t)$

The abstract heat bath coordinate variables $R_p(t)$ are *defined* recursively in terms of $r_0(t)$ via a sequence of MTGLE's. $R_2(t)$ is, for example, defined in terms of $R_1(t)$ by

$$\ddot{R}_1(t) = -\omega_{e_1}^2 R_1(t) + \omega_{c_2}^4 \int_0^t \theta_2(t-\tau) R_1(\tau)\,d\tau + \omega_{c_2}^2 R_2(t) \ . \tag{6.4}$$

The general coordinate variable $R_{p+1}(t)$ is defined in terms of $R_p(t)$ by the MTGLE

$$\ddot{R}_p(t) = -\omega_{e_p}^2 R_p(t) + \omega_{c_{p+1}}^4 \int_0^t \theta_{p+1}(t-\tau) R_p(\tau)\,d\tau + \omega_{c_{p+1}}^2 R_{p+1}(t) \ . \tag{6.5}$$

The content of Eqs. (6.4) and (6.5) arises from the following orthogonality and fluctuation–dissipation theorems [note $R_0 \equiv r_0$]:

$$\langle R_p(t)\dot{R}_{p-1}\rangle = 0, \quad p \geq 1 \ , \tag{6.6}$$

$$\langle \dot{R}_p(t)\dot{R}_p\rangle / \langle \dot{r}_0^2\rangle = \dot{\theta}_p(t), \quad p \geq 1 \ . \tag{6.7}$$

An immediate consequence of Eqs. (6.5) and (6.6) is orthogonality of $\dot{R}_p$ to all higher heat bath coordinate variables $R_{p+1}(t)$, $R_{p+2}(t)$, etc., i.e.,

$$\langle R_q(t)\dot{R}_p\rangle = 0, \quad p \geq 0, \quad q \geq p+1 \ . \tag{6.8}$$

The simple method of proof (Appendix C) used to demonstrate Eqs. (6.2) and (6.3) unfortunately cannot be used without detailed justification to prove Eqs. (6.6) and (6.7). This is because the proof of Eq. (6.3) uses Eq. (3.3) which is a consequence of the stationary property of the process $\dot{r}_0(t)$ [Eq. (3.1)]. We will show in Sec. XI below that the processes $\dot{R}_p(t)$ are *not* stationary if the inner product is $\langle\ \rangle$. Thus, Eqs. (6.6) and (6.7) will be established in Sec. X below by a method which does not require $\dot{R}_p(t)$ to be stationary.

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VII. EQUIVALENT HARMONIC CHAIN REPRESENTATION FOR DYNAMICAL VARIABLES

We next develop equivalent harmonic chain representations for the coordinate variables $r_0(t)$, $R_1(t)$, ... Our treatment closely parallels the complementary development for response functions given in Sec. V.

The chain representations depend only on the defining relations for the $R_p(t)$, [the MTGLE's of Eqs. (6.1), (6.4), and (6.5)] and on the results for response functions derived in Sec. IV. Thus, our proof that the chain representations exist *does not* depend on the validity of the orthogonality and fluctuation–dissipation theorems, Eqs. (6.6) and (6.7).

A. Chain representation for $r_0(t)$

We first develop the two atom chain equations for $r_0(t)$. We *define* the coordinate of chain atom 1, $r_1(t)$ by

$$r_1(t) = R_1(t) + \omega_{c_1}^2 \int_0^t \theta_1(t-\tau) r_0(\tau)\, d\tau \,. \tag{7.1}$$

Using Eq. (7.1), the MTGLE Eq. (6.1) may be rewritten as

$$\ddot{r}_0(t) = -\omega_{e_0}^2 r_0(t) + \omega_{c_1}^2 r_1(t) \,. \tag{7.2a}$$

We further note that since $\theta_1(0) = 0$, Eq. (7.1) implies

$$r_1 = R_1 \,, \quad \dot{r}_1 = \dot{R}_1 \,. \tag{7.3}$$

Equation (7.1) may be written in the Laplace domain[7] as

$$\hat{r}_1(z) = \hat{R}_1(z) + \omega_{c_1}^2 \hat{\theta}_1(z) \hat{r}_0(z) \,. \tag{7.4}$$

Using Eq. (4.17) (for $p = 1$) and Eqs. (7.3), Eq. (7.4) may be rewritten as

$$[z^2 \hat{r}_1(z) - z r_1 - \dot{r}_1] = -\omega_{e_1}^2 \hat{r}_1(z) + \omega_{c_2}^4 \hat{\theta}_2(z) \hat{r}_1(z) + \omega_{c_1}^2 \hat{r}_0(z) + [z^2 \hat{R}_1(z) - z R_1 - \dot{R}_1] + \omega_{e_1}^2 \hat{R}_1(z) - \omega_{c_2}^4 \hat{\theta}_2(z) \hat{R}_1(z) \,.$$

Laplace inversion of the above equation yields

$$\ddot{r}_1(t) = -\omega_{e_1}^2 r_1(t) + \omega_{c_1}^2 r_0(t) + \omega_{c_2}^4 \int_0^t \theta_2(t-\tau) r_1(\tau)\, d\tau + \ddot{R}_1(t) + \omega_{e_1}^2 R(t) - \omega_{c_2}^2 \int_0^t \theta_2(t-\tau) R_1(\tau)\, d\tau \,.$$

Using Eq. (6.4), the above equation simplifies to

$$\ddot{r}_1(t) = -\omega_{e_1}^2 r_1(t) + \omega_{c_1}^2 r_0(t) + \omega_{c_2}^4 \int_0^t \theta_2(t-\tau) r_1(\tau)\, d\tau + \omega_{c_2}^2 R_2(t) \,. \tag{7.2b}$$

Equations (7.2) are the two-atom harmonic chain equations for $r_0(t)$.

The general $(N+1)$-atom chain representation is derived by continuing the above procedure. It is

$$\begin{aligned}
&\ddot{r}_0(t) = -\omega_{e_0}^2 r_0(t) + \omega_{c_1}^2 r_1(t) \\
&\ddot{r}_1(t) = -\omega_{e_1}^2 r_1(t) + \omega_{c_1}^2 r_0(t) + \omega_{c_2}^2 r_2(t) \\
&\quad \vdots \\
&\ddot{r}_N(t) = -\omega_{e_N}^2 r_N(t) + \omega_{c_N}^2 r_{N-1}(t) + \omega_{c_{N+1}}^4 \times \int_0^t \theta_{N+1}(t-\tau) r_N(\tau)\, d\tau + \omega_{c_{N+1}}^2 R_{N+1}(t) \,.
\end{aligned} \tag{7.5}$$

The chain atom coordinates $r_p(t)$ are defined recursively in terms of $r_0(t)$ by

$$r_p(t) = R_p(t) + \omega_{c_p}^2 \int_0^t \theta_p(t-\tau) r_{p-1}(\tau)\, d\tau \,, \quad p \geq 1 \,. \tag{7.6}$$

Note that since $\theta_p(0) = 0$, Eq. (7.6) shows that

$$r_p = R_p \,, \quad \dot{r}_p = \dot{R}_p \,, \quad p \geq 1 \,. \tag{7.7}$$

B. Chain representation for $R_p(t)$

The chain representation for $R_p(t)$ may be derived from the MTGLE, Eq. (6.5), by paralleling our derivation of Eq. (7.5) from Eq. (6.1). The $(N+1)$-atom chain representation is

$$\begin{aligned}
&\ddot{r}_p^{(p)}(t) = -\omega_{e_p}^2 r_p^{(p)}(t) + \omega_{c_{p+1}}^2 r_{p+1}^{(p)}(t) \\
&\ddot{r}_{p+1}^{(p)}(t) = -\omega_{e_{p+1}}^2 r_{p+1}^{(p)}(t) + \omega_{c_{p+1}}^2 r_p^{(p)}(t) + \omega_{c_{p+2}}^2 r_{p+1}^{(p)}(t) \\
&\quad \vdots \\
&\ddot{r}_{p+N}^{(p)}(t) = -\omega_{e_{p+N}}^2 r_{p+N}^{(p)}(t) + \omega_{c_{p+N}}^2 r_{p+N-1}^{(p)}(t) + \omega_{c_{p+N+1}}^4 \int_0^t \theta_{p+N+1}(t-\tau) r_{p+N}^{(p)}(t)\, d\tau + \omega_{c_{p+N+1}}^2 R_{p+N+1}(t) \,.
\end{aligned} \tag{7.8}$$

The chain coordinates $r_q^{(p)}(t)$, $q \geq p$ are defined recursively in terms of $R_p(t)$ by

$$r_p^{(p)}(t) = R_p(t) \,, \tag{7.9a}$$

$$r_q^{(p)}(t) = R_q(t) + \omega_{c_q}^2 \int_0^t \theta_q(t-\tau) r_{q-1}^{(p)}(\tau)\, d\tau \,, \quad q \geq p+1 \,. \tag{7.9b}$$

Equations (7.7) and (7.9) further imply that

$$r_q^{(p)} = R_q = r_q \,, \quad \dot{r}_q^{(p)} = \dot{R}_q = \dot{r}_q \,. \tag{7.10}$$

VIII. NORMAL MODE REPRESENTATION FOR DYNAMICAL VARIABLES

We next develop normal mode representations for the dynamical variables $r_0(t)$, $R_1(t)$, ... Our development does not use the statistical theorems [Eqs. (6.6) and (6.7)]; the mode representation will, in fact, be used to prove these theorems.

