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Generalized Langevin theory for many-body problems in chemical dynamics: The quantum equivalent chain

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A quantum generalized Langevin representation for condensed phase atomic dynamics, which provides a physically useful formal framework for a quantum condensed phase molecular collision theory, is presented. Basic formal properties of the representation are worked out. A treatment of atomic quantum relaxation is presented.

I. INTRODUCTION

Recently, we have developed[1] and applied[2] a theoretical framework for dealing with the many-body problems which arise in molecular treatments of condensed phase chemical reaction dynamics. This framework is based on a new formulation[3] of generalized Brownian theory,[4-6] which we call the molecular timescale generalized Langevin equation (MTGLE) theory. The MTGLE theory provides an exact representation of irreversible dynamics which is particulary natural for describing the many-body problem on ultrashort timescales. Since chemically effective molecular encounters typically occur on short (subpico-second) timescales, the MTGLE theory provides a convenient theoretical language for describing condensed phase chemical reactions. The theory, moreover, provides practical algorithms[2] for reducing *classical mechanical* condensed phase chemical problems to physically realistic effective few-body trajectory problems.

The following question immediately arises. Can practical *quantum mechanical* many-body collision methods also be developed? Such a development would be of interest since quantum effects are probably important in such processes as atom energy transfer to low temperature solids,[7,8] vibrational energy relaxation in solids[9] and liquids,[10] chemical reactions in cold solid matrices,[11] etc.

The problem associated with the development of practical quantum many-body collision methods, however, appears challenging. This paper thus presents only modest first steps towards the development of such methods. What we do here is (i) formulate a quantum generalized Langevin representation which provides a formally exact and physically sound basis for further development and (ii) work out those basic properties of the representation which are likely to be useful in applications to condensed phase collision problems.

Future papers will present further developments.

The plan of this paper is as follows. Elementary properties of quantum time correlation functions are reviewed in Sec. II. The subsequent developments are based on these properties. Two quantum generalizations of the classical velocity autocorrelation function of an atom are defined in Sec. III. Corresponding to these two quantum velocity correlation functions are two exact quantum generalized Langevin representations of atomic dynamics. These quantum Langevin representations are presented and compared in Sec. IV. One of the two representations is found to be a natural basis for a quantum condensed phase collision theory. Statistical properties of this representation are presented in Secs. V and VI. The essential results of Secs. IV–VI may be summarized as follows. Atomic dynamics in an arbitrary quantum many-body system may be rigorously recast as the quantum dynamics of a fictitious equivalent harmonic chain. The equivalent chain has statistical properties which are identical to those of physical harmonic chains obeying quantum Boltzmann statistics. Finally, in Sec. VII, a treatment of atomic quantum relaxation based on the chain is presented. This treatment employs Wigner's[12] *c*-number representation of quantum statistical mechanics as succinctly formulated by Kubo.[13] The point of our treatment of quantum relaxation is that it illustrates, for a simple case, how one may deal with quantum noise problems. Such noise problems will arise in quantum treatments of condensed phase molecular collisions.

II. QUANTUM TIME CORRELATION FUNCTIONS

We develop in this paper a quantum generalized Langevin representation for the dynamics of a chemically active atom translating in an arbitrary many-body heatbath. The motivation for this development is that the quantum representation, like its classical analog,[1] provides a formal framework for the development of few-body mechanical models which simulate the influence of the many-body heatbath on the motion of the active atom. The use of these models in classical condensed phase collision problems has been discussed earlier.[2] We plan to discuss their use in quantum condensed phase collision problems elsewhere.

The classical generalized Langevin theory[1] may be derived from a small number of formal properties [see Eqs. (3.2) and (3.4) below] of the classical velocity response function of the atom. A parallel quantum development may be based on analogous formal properties [see Eqs. (3.7) and (3.9) below] of the quantum velocity response function.

To develop the formal properties of the quantum response function, we require several general properties of quantum time correlation functions. We next review[14] these general properties using notation which will be employed in the remainder of the paper.

We consider an arbitrary quantum many-body system at temperature T. Let the Hamiltonian operator of the system be $\hat{H}$ [Here and below we will denote the quantum operator which corresponds to a classical or Wigner variable A by $\hat{A}$]. The canonical ensemble density matrix of the system is [$\beta \equiv (k_B T)^{-1}$],

$$\hat{\rho}_{ca} = Z^{-1}(\beta) e^{-\beta \hat{H}} , \tag{2.1}$$

where $Z(\beta) = \mathrm{tr}\hat{\rho}_{ca}$ is the system partition function. Let $\hat{A}(t)$ and $\hat{B}(t)$ be two system observables, i.e., Hermitian Heisenberg operators. Their time correlation function $\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle$ is defined in the usual manner as

$$\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle = \mathrm{tr}[\hat{\rho}_{ca}\hat{A}(t+\tau)\hat{B}(\tau)] = \mathrm{tr}\left\{\hat{\rho}_{ca}\exp\left[\frac{i}{\hbar}\hat{H}(t+\tau)\right]\right.$$

$$\left. \hat{A}\exp\left[-\frac{i}{\hbar}\hat{H}(t+\tau)\right]\exp\left(\frac{i}{\hbar}\hat{H}\tau\right)\hat{B}\exp\left(-\frac{i}{\hbar}\hat{H}\tau\right)\right\} . \tag{2.2}$$

The time correlation function has the stationary property [here and below $\hat{A}(t=0) \equiv \hat{A}$ for all operators $\hat{A}(t)$], i.e., we have

$$\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle = \langle \hat{A}(t)\hat{B}\rangle . \tag{2.3}$$

Equation (2.3) follows from Eqs. (2.1) and (2.2) and the cyclic property of the trace. Since A and B are Hermitian, we additionally have

$$\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle = \langle \hat{B}(\tau)\hat{A}(t+\tau)\rangle^* . \tag{2.4}$$

Equations (2.3) and (2.4) yield the symmetry relation

$$\langle \hat{A}(-t)\hat{B}\rangle = \langle \hat{B}(t)\hat{A}\rangle^* . \tag{2.5}$$

We next define the symmetrized and antisymmetrized correlation functions $\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle_{\pm}$ by

$$\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle_+ \equiv \tfrac{1}{2}\langle [\hat{A}(t+\tau)\hat{B}(\tau) + \hat{B}(\tau)\hat{A}(t+\tau)]\rangle \tag{2.6a}$$

and

$$\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle_- \equiv \langle [\hat{A}(t+\tau)\hat{B}(\tau) - \hat{B}(\tau)\hat{A}(t+\tau)]\rangle . \tag{2.6b}$$

Equations (2.4) and (2.6) yield the additional relations

$$\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle_+ = \mathrm{Re}\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle , \tag{2.7a}$$

$$\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle_- = 2i\,\mathrm{Im}\langle \hat{A}(t+\tau)\hat{B}(\tau)\rangle . \tag{2.7b}$$

Finally, the following symmetry properties for auto-correlation functions follow from Eqs. (2.5) and (2.7):

$$\langle \hat{A}(-t)\hat{A}\rangle_+ = \langle \hat{A}(t)\hat{A}\rangle_+ , \tag{2.8a}$$

$$\langle \hat{A}(-t)\hat{A}\rangle_- = -\langle \hat{A}(t)\hat{A}\rangle_- . \tag{2.8b}$$

Differentiating Eq. (2.8b) yields

$$\langle \dot{\hat{A}}(-t)\hat{A}\rangle_- = \langle \dot{\hat{A}}(t)\hat{A}\rangle_- . \tag{2.9}$$

Thus, the symmetrized autocorrelation function of $\hat{A}(t)$ and the antisymmetrized correlation function of $\dot{\hat{A}}(t)$ and $\hat{A}(t)$ are even functions of the time.

III. VELOCITY CORRELATION FUNCTIONS

We next define time correlation functions which describe the translational motion of a tagged atom (mass $= m$) moving in a many-body system. Denote the classical coordinate and momentum of the tagged atom by $\mathbf{r}_0(t)$ and $\mathbf{p}_0(t) = m\dot{\mathbf{r}}_0(t)$, and the corresponding quantum operators by $\hat{\mathbf{r}}_0(t)$ and $\hat{\mathbf{p}}_0(t) = m\dot{\hat{\mathbf{r}}}_0(t)$.