A. Mode representation for $\dot{r}_0(t)$

We begin [(cf. Sec. V)] by rewriting Eq. (7.5) for the case of an infinite $(N \to \infty)$ chain as

$$\ddot{\mathbf{r}}(t) = -\boldsymbol{\omega}^2 \mathbf{r}(t) \,, \tag{8.1}$$

where $\mathbf{r}(t)$ is the following infinite column vector

$$\mathbf{r}(t) = \begin{pmatrix} r_0(t) \\ r_1(t) \\ \vdots \end{pmatrix} \,, \tag{8.2}$$

and where $\boldsymbol{\omega}^2$ is the definite symmetric matrix defined in Eq. (5.10).

The normal mode coordinates $\boldsymbol{\zeta}(t)$ are defined by

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$$\boldsymbol{\zeta}(t) = \mathbf{U}^T \mathbf{r}(t) = \begin{pmatrix} \zeta_0(t) \\ \zeta_1(t) \\ \vdots \end{pmatrix} , \tag{8.3}$$

where $\mathbf{U}$, the orthogonal transformation which diagonalizes ω^2, is defined in Sec. V A. The inverse of Eq. (8.3) is

$$\mathbf{r}(t) = \mathbf{U}\boldsymbol{\zeta}(t) . \tag{8.4}$$

Combining Eqs. (5.14), (8.1), and (8.3) shows that $\boldsymbol{\zeta}(t)$ obeys the following diagonal equation of motion:

$$\ddot{\boldsymbol{\zeta}}(t) = -\omega_D^2 \boldsymbol{\zeta}(t) , \tag{8.5a}$$

or equivalently,

$$\ddot{\zeta}_\lambda(t) = -\omega_\lambda^2 \zeta_\lambda(t) , \quad \lambda = 0, 1, \ldots . \tag{8.5b}$$

The solution of Eq. (8.5b) is

$$\zeta_\lambda(t) = \cos\omega_\lambda t \zeta_\lambda + \omega_\lambda^{-1} \sin\omega_\lambda t \dot{\zeta}_\lambda . \tag{8.6}$$

Combining Eqs. (8.4) and (8.6) shows that the velocity process $\dot{r}_0(t)$ has the following mode expansion

$$\dot{r}_0(t) = \sum_{\lambda=0}^{\infty} U_{0\lambda}(\cos\omega_\lambda t \dot{\zeta}_\lambda - \omega_\lambda \sin\omega_\lambda t \zeta_\lambda) . \tag{8.7}$$

B. Mode representation for $R_p(t)$

The mode representation for $R_p(t)$ may be derived in a parallel manner. We rewrite the chain Eq. (7.8) as $(N \to \infty)$

$$\mathbf{r}^{(p)}(t) = -[\omega^{(p)}]^2 \mathbf{r}^{(p)}(t) , \tag{8.8}$$

where $[\omega^{(p)}]^2$ is defined in Eq. (5.24), and where [see Eq. (7.9a)]

$$\mathbf{r}^{(p)}(t) = \begin{pmatrix} r_p^{(p)}(t) \\ r_{p+1}^{(p)}(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} R_p(t) \\ r_{p+1}^{(p)}(t) \\ \vdots \end{pmatrix} . \tag{8.9}$$

The normal mode coordinates $\boldsymbol{\zeta}^{(p)}(t)$ defined by

$$\boldsymbol{\zeta}^{(p)}(t) = \mathbf{U}^{(p)T} \mathbf{r}^{(p)}(t) = \begin{pmatrix} \zeta_p^{(p)}(t) \\ \zeta_{p+1}^{(p)}(t) \\ \vdots \end{pmatrix} \tag{8.10}$$

satisfy

$$\ddot{\zeta}_\lambda^{(p)}(t) = -[\omega_\lambda^{(p)}]^2 \zeta_\lambda^{(p)}(t) , \quad \lambda = p, p+1, \ldots . \tag{8.11}$$

Thus, the mode expansion of $\dot{R}_p(t)$ is

$$\dot{R}_p(t) = \sum_{\lambda=p}^{\infty} U_{p\lambda}^{(p)}[\cos\omega_\lambda^{(p)} t \dot{\zeta}_\lambda^{(p)} - \omega_\lambda^{(p)} \sin\omega_\lambda^{(p)} t \zeta_\lambda^{(p)}] . \tag{8.12}$$

Finally, we note that $R_p(t) = r_p^{(p)}(t)$ is the trajectory of the terminal atom in a chain with dynamical matrix $[\omega^{(p)}]^2$. This frequency matrix is obtained by striking out the first p columns and rows of the matrix ω^2. Thus, in accord with our discussion in Sec. V C, we say that $R_p(t)$ is the velocity of chain atom p given that chain atoms 0, 1, ..., $p-1$ are abstractly clamped at their equilibrium positions. For the case of physical harmonic chains this abstract clamping is identical to physical clamping of chain atoms 0, 1, ..., $p-1$.

IX. FORMAL STATISTICAL PROPERTIES OF ATOM AND MODE COORDINATES

The results of Secs. VII and VIII show that the abstract dynamics defined in Sec. II may be rigorously recast to resemble the dynamics of physical harmonic chains. This suggests that the abstract statistics defined by the inner product $\langle\ \rangle$ might resemble physical harmonic chain statistics. We now show that this is the case. We prove that the formal chain statistics resembles the physical statistics of real chains described by a *classical canonical* ensemble.

A. Mode statistics

We first discuss the formal statistics of the normal modes ζ_λ defined in Sec. VIII A. We prove in Appendix D, using the stationary property of velocity process $\dot{r}_0(t)$, that the following formal statistical properties hold,

$$\langle \dot{\zeta}_\lambda \dot{\zeta}_{\lambda'} \rangle = \delta_{\lambda\lambda'} \langle \dot{r}_0^2 \rangle , \tag{9.1a}$$

$$\langle \dot{\zeta}_\lambda \zeta_{\lambda'} \rangle = 0 , \tag{9.1b}$$

$$\langle \zeta_\lambda \zeta_{\lambda'} \rangle = \omega_\lambda^{-2} \langle \dot{r}_0^2 \rangle \delta_{\lambda,\lambda'} , \tag{9.1c}$$

where $\lambda, \lambda' = 0, 1, \ldots$, and where ω_λ is the frequency of the normal mode ζ_λ [see Eq. (8.5b)]. If one defines a formal temperature T by

$$\tfrac{1}{2} m \langle \dot{r}_0^2 \rangle = \tfrac{1}{2} k_B T , \tag{9.2}$$

then Eqs. (9.1) become identical to the classical Boltzmann averages expected for physical harmonic chain modes.

B. Atom statistics

The chain atom coordinates r_p and velocities $\dot{r}_p$ have the following formal statistical properties:

$$\langle \dot{r}_p \dot{r}_q \rangle = \delta_{pq} \langle r_0^2 \rangle , \tag{9.3a}$$

$$\langle r_p \dot{r}_q \rangle = 0 , \tag{9.3b}$$

$$\langle r_p r_q \rangle = \langle r_0^2 \rangle (\omega^{-2})_{pq} , \tag{9.3c}$$

where $p, q = 0, 1, \ldots$, and where ω^2 is defined in Eq. (5.10). Equations (9.3) follow directly from Eqs. (9.1) using Eqs. (5.14), (5.15), and (8.4).

The formal averages in Eqs. (9.3) are identical to the classical Boltzmann averages expected for physical harmonic chain atoms.

X. ORTHOGONALITY AND FLUCTUATION-DISSIPATION THEOREMS

We next prove the orthogonality and fluctuation–dissipation theorems, Eqs. (6.6) and (6.7). We begin by solving Eq. (8.8) to yield

$$\mathbf{r}^{(p)}(t) = \cos\omega^{(p)} t \mathbf{r}^{(p)} + \omega^{(p)-1} \sin\omega^{(p)} t \dot{\mathbf{r}}^{(p)} . \tag{10.1}$$

Since $r_p^{(p)}(t) = R_p(t)$ [Eq. (7.9)], Eq. (10.1) yields

$$R_p(t) = \sum_{q=p}^{\infty} \{[\cos\omega^{(p)} t]_{pq} r_q^{(p)} + [\omega^{(p)-1} \sin\omega^{(p)} t]_{pq} \dot{r}_q^{(p)}\} . \tag{10.2}$$

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According to Eq. (7.10), however, $r_q^{(p)} = r_q$ and $\dot{r}_q^{(p)} = \dot{r}_q$. Thus, Eq. (10.2) yields the following expansion of $R_p(t)$:

$$R_p(t) = \sum_{q=p}^{\infty} \{[\cos\omega^{(p)}t]_{pq} r_q + [\omega^{(p)-1}\sin\omega^{(p)}t]_{pq}\dot{r}_q\} . \quad (10.3)$$

Since $\dot{R}_{p-1} = \dot{r}_{p-1}$ [Eq. (7.7)], one has from Eq. (10.3),

$$\langle R_p(t)\dot{R}_{p-1}\rangle = \sum_{q=p}^{\infty} \{[\cos\omega^{(p)}t]_{pq}\langle r_q\dot{r}_{p-1}\rangle + [\omega^{(p)-1}\sin\omega^{(p)}t]_{pq}\langle\dot{r}_q\dot{r}_{p-1}\rangle\} . \quad (10.4)$$

According to Eqs. (9.3), however, $\langle r_q\dot{r}_{p-1}\rangle = 0$ and $\langle\dot{r}_q\dot{r}_{p-1}\rangle = 0$, for $q \geq p$. Thus, the right-hand side of Eq. (10.4) vanishes. This establishes Eq. (6.6).

Equation (6.7) may be similarly proven. The derivative of Eq. (10.3) is

$$\dot{R}_p(t) = \sum_{q=p}^{\infty} \{[\cos\omega^{(p)}t]_{pq}\dot{r}_q - [\omega^{(p)}\sin\omega^{(p)}t]_{pq} r_q\} . \quad (10.5)$$

Since $\dot{R}_p = \dot{r}_p$, Eq. (10.5) yields using Eqs. (9.3):

$$\frac{\langle\dot{R}_p(t)\dot{R}_p\rangle}{\langle\dot{r}_0^2\rangle} = [\cos\omega^{(p)}t]_{pp} . \quad (10.6)$$

Comparing Eqs. (5.25) and (10.6) proves the fluctuation–dissipation theorem [Eq. (6.7)].

XI. EIGENFUNCTIONS OF THE LIOUVILLE OPERATOR L

We next show that the normal mode coordinates ζ_λ and normal mode velocities $\dot{\zeta}_\lambda$ are simply related to the eigenfunctions ϕ_λ of the Liouville operator L [see Eq. (3.7)].[5] This connection provides a more fundamental understanding of the statistical relations [Eqs. (9.1) and Eqs. (9.3)]. We will see that the statistical properties are simple consequences of the fact that the eigenfunctions ϕ_λ form an orthonormal set since L is Hermitian.

Since the fluctuation–dissipation theorem of Eq. (6.7) was proven (Sec. X) using the statistical relations of Eqs. (9.3), our analysis yields a deep new insight into the origin of this fundamental theorem. The fluctuation-dissipation theorem is now seen to be a simple consequence of the orthonormality of the eigenfunctions of the Hermitian Liouville operator L.

We begin by noting that if ϕ_λ is an eigenfunction of L then ϕ_λ^*, its complex conjugate, is also an eigenfunction; i.e., if

$$L\phi_\lambda = \omega_\lambda\phi_\lambda , \quad (11.1a)$$

then

$$L\phi_{-\lambda} = \omega_\lambda\phi_{-\lambda} , \quad (11.1b)$$

where

$$\phi_{-\lambda} = \phi_\lambda^* . \quad (11.2)$$

Equation (11.1) and (11.2) imply that

$$\phi_\lambda(t) = e^{i\omega_\lambda t}\phi_\lambda , \quad (11.3a)$$

$$\phi_{-\lambda}(t) = e^{-i\omega_\lambda t}\phi_\lambda . \quad (11.3b)$$

The eigenfunctions (ϕ_λ) may be chosen to be orthonormal i.e.,

$$\langle\phi_\lambda\phi_{-\lambda'}\rangle = \delta_{\lambda\lambda'} . \quad (11.4)$$

Equation (11.4) implies the following expansions:

$$r_0(t) = \sum_{\text{all }\lambda}\phi_\lambda(t)\langle r_0\phi_{-\lambda}\rangle = \sum_{\text{all }\lambda}\phi_\lambda(t)\langle\phi_\lambda r_0\rangle^* \quad (11.5)$$

and

$$\dot{r}_0(t) = \sum_{\text{all }\lambda}\phi_\lambda(t)\langle\phi_\lambda\dot{r}_0\rangle^* . \quad (11.6)$$

Comparing Eqs. (11.3), (11.5), and (11.6) additionally yields

$$\langle\phi_\lambda\dot{r}_0\rangle^* = i\omega_\lambda\langle\phi_\lambda r_0\rangle^* , \quad (11.7)$$

or

$$|\langle\phi_\lambda\dot{r}_0\rangle| = \omega_\lambda|\langle\phi_\lambda r_0\rangle| . \quad (11.8)$$

Comparing Eqs. (3.8) and (5.18), however, gives the additional relationship

$$U_{0\lambda} = (2/\langle\dot{r}_0^2\rangle)^{1/2}|\langle\phi_\lambda\dot{r}_0\rangle| . \quad (11.9)$$

Equation (11.8) and (11.9) finally yield

$$|\langle\phi_\lambda r_0\rangle| = (\langle\dot{r}_0^2\rangle/2)^{1/2}(U_{0\lambda}/\omega_\lambda) . \quad (11.10)$$

We next note that since $r_0(t)$ is real, Eq. (11.5) may be rewritten as

$$r_0(t) = \sum_{\lambda=0}^{\infty}[\phi_\lambda(t)\langle\phi_\lambda r_0\rangle^* + \phi_{-\lambda}(t)\langle\phi_\lambda r_0\rangle] . \quad (11.11)$$

We further rewrite Eq. (11.11) as

$$r_0(t) = \sum_{\lambda=0}^{\infty}|\langle\phi_\lambda r_0\rangle|[\tilde{\phi}_\lambda(t) + \tilde{\phi}_{-\lambda}(t)] , \quad (11.12)$$

where

$$\tilde{\phi}_\lambda(t) = e^{i\chi_\lambda}\phi_\lambda(t) , \quad (11.13a)$$

$$\tilde{\phi}_{-\lambda}(t) = \tilde{\phi}_\lambda^*(t) = e^{-i\chi_\lambda}\phi_{-\lambda}(t) , \quad (11.13b)$$

and where the phase χ_λ is defined by

$$e^{-i\chi_\lambda} = \frac{\langle\phi_\lambda r_0\rangle}{|\langle\phi_\lambda r_0\rangle|} . \quad (11.14)$$

Notice that the new eigenfunctions $\tilde{\phi}_\lambda$ defined by Eqs. (11.13). satisfy the same orthonormality relations as the old eigenfunctions ϕ_λ, i.e.,

$$\langle\tilde{\phi}_\lambda\tilde{\phi}_{-\lambda'}\rangle = \delta_{\lambda\lambda'} . \quad (11.15)$$

Equations (11.10) and (11.12) finally yield

$$r_0(t) = \left(\frac{\langle\dot{r}_0^2\rangle}{2}\right)^{1/2}\sum_{\lambda=0}^{\infty}\frac{U_{0\lambda}}{\omega_\lambda}[\tilde{\phi}_\lambda(t) + \tilde{\phi}_{-\lambda}(t)] . \quad (11.16)$$

Equations (11.3) and (11.16) give the following expansion for $\dot{r}_0(t)$:

$$\dot{r}_0(t) = i\left(\frac{\langle\dot{r}_0^2\rangle}{2}\right)^{1/2}\sum_{\lambda=0}^{\infty}U_{0\lambda}[\tilde{\phi}_\lambda(t) - \tilde{\phi}_{-\lambda}(t)] . \quad (11.17)$$

We next define the *real* variables η_λ and $\dot{\eta}_\lambda$, $\lambda \geq 0$, by

$$\eta_\lambda = \frac{1}{\omega_\lambda}\left(\frac{\langle\dot{r}_0^2\rangle}{2}\right)^{1/2}[\tilde{\phi}_\lambda + \tilde{\phi}_{-\lambda}] , \quad (11.18a)$$

$$\dot{\eta}_\lambda = i\left(\frac{\langle\dot{r}_0^2\rangle}{2}\right)^{1/2}[\tilde{\phi}_\lambda - \tilde{\phi}_{-\lambda}] . \quad (11.18b)$$

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Combining Eqs. (11.3), (11.17), and (11.18) yields the following form for the eigenfunction expansion of $\dot{r}_0(t)$:

$$\dot{r}_0(t) = \sum_{\lambda=0}^{\infty} U_{0\lambda}(\cos\omega_\lambda t\dot{\eta}_\lambda - \omega_\lambda \sin\omega_\lambda t\eta_\lambda) \ . \tag{11.19}$$

Comparing Eq. (8.7) with Eq. (11.19) shows that

$$\zeta_\lambda = \eta_\lambda, \quad \dot{\zeta}_\lambda = \dot{\eta}_\lambda \ .$$

Thus [see Eq. (11.18)]. ζ_λ and $\dot{\zeta}_\lambda$ are related to the eigenfunctions $\tilde{\phi}_\lambda$ by

$$\zeta_\lambda = \frac{1}{\omega_\lambda}\left(\frac{\langle\dot{r}_0^2\rangle}{2}\right)^{1/2}(\tilde{\phi}_\lambda + \tilde{\phi}_{-\lambda}) \tag{11.20a}$$

and

$$\dot{\zeta}_\lambda = i\left(\frac{\langle\dot{r}_0^2\rangle}{2}\right)^{1/2}(\tilde{\phi}_\lambda - \tilde{\phi}_{-\lambda}) \ . \tag{11.20b}$$