The quantum operators satisfy canonical commutation rules. Thus

$$\langle [\hat{\mathbf{r}}_0 \cdot \hat{\mathbf{p}}_0 - \hat{\mathbf{p}}_0 \cdot \hat{\mathbf{r}}_0]\rangle = \langle \hat{\mathbf{r}}_0 \cdot \hat{\mathbf{p}}_0\rangle_- = 3i\hbar .$$

A. Classical correlation function

The normalized classical velocity correlation function of the atom $\dot{\chi}^{CL}(t)$ is defined by

$$\dot{\chi}^{CL}(t) = \frac{\langle \dot{\mathbf{r}}_0(t+\tau) \cdot \dot{\mathbf{r}}_0(\tau)\rangle_{CL}}{\langle \dot{r}_0^2\rangle_{CL}}$$

$$= \frac{\langle \dot{\mathbf{r}}_0(t) \cdot \dot{\mathbf{r}}_0\rangle_{CL}}{\langle \dot{r}_0^2\rangle_{CL}}$$

$$= \frac{m}{3k_B T}\langle \dot{\mathbf{r}}_0(t) \cdot \dot{\mathbf{r}}_0\rangle_{CL} , \tag{3.1}$$

where $\langle\ \rangle_{CL}$ denotes a classical canonical average. This is the classical limit of the quantum canonical average $\langle \cdots\rangle = \mathrm{tr}[\rho \dots]$.

An immediate consequence of the defining relation Eq. (3.1) is that $\dot{\chi}^{CL}(t)$ has the following formal properties:

$$\dot{\chi}^{CL}(-t) = \dot{\chi}^{CL}(t) ,$$

$$\dot{\chi}^{CL}(0) = 1 , \quad \ddot{\chi}^{CL}(0) = 0 . \tag{3.2}$$

Since $\dot{\chi}^{CL}(t)$ is an even function, its Fourier transform $\rho^{CL}(\omega)$ may be defined as the following cosine transform:

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

$$\equiv \frac{2}{\pi}\mathrm{Re}\left\{\lim_{\epsilon \to 0}\int_0^\infty \exp[-(i\omega + \epsilon)t]\dot{\chi}^{CL}(t)dt\right\} . \tag{3.3a}$$

The inverse of Eq. (3.3a) is

$$\dot{\chi}^{CL}(t) = \int_0^\infty \cos\omega t\,\rho^{CL}(\omega)d\omega . \tag{3.3b}$$

The transform $\rho^{CL}(\omega)$ may be shown to be non-negative.[1] Thus, $\rho^{CL}(\omega)$ is properly interpreted as the spectral density of $\dot{\chi}^{CL}(t)$. Also, $\rho^{CL}(-\omega) = \rho^{CL}(\omega)$ [Eq. (3.3)] and $\int_0^\infty \rho^{CL}(\omega)d\omega = 1$ [Eqs. (3.2) and (3.3b)]. Thus, $\rho^{CL}(\omega)$ has the following formal properties:

$$\rho^{CL}(\omega) \geq 0 , \tag{3.4a}$$

$$\rho^{CL}(-\omega) = \rho^{CL}(\omega) , \tag{3.4b}$$

$$\int_0^\infty \rho^{CL}(\omega)d\omega = 1 . \tag{3.4c}$$

The formal properties of $\dot{\chi}^{CL}(t)$ [Eq. (3.2)] and $\rho^{CL}(\omega)$ [Eqs. (3.4a)–(3.4c)] are sufficient to construct the classical generalized Langevin theory presented elsewhere.

B. Quantum correlation functions

We next define two quantum generalizations of the classical velocity autocorrelation function $\dot{\chi}^{CL}(t)$. We will denote these quantum correlation functions by $\dot{\chi}^{(+)}(t)$ and $\dot{\chi}^{(-)}(t)$. The quantity $\dot{\chi}^{(+)}(t)$ is the symmetrized velocity autocorrelation function defined by

$$\dot{\chi}^{(+)}(t) = \frac{\langle \dot{\hat{\mathbf{r}}}_0(t+\tau) \cdot \dot{\hat{\mathbf{r}}}_0(\tau)\rangle_+}{\langle \dot{\hat{r}}_0^2\rangle} = \frac{\langle \dot{\hat{\mathbf{r}}}_0(t) \cdot \dot{\hat{\mathbf{r}}}_0\rangle_+}{\langle \dot{\hat{r}}_0^2\rangle} . \tag{3.5}$$

The quantity $\dot{\chi}^{(-)}(t)$ is the *antisymmetrized* correlation function defined by

$$\dot{\chi}^{(-)}(t) = \frac{\langle \hat{\mathbf{r}}_0(t+\tau) \cdot \hat{\mathbf{p}}_0(\tau)\rangle_-}{\langle \hat{\mathbf{r}}_0 \cdot \hat{\mathbf{p}}_0 \rangle_-} = \frac{\langle \hat{\mathbf{r}}_0(t) \cdot \hat{\mathbf{p}}_0 \rangle_-}{3i\hbar} . \quad (3.6)$$

Both $\dot{\chi}^{(+)}(t)$ and $\dot{\chi}^{(-)}(t)$ reduce to $\dot{\chi}^{CL}(t)$ in the high temperature limit.[15]

We next show, using the general symmetry properties given in Eqs. (2.8) and (2.9), that both $\dot{\chi}^{(+)}(t)$ and $\dot{\chi}^{(-)}(t)$ have formal properties identical to $\dot{\chi}^{CL}(t)$. Setting $\tau = -t$ in Eq. (3.5) and using the symmetry property Eq. (2.8a) shows that $\dot{\chi}^{(+)}(t)$ is an even function. Similarly, setting $\tau = -t$ in Eq. (3.6) and using Eq. (2.9) shows that $\dot{\chi}^{(-)}(t)$ is also an even function. Moreover, both $\dot{\chi}^{(+)}(t)$ and $\dot{\chi}^{(-)}(t)$ are defined so that $\dot{\chi}^{(\pm)}(0) = 1$. Thus $\dot{\chi}^{(\pm)}(t)$ have formal properties identical to $\dot{\chi}^{CL}(t)$, i.e., we have

$$\dot{\chi}^{(\pm)}(-t) = \dot{\chi}^{(\pm)}(t) ,$$
$$\dot{\chi}^{(\pm)}(0) = 1 , \quad \chi^{(\pm)}(0) = 0 . \quad (3.7)$$

Moreover, since $\dot{\chi}^{(\pm)}(t)$ are even functions, their Fourier transforms $\rho^{(\pm)}(\omega)$ may be defined via cosine transform relations analogous to Eq. (3.3), i.e., we have

$$\rho^{(\pm)}(\omega) = \frac{2}{\pi} \int_0^\infty \cos \omega t \, \dot{\chi}^{(\pm)}(t) dt \quad (3.8a)$$

and

$$\dot{\chi}^{(\pm)}(t) = \int_0^\infty \cos \omega t \, \rho^{(\pm)}(\omega) d\omega . \quad (3.8b)$$

One may show by standard arguments[16] that $\rho^{(\pm)}(\omega)$ are non-negative. Moreover, $\rho^{(\pm)}(-\omega) = \rho^{(\pm)}(\omega)$ and $\int_0^\infty \rho^{(\pm)}(\omega) d\omega = 1$. Thus $\rho^{(\pm)}(\omega)$ have formal properties identical to $\rho^{CL}(\omega)$, i.e., we have

$$\rho^{(\pm)}(\omega) \geq 0 , \quad (3.9a)$$
$$\rho^{(\pm)}(-\omega) = \rho^{(\pm)}(\omega) , \quad (3.9b)$$
$$\int_0^\infty \rho^{(\pm)}(\omega) d\omega = 1 . \quad (3.9c)$$

Finally, $\rho^{(+)}(\omega)$ and $\rho^{(-)}(\omega)$ are not independent. Rather they are linked by the relation[17]

$$\rho^{(+)}(\omega) = \frac{3}{2} \frac{\epsilon(\omega)}{(\langle p_0^2 \rangle / 2m)} \rho^{(-)}(\omega) , \quad (3.10)$$

where $\epsilon(\omega)$ is the average thermal energy of a harmonic oscillator of frequency ω given by

$$\epsilon(\omega) = \tfrac{1}{2} \hbar \omega \coth(\tfrac{1}{2} \beta \hbar \omega) . \quad (3.11)$$

Notice that since $\lim_{T \to \infty} (\langle p_0^2 \rangle / 2m) = \tfrac{3}{2} k_B T$, Eqs. (3.10) and (3.11) show explicitly that $\rho^{(+)}(\omega) \to \rho^{(-)}(\omega)$ in the high temperature limit.