Equations (11.20) may be inverted to yield

$$\tilde{\phi}_\lambda = \left(\frac{1}{2\langle\dot{r}_0^2\rangle}\right)^{1/2}\omega_\lambda\left(\zeta_\lambda - \frac{i}{\omega_\lambda}\dot{\zeta}_\lambda\right) \tag{11.21a}$$

and

$$\tilde{\phi}_{-\lambda} = \left(\frac{1}{2\langle\dot{r}_0^2\rangle}\right)^{1/2}\omega_\lambda\left(\zeta_\lambda + \frac{i}{\omega_\lambda}\right)\dot{\zeta}_\lambda \ . \tag{11.21b}$$

Equations (11.20) show the fundamental significance of the MTGLE equivalent chain. The mode coordinates and velocities ζ_λ and $\dot{\zeta}_\lambda$ are linearly related to the eigenfunctions $\tilde{\phi}_\lambda$, $\tilde{\phi}_{-\lambda}$ of L. Thus, the MTGLE theory may be regarded as a formal algorithm for constructing the eigenfunctions of L.

Finally, Eqs. (11.15) and (11.20), permit one to rederive the statistical relations of Eqs. (9.1). Thus, these statistical relations follow directly from the orthonormality of the eigenfunctions of L.

XII. STATISTICAL DEFINITION OF ABSTRACT CLAMPING

A. Physical harmonic chains

To motivate the formal development in this section, we first discuss physical harmonic chains which obey classical Boltzmann statistics. We have mentioned in Sec. VIII that for such chains $\dot{R}_p(t)$ is the velocity of chain atom p given that chain atoms $0, 1, \ldots, p-1$ are physically clamped at equilibrium. Thus, the time development of $\dot{R}_p(t)$ is governed by the Hamiltonian $H^{(p)}$ of the *clamped* chain with dynamical matrix $[\omega^{(p)}]^2$. The inner product $\langle\ \rangle$ refers, in contrast, to a phase space average weighted by the Boltzmann factor $e^{-\beta H}$. The key point is that H is the Hamiltonian of the *full* chain with dynamical matrix ω^2. Thus, statistics and dynamics are governed by different Hamiltonians. An immediate consequence is that the process $\dot{R}_p(t)$ is *not* guaranteed to be stationary; i.e., we expect

$$\langle\dot{R}_p(t+\tau)\dot{R}_p(\tau)\rangle \neq \langle\dot{R}_p(t)\dot{R}_p\rangle \ , \quad \text{if } \tau \neq 0 \ . \tag{12.1}$$

The stationary property of $\dot{R}_p(t)$, with its many useful consequences, may be restored if we define a new inner product $\langle\ \rangle_{r_0, r_1, \ldots, r_{p-1}}$, which is a Boltzmann average over $e^{-\beta H^{(p)}}$ rather than $e^{-\beta H}$; i.e., we define

$$\langle\ \rangle_{r_0, r_1, \ldots, r_{p-1}} = (z^{(p)})^{-1} \times \int d\dot{r}_p d\dot{r}_{p+1} d\dot{r}_{p+1} \cdots e^{-\beta H^{(p)}}(\cdots) \ , \tag{12.2}$$

where $z^{(p)} = tr[e^{-\beta H^{(p)}}]$ is the partition function of the clamped chain.

Notice that $\langle\ \rangle_{r_0, r_1, \ldots, r_{p-1}}$ is a Boltzmann average, given that chain atoms $0, 1, \ldots, p-1$ are physically clamped at equilibrium.

Since statistics and dynamics are governed by the same Hamiltonian if the new inner product is used, the stationary property is restored. That is

$$\langle\dot{R}_p(t+\tau)\dot{R}_p(\tau)\rangle_{r_0, r_1, \ldots, r_{p-1}} = \langle\dot{R}_p(t)\dot{R}_p\rangle_{r_0, r_1, \ldots, r_{p-1}} \ . \tag{12.3}$$

Moreover one may additionally show that

$$\langle\dot{R}_p(t)\dot{R}_p\rangle_{r_0, r_1, \ldots, r_{p-1}} = \langle\dot{R}_p(t)\dot{R}_p\rangle \ . \tag{12.4}$$

The remainder of this section is concerned with extending this discussion of physical chains to the abstract chains of the MTGLE theory.

B. Proof that $R_1(t)$ is nonstationary

We begin by proving that $R_1(t)$ [and hence $\dot{R}_1(t)$] is nonstationary if the inner product is $\langle\ \rangle$. This is sufficient to show that the $R_p(t)$, $p = 2, 3, \ldots$ are also nonstationary for inner product $\langle\ \rangle$. The proof can be carried out in several ways; the present method leads to a "physically" interesting result.[10]

To prove $R_1(t)$ is nonstationary, we assume the converse and then show that this gives a contradiction. If $R_1(t)$ is stationary then by definition

$$\langle R_1(t+\tau)R_1(\tau)\rangle \stackrel{?}{=} -\langle R_1(t)R_1\rangle \ . \tag{12.5}$$

Equation (12.5) implies that [cf. Eq. (3.3)],

$$\langle\dot{R}_1(t)R_1\rangle \stackrel{?}{=} -\langle R_1(t)R_1\rangle \ . \tag{12.6}$$

Equation (6.3), however, shows that (since $\langle\dot{R}_1R_1\rangle = \langle\dot{r}_1r_1\rangle = 0$)

$$\langle R_1(t)\dot{R}_1\rangle = \langle\dot{r}_0^2\rangle\theta_1(t) \ . \tag{12.7}$$

Equations (12.6) and (12.7) thus predict that

$$\langle\dot{R}_1(t)R_1\rangle \stackrel{?}{=} -\langle\dot{r}_0^2\rangle\theta_1(t) \ . \tag{12.8}$$

We show in Appendix E, however, that

$$\langle\dot{R}_1(t)R_1\rangle = -\langle\dot{r}_0^2\rangle\left(\frac{\omega_{e0}}{\Omega_0}\right)^2\theta_1(t) \ . \tag{12.9}$$

Note that the adiabatic frequency Ω_0 appearing in Eq. (12.9) is defined by[1]

$$\Omega_0^{-2} = \hat{\chi}(z=0) \ . \tag{12.10}$$

Since $\Omega_0 < \omega_{e0}$ if $\omega_{c1}^2 > 0$ (Ref. 1) Eq. (12.9), which is exact, conflicts with Eq. (12.8). Equation (12.8), however, was derived assuming $R_1(t)$ is stationary. Thus, $R_1(t)$ is nonstationary.

C. Definition of $\langle\ \rangle_{r_0, r_1, \ldots, r_{p-1}}$

We next define a new inner product $\langle\ \rangle_{r_0, r_1, \ldots, r_{p-1}}$, $p = 1, 2, \ldots$, which renders the process $R_p(t)$ stationary.

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Our discussion of Sec. XII A suggests that the new inner product should have the following two properties [cf. Eqs. (12.3) and (12.4)]:

$$\langle \dot{R}_p(t+\tau)\dot{R}_p(\tau)\rangle_{r_0,r_1,\ldots,r_{p-1}} = \langle \dot{R}_p(t)\dot{R}_p\rangle_{r_0,r_1,\ldots,r_{p-1}} , \quad (12.11)$$

$$\langle \dot{R}_p(t)\dot{R}_p\rangle_{r_0,r_1,\ldots,r_{p-1}} = \langle \dot{R}_p(t)\dot{R}_p\rangle . \quad (12.12)$$

Using the MTGLE fluctuation–dissipation theorem [Eq. (6.7)] these properties may be summarized as

$$\dot{\theta}_p(t) = \frac{\langle \dot{R}_p(t)\dot{R}_p\rangle_{r_0,r_1,\ldots,r_{p-1}}}{\langle \dot{r}_0^2\rangle} = \frac{\langle \dot{R}_p(t+\tau)\dot{R}_p(\tau)\rangle_{r_0,r_1,\ldots,r_{p-1}}}{\langle \dot{r}_0^2\rangle} . \quad (12.13)$$

Notice the perfect analogy between Eqs. (3.1) and (12.13). Throughout this paper we have been developing the formal analogy between the velocity process $\dot{r}_0(t)$ and the processes $\dot{R}_p(t)$. Comparing Eqs. (3.1) and (12.13) shows that, with the introduction of the inner product $\langle\ \rangle_{r_0,r_1,\ldots,r_{m-1}}$, the formal analogy is now complete.