IV. QUANTUM MTGLE REPRESENTATIONS OF ATOMIC DYNAMICS

The last section shows that the two quantum velocity correlation functions $\chi^{(+)}(t)$ and $\chi^{(-)}(t)$ have formal properties identical to the classical velocity autocorrelation function. We have mentioned that the formal properties of $\dot{\chi}^{CL}(t)$ are sufficient to build our classical generalized Langevin representation.[1,3] Thus by paralleling the

arguments presented for the classical case,[1] two distinct quantum generalized Langevin representations may be constructed, one from $\dot{\chi}^{(+)}(t)$ and the other from $\dot{\chi}^{(-)}(t)$. To minimize repetition we will omit the detailed arguments and pass directly to the main results.

A. Hierarchy of heatbaths

We find that for each quantum representation there exists an infinite sequence of abstract heatbaths. The pth heatbath $(p = 1, 2, \ldots)$ for each representation is characterized by a response function. We denote the response function for the "+" representation by $\dot{\theta}_p^{(+)}(t)$ and the response function for the "−" representation by $\dot{\theta}_p^{(-)}(t)$. Associated with the pth response function is an abstract coordinate operator $\hat{R}_p^{(\pm)}(t)$.

The response functions $\dot{\theta}_p^{(\pm)}(t)$ have formal properties identical to those of $\dot{\chi}^{(\pm)}(t)$, i.e.,

$$\dot{\theta}_p^{(\pm)}(-t) = \dot{\theta}_p^{(\pm)}(t) , \quad \dot{\theta}_p^{(\pm)}(0) = 1 , \quad \theta_p^{(\pm)}(0) = 0 , \quad (4.1)$$

and

$$\sigma_p^{(\pm)}(\omega) \geq 0 , \quad (4.2a)$$
$$\sigma_p^{(\pm)}(-\omega) = \sigma_p^{(\pm)}(\omega) , \quad (4.2b)$$
$$\int_0^\infty \sigma_p^{(\pm)}(\omega) d\omega = 1 , \quad (4.2c)$$

where $\sigma_p^{(\pm)}(\omega)$ is the spectral density of $\dot{\theta}_p^{(\pm)}(t)$ and is defined by

$$\sigma_p^{(\pm)}(\omega) = \frac{2}{\pi} \int_0^\infty \cos \omega t \, \dot{\theta}_p^{(\pm)}(t) dt \quad (4.3a)$$

and

$$\dot{\theta}_p^{(\pm)}(t) = \int_0^\infty \cos \omega t \, \sigma_p^{(\pm)}(\omega) d\omega . \quad (4.3b)$$

The response functions $\dot{\theta}_p^{(\pm)}(t)$, as just discussed, have formal properties identical to those of $\dot{\chi}^{(\pm)}(t)$. The abstract coordinate operators $\hat{R}^{(\pm)}(t)$, analogously, have formal properties identical to those of the physical coordinate operator $\hat{r}_0(t)$. The statistical properties of $\hat{R}_p(t)$, for example, are determined in terms of $\dot{\theta}_p^{(+)}(t)$ via a fluctuation-dissipation theorem analogous[18] to Eq. (3.5). This theorem is

$$\dot{\theta}_p^{(+)}(t) = \frac{\langle \hat{\mathbf{R}}_p^{(+)}(t) \cdot \hat{\mathbf{R}}_p^{(+)} \rangle_+}{\langle \hat{r}_0^2 \rangle} . \quad (4.4)$$

The coordinate operator $\hat{R}_p^{(-)}(t)$ similarly satisfies a fluctuation-dissipation theorem which is identical in form to Eq. (3.6). This theorem is

$$[\hat{P}_p^{(-)}(t) \equiv m \hat{R}_p^{(-)}(t)] ,$$
$$\dot{\theta}_p^{(-)}(t) = \frac{\langle \hat{\mathbf{R}}_p(t+\tau) \cdot \hat{\mathbf{P}}_p(\tau)\rangle_-}{3i\hbar} = \frac{\langle \hat{\mathbf{R}}_p(t) \cdot \hat{\mathbf{P}}_p \rangle_-}{3i\hbar} . \quad (4.5)$$

The response functions $\dot{\theta}_p^{(\pm)}(t)$ are *defined* in terms of $\dot{\chi}^{(\pm)}(t)$ via a recursive sequence of effective equations of motion. The first member of the sequence, which defines $\dot{\theta}_1^{(\pm)}(t)$, is the following effective equation of motion for $\dot{\chi}^{(\pm)}(t)$:

$$\ddot{\chi}^{(\pm)}(t) = -[\omega_{e0}^{(\pm)}]^2 \chi^{(\pm)}(t) + [\omega_{e1}^{(\pm)}]^4 \int_0^t \dot{\theta}_1^{(\pm)}(t-\tau) \chi^{(\pm)}(\tau) d\tau . \quad (4.6a)$$

The force constants $[\omega_{e_0}^{(\pm)}]^2$ (the squared Einstein frequency) and $[\omega_{c_1}^{(\pm)}]^2$ (the coupling constant) which appear in Eq. (4.6a) are the first members of an infinite set of parameters $\{[\omega_{e_p}^{(\pm)}]^2\}$ and $\{[\omega_{c_{p+1}}^{(\pm)}]^2\}$, $p = 0, 1, 2, \ldots$, which play a basic role in MTGLE representations. All the parameters are expressable in terms of even moments of $\rho^{(\pm)}(\omega)$ using an algorithm presented elsewhere.[2] The general response function $\theta_{p+1}^{(\pm)}(t)$ is defined by the $(p + 1)$th member of the recursive sequence which is the following equation of motion for $\theta_p^{(\pm)}(t)$:

$$\dot{\theta}_p^{(\pm)}(t) = -[\omega_{e_p}^{(\pm)}]^2 \theta_p^{(\pm)}(t)$$
$$+ [\omega_{c_{p+1}}^{(\pm)}]^2 \int_0^t \theta_{p+1}^{(\pm)}(t - \tau)\theta_p^{(\pm)}(\tau)d\tau . \qquad (4.6b)$$

Equations (4.6) define the response functions $\theta_p^{(\pm)}(t)$ in terms of $\chi^{(\pm)}(t)$. The coordinate operators $\hat{R}_p^{(\pm)}(t)$ are defined in terms of $\hat{r}_0(t)$ by an analogous recursive sequence. The defining relation for $\hat{R}_1^{(\pm)}(t)$ is the following Heisenberg operator generalized Langevin equation of motion:

$$\hat{\ddot{r}}_0(t) = -[\omega_{e_0}^{(\pm)}]^2 \hat{r}_0(t)$$
$$+ [\omega_{c_1}^{(\pm)}]^4 \int_0^t \theta_1^{(\pm)}(t - \tau)\hat{r}_0(\tau)d\tau + [\omega_{c_1}^{(\pm)}]^2 \hat{R}_1^{(\pm)}(t) . \qquad (4.7a)$$

The defining relation for the general $(p + 1)$th coordinate operator $\hat{R}_{p+1}^{(\pm)}(t)$ is the following generalized Langevin equation for $\hat{R}_p^{(\pm)}(t)$:

$$\hat{\ddot{R}}_p^{(\pm)}(t) = -[\omega_{e_p}^{(\pm)}]^2 \hat{R}_p^{(\pm)}(t)$$
$$+ [\omega_{c_{p+1}}^{(\pm)}]^2 \int_0^t \theta_{p+1}^{(\pm)}(t - \tau)\hat{R}_p^{(\pm)}(\tau)d\tau + [\omega_{c_{p+1}}^{(\pm)}]^2 \hat{R}_{p+1}^{(\pm)}(t) . \qquad (4.7b)$$

Equations (4.7a) and (4.7b) constitute a recursive definition of the heatbath coordinate operators $\hat{R}_p^{(\pm)}(t)$ in terms of the atomic Heisenberg trajectory $\hat{r}_0(t)$.

B. Orthogonality theorems

The coordinate operators $\hat{R}_p^{(\pm)}(t)$ satisfy, in addition to the fluctuation-dissipation theorems, a second set of statistical constraints. These constraints are orthogonality theorems. The orthogonality constraints satisfied by the operators $\hat{R}_p^{(+)}(t)$ are

$$\langle \hat{R}_1^{(+)}(t) \cdot \hat{r}_0 \rangle_+ = 0 \qquad (4.8a)$$

and

$$\langle \hat{R}_{p+1}^{(+)}(t) \cdot \hat{R}_p^{(+)} \rangle_+ = 0 , \quad p = 1, 2, \ldots . \qquad (4.8b)$$

The orthogonality constraints satisfied by the operators $\hat{R}_p^{(-)}(t)$ are

$$\langle \hat{R}_1^{(-)}(t) \cdot \hat{r}_0 \rangle_- = \langle \hat{R}_1^{(-)}(t) \cdot \hat{\dot{r}}_0 \rangle_- = 0 \qquad (4.9a)$$

and

$$\langle \hat{R}_{p+1}^{(-)}(t) \cdot \hat{R}_p^{(-)} \rangle_- = \langle \hat{R}_{p+1}^{(-)}(t) \cdot \hat{\dot{R}}_p^{(-)} \rangle_- = 0 . \qquad (4.9b)$$

The above orthogonality theorems may be derived from the fluctuation-dissipation theorems and the equations of motion Eqs. (4.6) and (4.7).[19]

The fluctuation-dissipation theorems Eqs. (4.4) and (4.5), the equations of motion Eqs. (4.6) and (4.7), and the orthogonality theorems Eqs. (4.8) and (4.9) comprise the basic structure of the quantum generalized Langevin theory. An important consequence of this basic structure is the equivalent harmonic chain representation which we next present.

C. Equivalent chain representation

The generalized Langevin equation for $\hat{r}_0(t)$, Eq. (4.7a), may be rigorously recast as the Heisenberg equations of motion for an $(N + 1)$-atom fictitious harmonic chain (N can equal $N = 1, 2, \ldots$). The value of the quantum chain representation, like its classical counterpart,[1] is that it permits one to model the true many-body heatbath by an effective few-body system, namely, a truncated[2] chain. This modeling, in the classical case, permits one to reduce many-body collision problems to effective few-body collision problems.

The $(N + 1)$-atom equivalent chain equations are

$$\hat{\ddot{r}}_0(t) = -[\omega_{e_0}^{(\pm)}]^2 \hat{r}_0(t) + [\omega_{c_1}^{(\pm)}]^2 \hat{r}_1^{(\pm)}(t) ,$$
$$\hat{\ddot{r}}_1^{(\pm)}(t) = -[\omega_{e_1}^{(\pm)}]^2 \hat{r}_1^{(\pm)}(t) + [\omega_{c_1}^{(\pm)}]^2 \hat{r}_0(t) + [\omega_{c_2}^{(\pm)}]^2 \hat{r}_2^{(\pm)}(t) ,$$
$$\vdots \qquad (4.10)$$
$$\hat{\ddot{r}}_N^{(\pm)}(t) = -[\omega_{e_N}^{(\pm)}]^2 \hat{r}_N^{(\pm)}(t) + [\omega_{c_N}^{(\pm)}]^2 \hat{r}_{N-1}^{(\pm)}(t)$$
$$+ [\omega_{c_{N+1}}^{(\pm)}]^4 \int_0^t \theta_{N+1}^{(\pm)}(t - \tau)\hat{r}_N^{(\pm)}(\tau)d\tau + [\omega_{c_{N+1}}^{(\pm)}]^2 \hat{R}_{N+1}^{(\pm)}(t) .$$

Notice that the coordinate of the terminal chain atom $\hat{r}_0(t)$ is the physical atomic coordinate. The remaining chain atom coordinates $\hat{r}_p^{(\pm)}(t)$ are fictitious. These fictitious coordinates are defined recursively in terms of $\hat{r}_0(t)$ by the following sequence:

$$\hat{r}_1^{(\pm)}(t) = \hat{R}_1^{(\pm)}(t) + [\omega_{c_1}^{(\pm)}]^4 \int_0^t \theta_1^{(\pm)}(t - \tau)\hat{r}_0(\tau)d\tau \qquad (4.11a)$$

and

$$\hat{r}_p^{(\pm)}(t) = \hat{R}_p^{(\pm)}(t) + [\omega_{c_p}^{(\pm)}]^4 \int_0^t \theta_p^{(\pm)}(t - \tau)\hat{r}_{p-1}^{(\pm)}(\tau)d\tau . \qquad (4.11b)$$

For the purpose of formal discussions it is often convenient to pass to the limit of an infinite ($N \to \infty$) chain. In this limit, the chain Eqs. (4.10) may be written in matrix notation as

$$\hat{\ddot{r}}^{(\pm)}(t) = -[\omega^{(\pm)}]^2 \hat{r}^{(\pm)}(t) , \qquad (4.12)$$

where

$$\hat{r}^{(\pm)}(t) = \begin{pmatrix} \hat{r}_0(t) \\ \hat{r}_1^{(\pm)}(t) \\ \vdots \end{pmatrix} , \qquad (4.13)$$

and where

$$[\omega^{(\pm)}]^2 = \begin{pmatrix} [\omega_{e_0}^{(\pm)}]^2 & [\omega_{c_1}^{(\pm)}]^2 & 0 & 0 & \cdot & \cdot \\ [\omega_{c_1}^{(\pm)}]^2 & [\omega_{e_1}^{(\pm)}]^2 & [\omega_{c_2}^{(\pm)}]^2 & 0 & \cdot & \cdot \\ 0 & [\omega_{c_2}^{(\pm)}]^2 & [\omega_{e_2}^{(\pm)}]^2 & [\omega_{c_3}^{(\pm)}]^2 & \cdot & \cdot \\ \vdots & & & & & \end{pmatrix} . \qquad (4.14)$$

For formal discussions,[1] it is often convenient to deal with the normal mode coordinates $\hat{\xi}_\lambda^{(\pm)}$ and corresponding normal mode frequencies $\omega_\lambda^{(\pm)}$, $\lambda = 0, 1, 2, \ldots$, of the in-

finite chain. These may be determined by the orthogonal transformation $\mathbf{U}^{(\pm)}$ which diagonalizes the symmetric matrix $[\boldsymbol{\omega}^{(\pm)}]^2$. For example, the normal mode coordinates $\hat{\boldsymbol{\zeta}}^{(\pm)}$ are related to the atom coordinates $\hat{\mathbf{r}}_p^{(\pm)}$ by

$$\hat{\boldsymbol{\zeta}}^{(\pm)} \equiv \begin{pmatrix} \hat{\zeta}_0 \\ \hat{\zeta}_1 \\ \vdots \end{pmatrix} = [\mathbf{U}^{\pm}]^T \hat{\mathbf{r}}^{(\pm)} \ . \tag{4.15}$$

Finally, the spectral density $\rho^{(\pm)}(\omega)$ may be expanded in terms of the normal mode spectrum via the relation

$$\rho^{(\pm)}(\omega) = \sum_{\lambda=0}^{\infty} U_{0\lambda}^{(\pm)} U_{0\lambda}^{(\pm)} \delta[\omega - \omega_\lambda^{(\pm)}] \ . \tag{4.16}$$

Equation (4.16) shows that the spectral density $\rho^{(\pm)}(\omega)$ may be interpreted as the local density of modes at chain atom 0.

D. Commutator vs anticommutator representations

We have just constructed two formally exact quantum MTGLE representations, the "+" representation and the "−" representation. The two representations are mathematically equivalent but physically distinct. The two generalized Langevin equations (4.7a), for example, amount to two different decompositions of the total force operator acting on the atom into random $[(\omega_{c1}^{\pm})^2 R_1^{(\pm)}(t)]$ and systematic components. The following questions immediately arise.