We now give a formal definition of $\langle\ \rangle_{r_0,r_1,\ldots,r_{m-1}}$. This definition has two parts. (i) $\langle\ \rangle_{r_0,r_1,\ldots,r_{m-1}}$ has basic properties identical to those of $\langle\ \rangle$ given in Eq. (2.2). (ii) The modes $\zeta_\lambda^{(p)}$ of the clamped chain [see Eq. (8.11)] have the following formal statistical properties:

$$\langle \dot{\zeta}_\lambda^{(p)}\dot{\zeta}_{\lambda'}^{(p)}\rangle_{r_0,r_1,\ldots,r_{p-1}} = \delta_{\lambda\lambda'}\langle \dot{r}_0^2\rangle , \quad (12.14a)$$

$$\langle \dot{\zeta}_\lambda^{(p)}\zeta_{\lambda'}^{(p)}\rangle_{r_0,r_1,\ldots,r_{p-1}} = 0 , \quad (12.14b)$$

$$\langle \zeta_\lambda^{(p)}\zeta_{\lambda'}^{(p)}\rangle_{r_0,r_1,\ldots,r_{p-1}} = [\omega_\lambda^{(p)}]^{-2}\langle \dot{r}_0^2\rangle . \quad (12.14c)$$

Note the formal similarity of Eqs. (9.1), the statistical properties of unclamped modes ζ_λ, and Eqs. (12.14).

We have stated that Eqs. (12.14) *define* $\langle\ \rangle_{r_0,r_1,\ldots,r_{p-1}}$. This is because $[\zeta_\lambda^{(p)}]$ and $[\dot{\zeta}_\lambda^{(p)}]$ form a set of orthogonal basis vectors which are expected to span a subspace of the full space spanned by $[\zeta_\lambda]$, $[\dot{\zeta}_\lambda]$. This is the subspace which is orthogonal to the vectors $\dot{r}_0, \dot{r}_1, \ldots, \dot{r}_{p-1}$. Thus, $[\zeta_\lambda^{(p)}]$, $[\dot{\zeta}_\lambda^{(p)}]$ should provide a complete expansion basis for dynamical variables $A_i^{(p)}$ which lie in the subspace. Thus, Eqs. (12.14) should determine *all* correlations $\langle A_i^{(p)}A_j^{(p)}\rangle_{r_0,r_1,\ldots,r_{p-1}}$. This is why Eqs. (12.14) *define* $\langle\ \rangle_{r_0,r_1,\ldots,r_{p-1}}$. Using the mode statistics [Eqs. (12.14)] one may readily establish the following atom statistics [cf. Eqs. (9.3)] for $q, q' \geq p$:

$$\langle \dot{r}_q\dot{r}_{q'}\rangle_{r_0,r_1,\ldots,r_{p-1}} = \delta_{qq'}\langle \dot{r}_0^2\rangle , \quad (12.15a)$$

$$\langle r_q\dot{r}_{q'}\rangle_{r_0,r_1,\ldots,r_{p-1}} = 0 , \quad (12.15b)$$

$$\langle r_q r_{q'}\rangle_{r_0,r_1,\ldots,r_{p-1}} = \langle \dot{r}_0^2\rangle(\omega^{-2})_{qq'} . \quad (12.15c)$$

Finally, we establish that the definition [Eqs. (12.14)] yields Eq. (12.13), the desired form of the MTGLE fluctuation–dissipation theorem.

We employ Eq. (8.12) written as

$$\dot{R}_p(t+\tau) = \sum_{\lambda=p}^{\infty} U_{p\lambda}^{(p)}[\cos\omega_\lambda^{(p)}(t+\tau)\dot{\zeta}_\lambda^{(p)} - \omega_\lambda^{(p)}\sin\omega_\lambda^{(p)}(t+\tau)\zeta_\lambda^{(p)}] . \quad (12.16)$$

Equations (12.14) and (12.16) show that $\langle \dot{R}_p(t+\tau)\dot{R}_p(\tau)\rangle_{r_0,r_1,\ldots,r_{p-1}}$ may be reduced to

$$\frac{\langle \dot{R}_p(t+\tau)\dot{R}_p(\tau)\rangle_{r_0,r_1,\ldots,r_{p-1}}}{\langle \dot{r}_0^2\rangle} = \sum_{\lambda=p}^{\infty} U_{p\lambda}^{(p)}U_{p\lambda}^{(p)}[\cos\omega_\lambda^{(p)}(t+\tau)\cos\omega_\lambda^{(p)}\tau + \sin\omega_\lambda^{(p)}(t+\tau)\sin\omega_\lambda^{(p)}\tau] = \sum_{\lambda=p}^{\infty} U_{p\lambda}^{(p)}U_{p\lambda}^{(p)}\cos\omega_\lambda^{(p)}t = \dot{\theta}_p(t) . \quad (12.17)$$

Equation (12.17) is equivalent to Eq. (12.13).

Finally, we note that our development of the inner product $\langle\ \rangle_{r_0,r_1,\ldots,r_{p-1}}$ extends the concept of abstract clamping, originally defined dynamically in Sec. V, to statistics. That is we may regard $\langle\ \rangle_{r_0,r_1,\ldots,r_{p-1}}$ as a formal average over chain phase space coordinates given that chain atoms $r_0, r_1, \ldots, r_{p-1}$ are abstractly clamped at equilibrium.

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APPENDIX A: DERIVATION OF EQ. (3.8)

We derive Eq. (3.8) in this Appendix. Combining Eqs. (2.1b), (3.1), and (3.4a) yields

$$\rho(\omega) = \frac{1}{\langle \dot{r}_0^2\rangle}\frac{2}{\pi}\mathrm{Re}\left[\lim_{\epsilon\to 0}\int_0^\infty dt\exp[-(i\omega+\epsilon)t]\langle \dot{r}_0 e^{iLt}\dot{r}_0\rangle\right] . \quad (A1)$$

This may be rewritten as

$$\rho(\omega) = -\frac{1}{\langle \dot{r}_0^2\rangle}\frac{2}{\pi}\mathrm{Im}\left\langle \dot{r}_0\frac{1}{L-\omega+i\epsilon}\dot{r}_0\right\rangle . \quad (A2)$$

If one assumes the eigenfunctions of L, ϕ_λ, are complete then

$$\mathrm{Im}\left\langle \dot{r}_0\frac{1}{L-\omega+i\epsilon}\dot{r}_0\right\rangle = \mathrm{Im}\sum_\lambda \frac{\langle \dot{r}_0\phi_\lambda\rangle\langle \phi_\lambda\dot{r}_0\rangle}{\omega_\lambda-\omega+i\epsilon} = -\pi\sum_\lambda \langle \dot{r}_0\phi_\lambda\rangle|^2\delta(\omega-\omega_\lambda) . \quad (A3)$$

The final equality in Eq. (A3) holds because the ω_λ are real. Combining Eqs. (A2) and (A3) yields Eq. (3.8).

APPENDIX B: ANALYTICITY PROPERTIES OF $\hat{\theta}_1(z)$

We show that the defining relation for $\hat{\theta}_1(z)$ [Eq. (4.3)] implies that $\hat{\theta}_1(z)$ has analyticity properties identical to those of $\hat{\chi}(z)$.[7] We begin with the following expression for $\hat{\chi}(z)$:

$$\hat{\chi}(z) = \int_0^\infty \frac{\rho(\omega)d\omega}{z^2+\omega^2} . \quad (B1)$$

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Equation (B1) follows by taking the Laplace transform of Eq. (3.4b) and using $\mathcal{L}\dot{\chi}(t) = z\hat{\chi}(z)$. Equation (B1) shows that $\hat{\chi}(z)$ has the following properties:

(i) $\lim_{z\to 0}\hat{\chi}(z) = z^{-2}$.

(ii) $\hat{\chi}(z)$ is analytic off the imaginary z axis. On the imaginary z axis, $\hat{\chi}(z)$ simple poles at $z = \pm i\omega_\lambda$ [see Eq. (3.8)].[11]

(iii) $\hat{\chi}(z)$ has simple zeroes on the imaginary z axis at points $z = \pm i\tilde{\omega}_\lambda$. These zeroes interleave the poles.

(iv) $\hat{\chi}(z) > 0$ on the real z axis.

We next show that $\hat{\chi}(z)$ is free of zeroes except on the imaginary z axis. Letting $z = x + iy$, we find from Eq. (B1) that

$$\mathrm{Im}\,\hat{\chi}(x+iy) = -2xy\int_0^\infty \frac{\rho(\omega)\,d\omega}{(x^2 - y^2 + \omega^2)^2 + 4x^2y^2}\,. \tag{B2}$$

Equation (B2) shows that $\mathrm{Im}\,\hat{\chi}(x+iy) \neq 0$ unless z is either real ($y = 0$) or pure imaginary ($x = 0$). This result along with point (iv) shows that all zeroes of $\hat{\chi}(z)$ occur on the imaginary z axis.