(i) Which of the two force decompositions provides the physically more useful description of the many-body problem. For example, which random force operator, $[\omega_{c1}^{(+)}]^2 \hat{R}_1^{(+)}(t)$ or $[\omega_{c1}^{(-)}]^2 \hat{R}_1^{(-)}(t)$, may be more realistically modeled by stochastic methods?

(ii) Which representation provides the more natural basis for a quantum condensed phase collision theory?

We assert that the "−" representation is more useful physically and thus provides the natural foundation for a quantum many-body collision theory. There are several reasons for this assertion. The most important are:

(i) Suppose the many-body system is a *physical* nearest neighbor harmonic chain and the atom of interest is the terminal chain atom. For this case, the mathematical chain equations (4.12) of the "−" representation are *identical* to the true Heisenberg equations of motion of the physical chain. The "+" equations, in contrast, have no physical meaning.

This observation has implications for general (non-chain) many-body systems. Its importance is that only the "−" equations have a simple physical meaning. The Einstein frequency $\omega_{e0}^{(-)}$, for example, like its classical counterpart, is properly interpreted (within limits imposed by the uncertainty principle) for *general systems* as the frequency governing the initial oscillatory motion of the atom (this is the cage effect for an atom in a liquid). The frequency $\omega_{e0}^{(+)}$, in contrast, does not have this interpretation (except, of course, as $T \to \infty$).

(ii) The antisymmetrized correlation function $\dot{\chi}^{(-)}(t)$ rather than the symmetrized correlation function $\dot{\chi}^{(+)}(t)$ is the linear response function[14] which determines the

atomic drift velocity induced by a weak applied force $\hat{\mathbf{f}}(t)$. Thus if a weak force $\hat{\mathbf{f}}(t)$ is added to the right-hand side of the "−" generalized Langevin Eq. (4.7a), one correctly predicts that $\dot{\chi}^{(-)}(t)$ governs the induction of the drift velocity. If the analogous addition is made to the "+" equation, then the incorrect prediction that $\dot{\chi}^{(+)}(t)$ governs the velocity induction results. This point is basic for applications of quantum generalized Langevin equations to chemical dynamics. This is because, in such applications, one typically adds nonlinear forces to the generalized Langevin equation. These forces are just the gradients of the potential of mean force surfaces which couple the atoms involved in the reaction. The effects of the nonlinear forces must reduce to the linear response theory prediction in the weak coupling limit. This occurs only if the "−" rather than the "+" representation is used.

Given this discussion, our further work in this paper will be restricted to the "−" representation. For the sake of notational brevity, the "−" superscripts will be omitted below. Thus, as an example, Eq. (4.12) for the "−" case will be written as

$$\ddot{\hat{\mathbf{r}}}(t) = -\omega^2 \hat{\mathbf{r}}(t) \ . \tag{4.17}$$

V. STATISTICAL PROPERTIES OF THE QUANTUM EQUIVALENT CHAIN

To use the quantum equivalent chain in stochastic calculations (Sec. VII), we require the statistical properties of the chain. We find that binary averages involving equivalent chain phase space coordinates are identical in form to corresponding averages for *physical* harmonic chains obeying quantum Boltzmann statistics. The proof of this assertion parallels our earlier work[20] and thus will be omitted.

We first present thermal averages of phase space commutators; we then present averages of phase space anticommutators.

A. Thermal commutators

The phase space coordinates $\hat{\zeta}_\lambda$, $\dot{\hat{\zeta}}_\lambda$ of the normal modes of a *physical* harmonic chain obey canonical commutation rules, i.e.,

$$[\hat{\zeta}_\lambda, \dot{\hat{\zeta}}_{\lambda'}] = \frac{i\hbar}{m}\delta_{\lambda\lambda'}\hat{1} \ , \quad \text{physical chains} \ . \tag{5.1}$$

One might expect that canonical commutation rules are also obeyed by the mode phase space coordinates of the quantum equivalent chain. This is *not* true, however, unless the underlying many-body system is harmonic. The modes of the equivalent chain, however, do satisfy canonical commutation rules, *on the average*, i.e., the following statistical theorems hold for the equivalent chain modes:

$$\langle \hat{\zeta}_\lambda \cdot \hat{\zeta}_{\lambda'} \rangle_- = \langle \dot{\hat{\zeta}}_\lambda \cdot \dot{\hat{\zeta}}_{\lambda'} \rangle_- = 0 \ ,$$

$$\langle \hat{\zeta}_\lambda \cdot \dot{\hat{\zeta}}_{\lambda'} \rangle_- = \frac{3i\hbar}{m}\delta_{\lambda\lambda'} \ . \tag{5.2a}$$

The phase space chain atom coordinates $\hat{\mathbf{r}}_q$, $\hat{\mathbf{p}}_q = m\dot{\hat{\mathbf{r}}}_q$ are related to the mode coordinates by the orthogonal transformation $\mathbf{U} \equiv \mathbf{U}^{(-)}$. Thus, the chain atom coordinates

also obey canonical commutation rules on the average, i.e.,

$$\langle \hat{\mathbf{r}}_q \cdot \hat{\mathbf{r}}_{q'} \rangle_- = \langle \hat{\mathbf{r}}_q \cdot \hat{\mathbf{r}}_{q'} \rangle_- = 0 ,$$

$$\langle \hat{\mathbf{r}}_q \cdot \hat{\mathbf{p}}_{q'} \rangle_- = 3 i \hbar \, \delta_{qq'} . \tag{5.2b}$$

B. Thermal anticommutators

The symmetrized statistical averages of $\hat{\zeta}_\lambda$ and $\hat{\zeta}_\lambda$ are identical to the corresponding averages of physical harmonic chains, i.e.,

$$\tfrac{1}{2} m \langle \hat{\zeta}_\lambda \cdot \hat{\zeta}_{\lambda'} \rangle_+ = \tfrac{3}{2} \epsilon(\omega_\lambda) \delta_{\lambda\lambda'} ,$$

$$\langle \hat{\zeta}_\lambda \cdot \hat{\zeta}_{\lambda'} \rangle_+ = 0 , \tag{5.3a}$$

$$\tfrac{1}{2} m \, \omega_\lambda^2 \langle \hat{\zeta}_\lambda \cdot \hat{\zeta}_{\lambda'} \rangle = \tfrac{3}{2} \epsilon(\omega_\lambda) \delta_{\lambda\lambda} ,$$

where $\epsilon(\omega_\lambda)$ [recall Eq. (3.11)] is the average energy of a one-dimensional quantum harmonic oscillator with frequency ω_λ and temperature T.

The symmetrized statistical averages of the chain atom phase space coordinates are also identical to those of physical chains, i.e.,

$$\frac{\langle \hat{\mathbf{p}}_q \cdot \hat{\mathbf{p}}_{q'} \rangle_+}{2m} = \tfrac{3}{2} \hbar \left[\omega \coth\!\left(\frac{\beta \hbar \omega}{2} \right) \right]_{qq'} ,$$

$$\langle \hat{\mathbf{r}}_q \cdot \hat{\mathbf{p}}_{q'} \rangle_+ = 0 , \tag{5.3b}$$

$$\tfrac{1}{2} m \langle \hat{\mathbf{r}}_q \cdot \hat{\mathbf{r}}_{q'} \rangle_+ = \tfrac{3}{2} \hbar \left[\omega^{-1} \coth\!\left(\frac{\beta \hbar \omega}{2} \right) \right]_{qq'} ,$$

where $\omega \equiv \omega^{(-)}$ is defined by Eq. (4.14).

VI. QUANTUM EQUIPARTITION THEOREMS

The phase space coordinates $\hat{r}_0$, $\hat{p}_0$ of the chemically active atom fluctuate about their expected values due to both quantum and thermal effects. We next develop exact chain formalism expressions for the equilibrium fluctuations of the phase space coordinates. These expressions are required if one wishes to use the quantum chain in stochastic treatments of atomic relaxation and dynamics. This is because at long times nonequilibrium fluctuations must relax to these equilibrium results [see, e.g., Eq. (7.36)].

The fluctuation expressions are derived in Appendix A. The results are

$$\frac{\langle \hat{p}_0^2 \rangle_+}{2m} = \tfrac{3}{2} \epsilon_0(T) , \tag{6.1a}$$

$$\langle \hat{r}_0 \cdot \hat{p}_0 \rangle_+ = 0 , \tag{6.1b}$$

$$\tfrac{1}{2} m [\Omega_0^{(+)}]^2 \langle \hat{r}_0^2 \rangle_+ = \tfrac{3}{2} \epsilon_0(T) , \tag{6.1c}$$

where

$$\epsilon_0(T) = \int_0^\infty \epsilon(\omega) \rho^{(-)}(\omega) d\omega , \tag{6.2}$$

and where

$$[\Omega_0^{(+)}]^{-2} = \int_0^\infty \omega^{-2} \rho^{(+)}(\omega) d\omega . \tag{6.3}$$

Equations (6.1)–(6.3) have a quasiphysical interpretation. Since $\rho^{(-)}(\omega)$ may be interpreted as the normal

mode density which is localized at atom 0 [Eq. (4.16)], and since $3\epsilon(\omega)$ [see Eq. (3.11)] is the average energy of a three-dimensional quantum harmonic oscillator at temperature T, the quantity $3\epsilon_0(T)$ may be interpreted as the mean energy of atom 0. Moreover, $\Omega_0^{(+)}$ is the adiabatic frequency[21] associated with the "+" representation. Thus, one may interpret Eqs. (6.1) as formal equipartition theorems for a three-dimensional quantum oscillator with frequency $\Omega_0^{(+)}$ and total energy $\epsilon_0(T)$.

Finally, note that the energy function $\epsilon_0(T)$ properly reduces in the classical $(T \to \infty)$ and extreme quantum $(T \to 0)$ limits. As $T \to \infty$, $\epsilon_0(T) \to k_B T$, the classical thermal energy of a one-dimensional harmonic oscillator. As $T \to 0$, the energy arises completely from zero point motion of the chain and $\epsilon_0(T) \to \tfrac{1}{2} \hbar \langle \omega \rangle$, where $\langle \omega \rangle \equiv \int_0^\infty \rho^{(-)}(\omega) \omega \, d\omega$.

VII. CHAIN FORMALISM TREATMENT OF ATOMIC DYNAMICS

We next discuss how the quantum chain formalism may be used as a framework for stochastic modeling of relaxation and dynamics of the chemically active atom. We assume that chemical, i.e., explicit nonlinear, forces on the atom are absent. This simplified calculation is preliminary to a detailed treatment of the quantum condensed phase collision problem which we reserve for future publications. Our present calculation employs Wigner's[12] c-number representation of quantum statistical mechanics. We begin, therefore, by briefly reviewing basic aspects of the Wigner theory. We use a formulation similar to that introduced by Kubo.[13] This formulation makes the structure of the Wigner theory easy to see.

We discuss the Wigner representation for an arbitrary $(N + 1)$-atom many-body system characterized by a Hamiltonian $\hat{H}$ and a density matrix $\hat{\rho}(t)$. The coordinate and momentum operators of the atoms will be collectively denoted by $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ [e.g., $\hat{\mathbf{r}} = (\hat{\mathbf{r}}_0 \hat{\mathbf{r}}_1 \cdots \hat{\mathbf{r}}_N)$]. The Wigner equivalents of these operators will be denoted by $\mathbf{r}$ and $\mathbf{p}$. Similarly, the Wigner equivalent of an arbitrary Heisenberg operator $\hat{A}[\hat{\mathbf{r}}, \hat{\mathbf{p}}]$ will be written as $A[\mathbf{r}, \mathbf{p}]$. Finally, the symmetry of the Wigner representation will be most clear if we write quantum traces in the following way:

$$h^{3(N+1)} \text{tr}[\cdots] = \int_{op} d\hat{\mathbf{r}} \, d\hat{\mathbf{p}} [\cdots] . \tag{7.1}$$

Equation (7.1) *defines* the symbol $\int_{op} d\hat{\mathbf{r}} \, d\hat{\mathbf{p}}$. The reason for introducing this symbol is that it is the quantum analogue of the c-number phase space integral

$$\int d\mathbf{r} \, d\mathbf{p} \equiv \int_{-\infty}^\infty d\mathbf{r}_0 \int_{-\infty}^\infty d\mathbf{p}_0 \cdots \int_{-\infty}^\infty d\mathbf{r}_N \int_{-\infty}^\infty d\mathbf{p}_N .$$

A. Wigner representation

The essence of the Wigner representation is a transformation [Eqs. (7.4a) and (7.4b) below] between the Heisenberg operators $\hat{A}[\hat{\mathbf{r}}, \hat{\mathbf{p}}]$ and their c-number equivalents $A[\mathbf{r}, \mathbf{p}]$. The basic element in this transformation is Kubo's[13] Δ function defined by

$$\Delta[\hat{p}-p, \hat{r}-r] = (2\pi\hbar)^{-3(N+1)}$$

$$\times \int d\lambda \, d\mu \, \exp\left\{-\frac{1}{\hbar}[(\hat{p}-p)\cdot\lambda + (\hat{r}-r)\cdot\mu]\right\} . \quad (7.2)$$

The Δ function is a generalization of the classical phase space δ function, $\delta[p-p']\delta[r-r']$. [Note that the Δ function becomes the δ function if the substitutions $\hat{p}-p'$ and $\hat{r}-r'$ are made in Eq. (7.2).] The Δ function, for example, has formal properties which resemble those of the δ function. The most important properties are[13]

$$\int dr \, dp \, \Delta[\hat{p}-p, \hat{r}-r] = \hat{1} , \quad (7.3a)$$

$$\int_{op} d\hat{r} \, d\hat{p} \, \Delta[\hat{p}-p, \hat{r}-r] = 1 , \quad (7.3b)$$

$$\int_{op} d\hat{r} \, d\hat{p} \, \Delta[p'-\hat{p}, r'-\hat{r}]\Delta[p-\hat{p}, r-\hat{r}]$$
$$= \delta[p'-p]\delta[r'-r] , \quad (7.3c)$$

where 1 is the unit matrix and $\hat{1}$ is the unit matrix times the unit operator.

The transformation between Wigner equivalents and quantum operators is[13]

$$A[r,p] = \int_{op} d\hat{r} \, d\hat{p} \, \hat{A}[\hat{r},\hat{p}]\Delta[p-\hat{p}, r-\hat{r}] , \quad (7.4a)$$

$$\hat{A}[\hat{r},\hat{p}] = \int dr \, dp \, A[r,p]\Delta[p-\hat{p}, r-\hat{r}] . \quad (7.4b)$$

The interpretation of the Δ function is made clear by comparing Eqs. (7.3c) and (7.4a). If one regards the phase space δ function $\delta[p-p']\delta[r-r']$ as the Wigner equivalent of some Heisenberg operator, then that operator is $\Delta[p-\hat{p}, r-\hat{r}]$.

The basic theorems of the Wigner theory concern the Wigner transforms of operator products. These theorems may be derived from Eqs. (7.3) and (7.4).

To develop these theorems we begin with Eq. (7.4b) rewritten for an arbitrary operator $\hat{B}[\hat{r},\hat{p}]$ as

$$\hat{B}[\hat{r},\hat{p}] = \int dr' \, dp' \, B[r',p']\Delta[p'-\hat{p}, r'-\hat{r}] . \quad (7.5)$$

Taking the product of Eqs. (7.4b) and (7.5), "integrating" both sides of this product over $\hat{r}$ and $\hat{p}$, and then using Eq. (7.3c) to simplify the result yields the first basic theorem

$$\int dr \, dp \, A[r,p]B[r,p] = \int_{op} d\hat{r} \, d\hat{p} \, \hat{A}[\hat{r},\hat{p}]\hat{B}[\hat{r},\hat{p}] . \quad (7.6)$$

The second basic theorem relates the Wigner equivalent of $\hat{A}\hat{B}$, which we call $AB[r,p]$, to $A[r,p]$ and $B[r,p]$. The result is

$$AB[r,p] = A[r,p]\exp\left[\frac{i\hbar}{2}\Lambda\right]B[r,p] , \quad (7.7)$$

where Λ is the Poisson bracket operator defined by

$$B[r,p]\Lambda A[r,p] = \sum_{k=0}^{N}\left\{\frac{\partial B}{\partial r_k}\cdot\frac{\partial A}{\partial p_k} - \frac{\partial B}{\partial p_k}\cdot\frac{\partial A}{\partial r_k}\right\} . \quad (7.8)$$

The derivation of Eq. (7.7) nicely illustrates how the Δ-function notation simplifies calculations. Thus, it is included as Appendix B.