Next consider $\hat{\chi}^{-1}(z)$. The above results show $\hat{\chi}^{-1}(z)$ is analytic except at $z = \pm i\tilde{\omega}_\lambda$ where it has simple poles. Also, for large z,

$$\lim_{z\to 0}\hat{\chi}^{-1}(z) = z^2 + \omega_{e_0}^2 - \frac{\omega_{c_1}^4}{z^2} + O(z^{-4})\,. \tag{B3}$$

Equation (B3) follows from Eq. (B1) using Eq. (4.1). Thus, the function $\hat{\theta}_1(z)$ defined by Eq. (4.3) or equivalently by

$$\hat{\chi}^{-1}(z) = z^2 + \omega_{e_0}^2 - \omega_{c_1}^4\hat{\theta}_1(z) \tag{B4}$$

has the following properties:

(i) $\lim_{z\to 0}\hat{\theta}_1(z) = z^{-2}$. (B5)

(ii) $\hat{\theta}_1(z)$ is analytic except for simple poles at the points $z = \pm i\tilde{\omega}_\lambda$. Thus, $\hat{\theta}_1(z)$ has the following Mittag–Leffler representation:

$$\hat{\theta}_1(z) = \int_0^\infty \frac{\sigma_1(\omega)\,d\omega}{z^2 + \omega^2}\,. \tag{B6}$$

The spectrum $\sigma_1(\omega)$ has nonzero weight only at the points $\omega = \pm\tilde{\omega}_\lambda$. Moreover, further analysis yields $\sigma_1(-\omega) = \sigma_1(\omega)$, and $\sigma_1(\omega) \geq 0$. These results and Eq. (B6) show that $\hat{\theta}_1(z)$ is a meromorphic function which is free of poles and zeroes except on the imaginary z axis, where it has an interleaving sequence of simple poles and zeroes. Thus, $\hat{\theta}_1(z)$ has analyticity properties identical to $\hat{\chi}(z)$. Finally, since $\mathcal{L}^{-1}(z/z^2 + \omega^2) = \cos\omega t$, Eq. (B6) implies

$$\dot{\theta}_1(t) = \int_0^\infty \sigma_1(\omega)\cos\omega t\,d\omega\,. \tag{B7}$$

Equation (B7) justifies the formal Laplace inversion of Eq. (4.3) to yield Eq. (4.4).

APPENDIX C: PROOF OF ORTHOGONALITY AND FLUCTUATION-DISSIPATION THEOREMS

We here establish Eqs. (6.2) and (6.3). Equation (6.2) is readily proven by multiplying Eq. (6.1) on the right-hand side by $\dot{r}_0\langle\dot{r}_0^2\rangle^{-1}$, taking the inner product $\langle\ \rangle$ and using Eq. (3.1). This yields (since $\langle r_0\dot{r}_0\rangle = 0$,

$$\ddot{\chi}(t) = -\omega_{e_0}^2\chi(t) + \omega_{c_1}^4\int_0^t \theta_1(t-\tau)\chi(\tau)d\tau + \omega_{c_1}^2\langle R_1(t)\dot{r}_0\rangle\,. \tag{C1}$$

Comparing Eq. (C1) with Eq. (4.4) yields Eq. (6.2).

We next establish the MTGLE second fluctuation–dissipation theorem [Eq. (6.3)]. Our derivation is suggested by Kubo's proof[3] of the conventional second fluctuation–dissipation theorem. Differentiating Eq. (6.1) and evaluating the result at $t = 0$ yields

$$\omega_{c_1}^2\dot{R}_1 = \dddot{r}_0 + \omega_{e_0}^2\dot{r}_0\,. \tag{C2}$$

Combining Eqs. (6.1) and (C2) thus yields

$$\frac{\langle\ddot{r}_0(t)(\dddot{r}_0 + \omega_{e_0}^2\dot{r}_0)\rangle}{\langle\dot{r}_0^2\rangle} = -\omega_{e_0}^2\frac{\langle r_0(t)(\dddot{r}_0 + \omega_{e_0}^2\dot{r}_0)\rangle}{\langle\dot{r}_0^2\rangle} + \omega_{c_1}^4\int_0^t\theta_1(t-\tau)\frac{\langle r_0(\tau)(\dddot{r}_0 + \omega_{e_0}^2\dot{r}_0)\rangle\,d\tau}{\langle\dot{r}_0^2\rangle} + \omega_{c_1}^2\frac{\langle R_1(t)\dot{R}_1\rangle}{\langle\dot{r}_0^2\rangle}\,. \tag{C3}$$

Using Eqs. (3.1), (3.3), and (4.4), Eq. (C3) may be simplified to

$$\dddot{\chi}(t) = -\omega_{e_0}^2\dot{\chi}(t) + \omega_{c_1}^4\int_0^t\dot{\chi}(t-\tau)\theta_1(\tau)\,d\tau + \omega_{c_1}^4\frac{\langle R_1(t)\dot{R}_1\rangle}{\langle\dot{r}_0^2\rangle}\,. \tag{C4}$$

Comparing Eq. (C4) and Eq. (4.5) yields

$$\frac{\langle R_1(t)\dot{R}_1\rangle}{\langle\dot{r}_0^2\rangle} = \theta_1(t)\,. \tag{C5}$$

The time derivative of Eq. (C5) is Eq. (6.3).

APPENDIX D: PROOF OF MODE STATISTICAL PROPERTIES

We here prove Eqs. (9.1). We begin with the relation

$$\langle\dot{r}_0^2(\tau)\rangle = \langle\dot{r}_0^2\rangle\,, \tag{D1}$$

which is valid for all times τ. Equation (D1) follows by setting $t = 0$ in Eq. (3.1). Using Eq. (8.7), we may write $\langle\dot{r}_0^2(\tau)\rangle$ as

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$$\langle \dot{r}_0^2(\tau)\rangle = \langle \dot{r}_0^2\rangle = \sum_\lambda \sum_{\lambda'} U_{0\lambda}U_{0\lambda'}\langle \cos\omega_\lambda t \cos\omega_{\lambda'} t\langle \dot{\xi}_\lambda \dot{\xi}_{\lambda'}\rangle + \omega_\lambda\omega_{\lambda'} \sin\omega_\lambda t \sin\omega_{\lambda'} t\langle \zeta_\lambda \zeta_{\lambda'}\rangle$$
$$- \omega_\lambda \sin\omega_\lambda t \cos\omega_{\lambda'} t\langle \zeta_\lambda \dot{\zeta}_{\lambda'}\rangle - \omega_{\lambda'} \sin\omega_{\lambda'} t \cos\omega_\lambda t\langle \dot{\zeta}_\lambda \zeta_{\lambda'}\rangle) \ . \tag{D2}$$

Equation (D2) may be rewritten as

$$\langle \dot{r}_0^2\rangle = \frac{1}{2}\sum_\lambda \sum_{\lambda'} U_{0\lambda}U_{0\lambda'} \{\cos(\omega_\lambda - \omega_{\lambda'})t[\langle \dot{\zeta}_\lambda \dot{\zeta}_{\lambda'}\rangle + \omega_\lambda\omega_{\lambda'}\langle \zeta_\lambda \zeta_{\lambda'}\rangle] + \cos(\omega_\lambda + \omega_{\lambda'})t[\langle \dot{\zeta}_\lambda \dot{\zeta}_{\lambda'}\rangle - \omega_\lambda\omega_{\lambda'}\langle \zeta_\lambda \zeta_{\lambda'}\rangle]$$
$$- \sin(\omega_\lambda + \omega_{\lambda'})t[\omega_\lambda\langle \zeta_\lambda \dot{\zeta}_{\lambda'}\rangle + \omega_{\lambda'}\langle \dot{\zeta}_\lambda \zeta_{\lambda'}\rangle] - \sin(\omega_\lambda - \omega_{\lambda'})t[\omega_\lambda\langle \zeta_\lambda \dot{\zeta}_{\lambda'}\rangle - \omega_{\lambda'}\langle \dot{\zeta}_\lambda \zeta_{\lambda'}\rangle]\} \ . \tag{D3}$$

The left- and right-hand sides of Eq. (D3) can only agree if the coefficients of the periodic terms vanish. This requirement yields (since $\omega_\lambda \geq 0$)

$$\langle \dot{\zeta}_\lambda \dot{\zeta}_{\lambda'}\rangle = -\omega_\lambda\omega_{\lambda'}\langle \zeta_\lambda \zeta_{\lambda'}\rangle \ , \quad \lambda \neq \lambda' \ , \tag{D4a}$$

$$\langle \dot{\zeta}_\lambda \dot{\zeta}_{\lambda'}\rangle = \omega_\lambda\omega_{\lambda'}\langle \zeta_\lambda \zeta_{\lambda'}\rangle \ , \tag{D4b}$$

$$\omega_\lambda\langle \zeta_\lambda \dot{\zeta}_{\lambda'}\rangle = \omega_{\lambda'}\langle \dot{\zeta}_\lambda \zeta_{\lambda'}\rangle \ , \quad \lambda \neq \lambda' \ , \tag{D4c}$$

$$\omega_\lambda\langle \zeta_\lambda \dot{\zeta}_{\lambda'}\rangle = -\omega_{\lambda'}\langle \dot{\zeta}_\lambda \zeta_{\lambda'}\rangle \ . \tag{D4d}$$