To use the basic results of the Wigner theory in quantum statistical calculations, we introduce the Wigner distribution function (wdf) $f[r,p;t]$. This function is defined in terms of the Wigner equivalent of the density matrix $\rho[r,p;t]$ by

$$f[r,p;t] = h^{-3(N+1)}\rho[r,p;t] . \quad (7.9)$$

The wdf is the quantum analog of the classical phase space distribution function. For example, statistical averages may be constructed from the wdf by the following prescription:

$$tr[\hat{\rho}(t)\hat{A}] \equiv \frac{1}{h^{3(N+1)}}\int_{op} d\hat{r} \, d\hat{p} \, \hat{\rho}[\hat{r},\hat{p};t]\hat{A}[\hat{r},\hat{p}]$$
$$= \int dr \, dp \, f[r,p]A[r,p] . \quad (7.10)$$

Equation (7.10) follows from Eqs. (7.6) and (7.9). Setting $\hat{A} = \hat{1}$ in Eq. (7.10) shows that the wdf, like its classical analog, is unit normalized, i.e.,

$$\int dr \, dp \, f[r,p;t] = 1 . \quad (7.11)$$

Canonical averages may, in particular, be constructe from Eq. (7.6) using the wdf, $f_{ca}[r,p]$, which corresponds to the canonical ensemble density matrix $\hat{\rho}_{ca}$. The following canonical averages will be used below:

$$\langle \hat{r}\cdot\hat{r}^T\rangle_{+} = \int dr \, dp \, f_{ca}[r,p]r\cdot r^T ,$$

$$\langle \hat{r}\cdot\hat{p}^T\rangle_{+} = \int dr \, dp \, f_{ca}[r,p]r\cdot p^T = 0 , \quad (7.12)$$

$$\langle \hat{p}\cdot\hat{p}^T\rangle_{+} = \int dr \, dp \, f_{ca}[r,p]p\cdot p^T .$$

Equations (7.12) may be derived by applying Eq. (7.7) to determine the Wigner transforms of the operator products $\hat{r}\hat{r}^T$, $\hat{r}\hat{p}^T$, and $\hat{p}\hat{p}^T$.

Finally, taking the Wigner transform of the quantum Liouville equation for the density matrix, which is

$$\frac{\partial\hat{\rho}(t)}{\partial t} = \frac{i}{\hbar}[\hat{\rho}(t), \hat{H}] , \quad (7.13)$$

yields [using Eq. (7.7)] the following c-number equation of motion for the wdf:

$$\frac{\partial f[r,p;t]}{\partial t} = -\frac{2}{\hbar}f[r,p;t]\sin\left[\frac{\hbar}{2}\Lambda\right]H[r,p] . \quad (7.14)$$

This concludes our brief review of the Wigner theory.

B. Gaussian mechanical models

One use of rigorous representations like the chain is that such representations provide a formal framework for the construction of simplified but physically meaningful model treatments of the many-body problem.

To use the quantum chain in explicit calculations one apparently requires two modelistic assumptions. These are as follows:

(i) The canonical commutation rules for the phase space coordinates of the chain, which rigorously hold statistically [Eqs. (5.2)], are assumed to also hold in detail, i.e., we assume Eq. (5.1) is valid for the

equivalent chain. This assumption converts the infinite chain from a mathematical representation into a true mechanical system. All of the standard results of quantum mechanics are valid for this mechanical system including the results of the Wigner representation just presented.

(ii) The Wigner equivalents r, p of the chain atom phase space Heisenberg coordinates $\hat{r}, \hat{p}$ are assumed to be Gaussian random variables with zero mean. This assumption is the quantum analog of the Gaussian noise model familiar from phenomenological Brownian motion theory. The quantum Gaussian noise assumption greatly simplifies stochastic calculations based on the equivalent chain.

C. Equilibrium Wigner distribution functions

Given these assumptions, one may readily write down equilibrium Wigner distribution functions for the chain atom phase space coordinates. The equilibrium *wdf* for the full infinite chain has the following Gaussian form:

$$f_{ca}[r, p] = \left\{ \det\left[\frac{3}{2\pi}\langle \hat{r} \cdot \hat{r}^T \rangle_+^{-1}\right] \det\left[\frac{3}{2\pi}\langle \hat{p} \cdot \hat{p}^T \rangle_+^{-1}\right]\right\}^{3/2}$$

$$\times \exp[-\tfrac{3}{2} p^T \cdot \langle \hat{p} \cdot \hat{p}^T \rangle_+^{-1} \cdot p + r^T \cdot \langle \hat{r} \cdot \hat{r}^T \rangle_+^{-1} \cdot r] . \tag{7.15}$$

Notice that $f_{ca}[r, p]$ is unit normalized in accord with Eq. (7.11). Moreover, the second moments of the distribution, e.g., $\int dr\, dp\, r \cdot r^T f_{ca}[r, p]$, have been evaluated using Eq. (7.12). The quantities $\langle \hat{r} \cdot \hat{r}^T \rangle_+$ and $\langle \hat{p} \cdot \hat{p}^T \rangle_+$ may be explicitly evaluated using the rigorous statistical properties of the chain atom coordinates, Eqs. (5.3b). This yields the following result for Eq. (5.3b):

$$f_{ca}[r, p] = \det\left[\left(\frac{\hat{\beta}\omega}{2\pi}\right)^3\right]$$

$$\times \exp\left\{-\left[\frac{p^T \cdot \hat{\beta} \cdot p}{2m} + \tfrac{1}{2}m\, r^T \cdot \hat{\beta}\omega^2 \cdot r\right]\right\} . \tag{7.16}$$

The matrix $\hat{\beta}$ appearing in Eq. (7.16) is defined in terms of the frequency matrix ω of the chain by

$$\hat{\beta} = 2(\hbar\omega)^{-1} \tanh\left[\frac{\beta\hbar\omega}{2}\right] . \tag{7.17}$$

Note that as $T \to \infty$, $\hat{\beta} = \beta 1$ and $f_{ca}[r, p]$ properly reduces to the classical Boltzmann distribution for the Gaussian chain model.

Chain atoms $1, 2, \ldots$ function as a Gaussian heatbath for the physical atom, i.e., chain atom 0. To study the relaxation of the physical atom, we thus require the equilibrium *wdf* of the heatbath. Collectively denote the Wigner phase space coordinates of the chain heatbath by r_Q and p_Q, where

$$r_Q = \begin{pmatrix} r_1 \\ r_2 \\ \vdots \end{pmatrix}, \quad p_Q = \begin{pmatrix} p_1 \\ p_2 \\ \vdots \end{pmatrix} . \tag{7.18}$$

Then the equilibrium *wdf*, $f_{ca}^{(1)}[r_Q, p_Q]$, of the heatbath is [cf. Eq. (7.16)]

$$f_{ca}^{(1)}[r_Q, p_Q] = \det\left[\left(\frac{\hat{\beta}^{(1)}\omega^{(1)}}{2\pi}\right)^3\right]$$

$$\times \exp\left[\frac{-p_Q^T \cdot \hat{\beta}^{(1)} \cdot p_Q}{2m} + \tfrac{1}{2}m\, r_Q^T \cdot \hat{\beta}^{(1)}[\omega^{(1)}]^2 \cdot r_Q\right] . \tag{7.19}$$