Equations (D4c) and (D4d) yield

$$\langle \zeta_\lambda \dot{\zeta}_{\lambda'}\rangle = 0 \ . \tag{D5}$$

Equations (D4a) and (D4b) yield

$$\langle \dot{\zeta}_\lambda \dot{\zeta}_{\lambda'}\rangle = 0 \ , \quad \lambda \neq \lambda' \tag{D6}$$

and

$$\langle \zeta_\lambda \zeta_{\lambda'}\rangle = 0 \ , \quad \lambda \neq \lambda' \ . \tag{D7}$$

Finally, Eq. (D4b) shows that

$$\langle \dot{\zeta}_\lambda^2\rangle = \omega_\lambda^2\langle \zeta_\lambda^2\rangle \ . \tag{D8}$$

We next show

$$\langle \dot{\zeta}_\lambda^2\rangle = \langle \dot{r}_0^2\rangle \ . \tag{D9}$$

We use [see Eqs. (8.3) and (8.4)]

$$\dot{r}_0 = \sum_{\lambda'} U_{0\lambda'}\dot{\zeta}_{\lambda'} \ , \tag{D10a}$$

$$\dot{\zeta}_\lambda = \sum_\rho U_{\rho\lambda}\dot{r}_\rho \ . \tag{D10b}$$

Equations (D10) imply that

$$\langle \dot{\zeta}_\lambda \dot{r}_0\rangle = \sum_{\lambda'} U_{0\lambda'}\langle \dot{\zeta}_\lambda \dot{\zeta}_{\lambda'}\rangle = \sum_\rho U_{\rho\lambda}\langle \dot{r}_\rho \dot{r}_0\rangle \ . \tag{D11}$$

We show below, however, that

$$\langle \dot{r}_\rho \dot{r}_0\rangle = \delta_{0\rho}\langle \dot{r}_0^2\rangle \ . \tag{D12}$$

Equations (D6), (D8), and (D11) thus yield Eq. (D9). Equations (D5)–(D9) are equivalent to Eq. (9.1).

We conclude by proving Eq. (D12). We employ

$$\langle R_1(t)\dot{r}_0\rangle = 0 \tag{D13}$$

which has been established by an independent argument in Appendix C. Equation (D13) and the MTGLE Eq. (6.4) imply

$$\langle R_2(t)\dot{r}_0\rangle = 0 \ .$$

Continuing this argument we have, in general,

$$\langle R_p(t)\dot{r}_0\rangle = 0 \ , \quad p = 1, 2, \ldots \ , \tag{D14}$$

which implies [use Eq. (7.7)]

$$\langle \dot{R}_p \dot{r}_0\rangle = \langle \dot{r}_p \dot{r}_0\rangle = 0 \ , \quad p = 1, 2, \ldots \ . \tag{D15}$$

Equation (D15) is equivalent to Eq. (D12).

Finally, we note that our proof tacitly assumes that

(i) $\omega_\lambda \neq 0$,

(ii) the ζ_λ are nondegenerate.

Assumption (i) may be removed by further analysis. Assumption (ii) may be lifted if (as is expected) we can form linear combinations of degenerate modes which satisfy the orthogonality relations Eqs. (9.1).

APPENDIX E: PROOF OF EQ. (12.9)

Here, we prove Eq. (12.9). We begin by evaluating Eq. (6.1) at $t = 0$. This gives

$$\omega_{c_1}^2 R_1 = \ddot{r}_0 + \omega_{e_0}^2 r_0 \ . \tag{E1}$$

Taking the derivative of Eq. (6.1) yields the additional relationship

$$\dddot{r}_0(t) = -\omega_{e_0}^2 \dot{r}_0(t) + \omega_{c_1}^4 \times \int_0^t \dot{\theta}_1(t-\tau) r_0(\tau)\, d\tau + \omega_{c_1}^2 \dot{R}_1(t) \ . \tag{E2}$$

Combining Eqs. (E1) and (E2) and simplifying as in Appendix C yields

$$\dddot{\chi}(t) = -\omega_{e_0}^2 \ddot{\chi}(t) + \omega_{c_1}^4 \int_0^t \theta_1(t-\tau)\ddot{\chi}(\tau)\, d\tau + \omega_{c_1}^4 \theta_1(t) - \omega_{e_0}^2 \omega_{c_1}^4 \theta_1(t) \frac{\langle r_0^2\rangle}{\langle \dot{r}_0^2\rangle} - \omega_{c_1}^4 \frac{\langle \dot{R}_1(t) R_1\rangle}{\langle \dot{r}_0^2\rangle} \ . \tag{E3}$$

Comparing Eq. (4.5) with Eq. (E3) gives

$$\frac{\langle \dot{R}_1(t) R_1\rangle}{\langle \dot{r}_0^2\rangle} = -\omega_{e_0}^2 \theta_1(t) \frac{\langle r_0^2\rangle}{\langle \dot{r}_0^2\rangle} \ . \tag{E4}$$

Finally, Eqs. (3.1) and (3.3) give

$$\chi(t) = \frac{\langle r_0(t)\dot{r}_0\rangle}{\langle \dot{r}_0^2\rangle} = -\frac{\langle \dot{r}_0(t) r_0\rangle}{\langle \dot{r}_0^2\rangle} \ . \tag{E5}$$

Thus,

$$\hat{\chi}(z=0) = \lim_{z\to 0} \int_0^\infty e^{-zt} \frac{\langle \dot{r}_0(t) r_0\rangle\, dt}{\langle \dot{r}_0^2\rangle} = \frac{\langle r_0^2\rangle}{\langle \dot{r}_0^2\rangle} = \Omega_0^{-2} \ , \tag{E6}$$

where we have used Eq. (12.10). Equations (E4) and (E6) yield Eq. (12.9).

APPENDIX F: RELATION TO MORI THEORY

We sketch here the relation between the MTGLE and Mori[2] representations of Brownian motion theory.

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We begin with Mori's[2] general identity for an arbitrary vector variable A, namely

$$\frac{d\mathbf{A}(t)}{dt} = i\omega\mathbf{A} - \int_0^t \Phi(t-\tau)\,\mathbf{A}(\tau)\,d\tau + \mathbf{F}_1(t)\ , \tag{F1}$$

All quantities appearing in Eq. (F1) are defined in Mori's paper. We choose

$$A = \begin{pmatrix} r_0 \\ p_0 \end{pmatrix} \equiv \begin{pmatrix} r_0 \\ m\dot{r}_0 \end{pmatrix}\ . \tag{F2}$$

Then, evaluating Eq. (F1) yields the following equation of motion for $r_0(t)$:

$$\ddot{r}_0(t) = -\Omega_0^2 r_0(t) - \int_0^t \beta_1(t-\tau)\,\dot{r}_0(\tau)\,d\tau + \frac{F_1(t)}{m}\ . \tag{F3}$$

Note that the Mori random force $F_1(t)$ is given by

$$F_1(t) = e^{QiLt}\,Q\,\dot{p}_0\ , \tag{F4}$$

where Q is Mori's projection operator which orthogonalizes a dynamical variable to A.

The Mori random force $F_1(t)$ satisfies the statistical constraints

$$\langle F_1(t) r_0\rangle = \langle F_1(t)\,\dot{r}_0\rangle = 0\ , \tag{F5}$$

$$\beta_1(t) = \frac{\langle F_1(t+\tau)\,F_1(\tau)\rangle}{\langle p_0^2\rangle}\ . \tag{F6}$$

Equation (F6) is Mori's second fluctuation–dissipation theorem. The adiabatic frequency Ω_0 appearing in Eq. (F3) is determined via the Mori prescription as [cf. Eq. (E6)]

$$\Omega_0^2 = \langle \dot{r}_0^2\rangle/\langle r_0^2\rangle\ . \tag{F7}$$

Equations (3.1), (F3), and (F5) yield the following equation of motion for $\dot{\chi}(t)$:

$$\ddot{\chi}(t) = -\Omega_0^2\chi(t) - \int_0^t \beta_1(t-\tau)\,\dot{\chi}(\tau)\,d\tau\ . \tag{F8}$$

We next define ω_{e0}^2 and $\omega_{c1}^4\,\theta_1(t)$ by

$$\omega_{e0}^2 = \beta_1(0) + \Omega_0^2\ , \tag{F9a}$$

$$\dot{\beta}_1(t) = -\omega_{c1}^4\,\theta_1(t)\ . \tag{F9b}$$

Using Eq. (F6), one may establish $\beta_1(-t) = \beta_1(t)$. Hence, $\dot{\theta}_1(-t) = \dot{\theta}_1(t)$. Thus, we may choose

$$\dot{\theta}_1(0) = 1\ . \tag{F10}$$

Equations (F9) and (F10) determine the MTGLE quantities ω_{e0}^2, ω_{c1}^4, and $\theta_1(t)$ in terms of the Mori quantities Ω_0^2 and $\beta_1(t)$.

Integrating Eq. (F8) by parts and using Eqs. (F9) and (F10) yields

$$\ddot{\chi}(t) = -\omega_{e0}^2\chi(t) + \omega_{c1}^4\int_0^t \theta_1(t-\tau)\chi(\tau)d\tau\ . \tag{F11}$$

Equation (F11) is identical to Eq. (4.4). Thus, we have derived the MTGLE relation Eq. (4.4) from the Mori theory. This derivation provides still another justification for Eq. (4.4).

To complete the connection between the first Mori GLE [Eq. (F3)] and the first MTGLE [Eq. (6.1)], we must derive the MTGLE statistical relations [Eqs. (6.2) and (6.3)] from the Mori statistical relations [Eqs. (F5) and (F6)]. This may be accomplished by integrating Eq. (F3) by parts to yield

$$\ddot{r}_0(t) = -\omega_{e0}^2 r_0(t) + \omega_{c1}^4\int_0^t \theta_1(t-\tau)\,r_0(\tau)\,d\tau + \omega_{c1}^2 R_1(t)\ . \tag{F12}$$

The quantity $\omega_{c1}^2 R_1(t)$ is *defined* by

$$\omega_{c1}^2 R_1(t) = F_1(t)/m + \beta_1(t)\,r_0\ . \tag{F13}$$

Equations (F5) and (F13) and the fact that $\langle r_0\dot{r}_0\rangle = 0$ immediately imply Eq. (6.2), i.e.,

$$\langle R_1(t)\,\dot{r}_0\rangle = 0\ . \tag{F14}$$

Note, however, that $\langle R_1(t)\,r_0\rangle \neq 0$. To prove Eq. (6.3), we differentiate Eq. (F13) to yield

$$\omega_{c1}^2\dot{R}_1(t) = \dot{F}_1(t)/m + \dot{\beta}_1(t)\,r_0\ . \tag{F15}$$

Notice that since $F_1(t)$ is stationary [see Eq. (F6)], Eq. (F15) shows immediately that $R_1(t)$ is nonstationary as discussed in Sec. XII.

Since $\dot{\beta}_1(t)$ is an odd function, Eq. (F15) yields at $t=0$,

$$\omega_{c1}^2\dot{R}_1 = \dot{F}_1/m\ . \tag{F16}$$

Equations (F15) and (F16) yield

$$\omega_{c1}^4\frac{\langle \dot{R}_1(t)\,\dot{R}_1\rangle}{\langle \dot{r}_0^2\rangle} = \frac{\langle[\dot{F}_1(t) + m\dot{\beta}_1(t)\,r_0]\,\dot{F}_1\rangle}{\langle p_0^2\rangle} = \frac{\langle \dot{F}_1(t)\,\dot{F}_1\rangle}{\langle p_0^2\rangle}\ . \tag{F17}$$

Equations (F6) and (F9), however, give

$$\ddot{\beta}_1(t) = \frac{\langle \ddot{F}_1(t)\,F_1\rangle}{\langle p_0^2\rangle} = -\frac{\langle \dot{F}_1(t)\,\dot{F}_1\rangle}{\langle p_0^2\rangle} = -\omega_{c1}^4\,\dot{\theta}_1(t)\ . \tag{F18}$$

Equations (F17) and (F18) yield

$$\frac{\langle \dot{R}_1(t)\,\dot{R}_1\rangle}{\langle \dot{r}_0^2\rangle} = \dot{\theta}_1(t)\ , \tag{F19}$$

which is the MTGLE second fluctuation–dissipation theorem Eq. (6.3). Thus, we have proven the complete equivalence between the MTGLE and Mori theories at the first level of the hierarchy. The proof may be continued by considering the Mori equations derived by projecting onto F_1 and $\dot{F}_1$, F_2, and $\dot{F}_2$, etc.

We find that the pth Mori random force $F_p(t)$ satisifes

$$\ddot{F}_p(t) = -\Omega_p^2 F_p(t) - \int_0^t \beta_{p+1}(t-\tau)\,\dot{F}_p(\tau)\,d\tau + F_{p+1}(t)\ , \tag{F20}$$

where

$$\langle F_p(t)\,F_{p-1}\rangle = \langle F_p(t)\,\dot{F}_{p-1}\rangle = 0\ , \tag{F21}$$

$$\beta_{p+1}(t) = \frac{\langle F_{p+1}(t+\tau)\,F_{p+1}(\tau)\rangle}{\langle F_p^2\rangle}\ . \tag{F22}$$

The relationship between MTGLE and Mori quantities at the pth level of the hierarchy is

$$\omega_{ep}^2 = \beta_{p+1}(0) + \Omega_p^2\ , \tag{F23}$$

$$\dot{\beta}_{p+1}(t) = -\omega_{cp+1}^4\,\theta_{p+1}(t)\ , \tag{F24}$$

$$R_{p+1}(t) = \frac{F_{p+1}(t)}{m[\omega_{c1}\omega_{c2}\cdots\omega_{cp+1}]^2} + \frac{\beta_{p+1}(t)}{\omega_{cp+1}^2}\,R_p\ . \tag{F25}$$

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[1]The MTGLE theory is developed in the following papers: (a) S. A. Adelman, J. Chem. Phys. **71**, 4471 (1979); (b) S. A. Adelman, Adv. Chem. Phys. **44**, 143 (1980); (c) S. A. Adelman, J. Chem. Phys. **73**, 3145 (1980). Applications of the MTGLE theory to modeling of time correlation functions has appeared in M. Berkowitz, C. L. Brooks III, and S. A. Adelman, J. Chem. Phys. **72**, 3889 (1980). Application to model simulations of chemical reaction dynamics has appeared in J. Chem. Phys. **73**, 4353 (1980). The MTGLE theory grew out of earlier work on gas–solid scattering. See S. A. Adelman and J. D. Doll, J. Chem. Phys. **61**, 4242 (1974); **64**, 2374 (1976); S. A. Adelman and B. J. Garrison, *ibid.* **65**, 3571 (1976); J. D. Doll and D. R. Dion, *ibid.* **65**, 3762 (1976); S. A. Adelman and J. D. Doll, Acc. Chem. Res. **10**, 378 (1977). The departure point for the gas–solid work was an important early paper by R. Zwanzig, J. Chem. Phys. **32**, 1173 (1960).

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[5]Eigenfunctions of the Liouville operator have been studied from a variational viewpoint in an interesting series of papers by Zwanzig. See for example, R. Zwanzig, Phys. Rev. **144**, 170 (1966).

[6]We follow the definitions used by Mori, Ref. 2.

[7]Here and below we denote the Laplace transform of an arbitrary function of time $f(t)$ by $\hat{f}(z)$, i.e., $\hat{f}(z) \equiv \mathcal{L}f(t) \equiv \int_0^\infty e^{-zt} f(t)\,dt$. Also, $\mathcal{L}^{-1}$ is defined by $f(t) = \mathcal{L}^{-1}\hat{f}(z)$.

[8]L. Kadanoff and P. C. Martin, Ann. Phys. (N. Y.) **24**, 419 (1963).

[9]Reference 1(a), Sec. VIC.

[10]Integration of Eq. (12.9) gives $\frac{1}{2} m\Omega_1^2 \langle R_1^2\rangle = \frac{1}{2} m \langle \dot{r}_0^2\rangle (\omega e_0/\Omega_0)^2 = \frac{1}{2} m \langle \dot{R}_1^2\rangle (\omega e_0/\Omega_0)^2$, where $\Omega_1^{-2} \equiv \hat{\theta}_1(z=0)$. The relation corresponding to Eq. (12.9) for $\langle\rangle_{r_0}$ is $\langle \dot{R}_0(t) R_1\rangle_{r_0} = -\langle \dot{r}_0^2\rangle \theta_1(t)$. Integration of this relation yields $\frac{1}{2} m\Omega_1^2 \langle R_1^2\rangle_{r_0} = \frac{1}{2} m \langle \dot{R}_1^2\rangle_{r_0} = \frac{1}{2} m \langle \dot{R}_1^2\rangle$. Notice this relation formally resembles the classical equipartition of kinetic and potential energy of a harmonic oscillator with frequency Ω_1 and coordinate R_1. The above relations show that $\langle R_1^2\rangle > \langle R_1^2\rangle_{r_0}$, since $\omega_{e_0} > \Omega_0$. The interpretation is as follows $\langle R_1^2\rangle$ is the mean square displacement of R_1 in the unclamped chain while $\langle R_1^2\rangle_{r_0}$ is the displacement in the clamped chain. On "physical" grounds we expect $\langle R_1^2\rangle > \langle R_1^2\rangle_{r_0}$.

[11]We have tacitly assumed here and elsewhere in this apper that $\rho(\omega)$ is a point spectrum. This is *not* true within classical mechanics unless the dynamical system of interest is harmonic. This point has been discussed by Zwanzig in Ref. 5(a). We are tacitly assuming that we have discretized the actual spectrum. The finite chain approximants yield such a discretized spectrum. The discretization scheme implicit in the chain approximants is generalized Gaussian qaudrature. For numerical applications of generalized Gaussian quadrature and related methods to obtain approximate spectral densities, see for example, the work of Gordon, e.g., R. G. Gordon, J. Math. Phys. (N. Y.) **9**, 655 (1968); **9**, 1087 (1968). For mathematical theorems related to Gordon's work and also the present work, see H. S. Wall, *Analytical Theory of Continued Fractions* (Van Nostrand, Princeton, 1948).

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