The force constant matrix of the heatbath is defined by [cf. Eq. (4.14)]

$$[\omega^{(1)}]^2 = \begin{pmatrix} \omega_{e_1}^2 & \omega_{c_2}^2 & 0 & 0 & 0 & \cdot & \cdot \\ \omega_{c_2}^2 & \omega_{e_2}^2 & \omega_{c_3}^2 & 0 & 0 & \cdot & \cdot \\ 0 & \omega_{c_3}^2 & \omega_{e_3}^2 & \omega_{c_4}^2 & 0 & \cdot & \cdot \\ \vdots & & & & & & \end{pmatrix} , \tag{7.20}$$

and $\hat{\beta}^{(1)}$ is defined in terms of $[\omega^{(1)}]^2$ by [cf. Eq. (7.17)]

$$\hat{\beta}^{(1)} = 2[\hbar\omega^{(1)}]^{-1} \tanh\left[\frac{\beta\hbar\omega^{(1)}}{2}\right] . \tag{7.21}$$

Finally, we will require the equilibrium *wdf*, $f_{ca}^{(0)}[r_0, p_0]$, for the chemically active atom [i.e., chain atom 0]. Using the statistical properties given in Eqs. (6.1), this is found to be

$$f_{ca}^{(0)}[r_0, p_0] = \left[\frac{\Omega_0^{(+)}}{2\pi\epsilon_0(T)}\right]^3$$

$$\times \exp\left\{-\frac{1}{\epsilon_0(T)}\left[\frac{p_0^2}{2m} + \tfrac{1}{2}m[\Omega_0^{(+)}]^2 r_0^2\right]\right\} . \tag{7.22}$$

D. Atomic relaxation

We next calculate the time dependent *wdf* of the chemically active atom using the chain formalism. Once this function is known, the reduced density matrix of the atom, and hence all statistical information concerning atomic dynamics, may be determined from the transformation Eq. (7.4b).

We begin with the general equation of motion, Eq. (7.14), for the *wdf*. This equation of motion simplifies to the classical Liouville equation

$$\frac{\partial f[r, p; t]}{\partial t} = -f[r, p; t]\Lambda H[r, p] \tag{7.23}$$

for harmonic Hamiltonians. Thus the time-dependent *wdf* of the chain satisfies Eq. (7.23). Let $f[r, p; r(0), p(0); t]$ denote the solution of Eq. (7.23) which satisfies the initial condition

$$f[r, p; r(0), p(0); t = 0] = \delta[r - r(0)]\delta[p - p(0)] . \tag{7.24}$$

This solution is

$$f[r, p; r(0), p(0); t] = \delta[r - r(t)]\delta[p - p(t)] , \tag{7.25}$$

where $r(t)$ is the classical trajectory of the chain which evolves out of the initial conditions $r(0), p(0)$ and where $p(t) = m\dot{r}(t)$ is the corresponding momentum, i.e.,

$$r(t) = \cos \omega t\, r(0) + (m\omega)^{-1} \sin \omega t\, p(0) \tag{7.26a}$$

and

$$p(t) = \cos \omega t\, p(0) - m\omega \sin \omega t\, r(0) . \tag{7.26b}$$

The time-dependent *wdf* of the atom is

$$f[\mathbf{r}_0, \mathbf{p}_0; \mathbf{r}(0), \mathbf{p}(0); t] = \int d\mathbf{r}_Q \, d\mathbf{p}_Q \, f[\mathbf{r}, \mathbf{p}; \mathbf{r}(0), \mathbf{p}(0); t]$$

$$= \delta[\mathbf{r}_0 - \mathbf{r}_0(t)]\delta[\mathbf{p}_0 - \mathbf{p}_0(t)] , \qquad (7.27)$$

where $\mathbf{r}_0(t)$ and $\mathbf{p}_0(t)$ are the atomic trajectory and atomic momentum. These may be evaluated from Eqs. (7.26). We write the results as

$$\mathbf{r}_0(t) = \mathbf{Z}_0(t) + \mathbf{R}_0(t) \qquad (7.28a)$$

and

$$\mathbf{p}_0(t) = m \, \mathbf{Z}_0(t) + \mathbf{P}_0(t) , \qquad (7.28b)$$

where we define

$$\mathbf{Z}_0(t) = \dot{\chi}^{(-)}(t)\mathbf{r}_0(0) + \chi^{(-)}(t)\frac{\mathbf{p}_0(0)}{m} \qquad (7.29)$$

and

$$\mathbf{R}_0(t) = (\cos \omega t)_{0Q}\mathbf{r}_Q(0) + (\omega^{-1} \sin \omega t)_{0Q}\frac{\mathbf{p}_Q(0)}{m} , \qquad (7.30a)$$

$$\mathbf{P}_0(t) = m\dot{\mathbf{R}}_0(t)$$

$$= (\cos \omega t)_{0Q}\mathbf{p}_Q(0) - m(\omega \sin \omega t)_{0Q}\mathbf{r}_Q(0) . \qquad (7.30b)$$

To obtain Eq. (7.29), we have used the exact result[22] $\dot{\chi}^{(-)}(t) = (\cos \omega t)_{00}$.

The trajectory $\mathbf{Z}_0(t)$ is the hypothetical "zero noise" trajectory that the atom would execute if the thermal bath had the initial conditions $\mathbf{r}_Q(0) = \mathbf{p}_Q(0) = 0$. The quantity $\mathbf{R}_0(t)$ is the fluctuation about the zero noise trajectory due to thermal motion and quantum uncertainty which causes a dispersion in the heatbath initial conditions $\mathbf{r}_Q(0), \mathbf{p}_Q(0)$ about zero.

We are now ready to treat atomic relaxation. This requires averaging of $f[\mathbf{r}_0, \mathbf{p}_0; \mathbf{r}(0), \mathbf{p}(0); t]$ over the fluctuations in $\mathbf{r}_Q(0)$ and $\mathbf{p}_Q(0)$. To do this we assume the distribution function $f_{ca}^{(1)}[\mathbf{r}_Q, \mathbf{p}_Q]$, Eq. (7.19), governs the distribution of $\mathbf{r}_Q(0)$ and $\mathbf{p}_Q(0)$. This leads to a new distribution function $f^{(0)}[\mathbf{r}_0, \mathbf{p}_0; \mathbf{r}_0(0), \mathbf{p}_0(0); t]$ defined by

$$f^{(0)}[\mathbf{r}_0, \mathbf{p}_0; \mathbf{r}_0(0), \mathbf{p}_0(0); t]$$

$$= \int\int f_{ca}^{(1)}[\mathbf{r}_Q(0), \mathbf{p}_Q(0)]f[\mathbf{r}_0, \mathbf{p}_0; \mathbf{r}(0), \mathbf{p}(0); t] . \qquad (7.31)$$

The above distribution function may be readily evaluated by noting that it must be a normalized Gaussian in the fluctuations

$$\rho_0(t) = \mathbf{r}_0 - \mathbf{Z}_0(t) , \qquad (7.32a)$$

$$\pi_0(t) = \mathbf{p}_0 - m\mathbf{Z}_0(t) \qquad (7.32b)$$

about the zero noise trajectory and momentum. Thus the distribution function must have the following form:

$$f^{(0)}[\mathbf{r}_0, \mathbf{p}_0; \mathbf{r}_0(0), \mathbf{p}_0(0); t] = \left[\left(\frac{3}{2\pi}\right)^2 \frac{1}{\det \mathbf{B}(t)}\right]^{3/2} \exp\left\{-\frac{3}{2}[\rho_0(t)\pi_0(t)] \cdot \mathbf{B}^{-1}(t) \cdot \begin{pmatrix} \rho_0(t) \\ \pi_0(t) \end{pmatrix}\right\} , \qquad (7.33)$$

where $\mathbf{B}(t)$ is the matrix of second moments of $f^{(0)}[\mathbf{r}_0, \mathbf{p}_0; \mathbf{r}_0(0), \mathbf{p}_0(0); t]$ defined by

$$\mathbf{B}(t) = \begin{pmatrix} \overline{\rho_0(t) \cdot \rho_0(t)} & \overline{\rho_0(t) \cdot \pi_0(t)} \\ \overline{\rho_0(t) \cdot \pi_0(t)} & \overline{\pi_0(t) \cdot \pi_0(t)} \end{pmatrix} , \qquad (7.34)$$

where, e.g.,

$$\overline{\rho_0(t) \cdot \rho_0(t)} = \int \rho_0(t) \cdot \rho_0(t)f^{(0)}[\mathbf{r}_0, \mathbf{p}_0; \mathbf{r}_0(0), \mathbf{p}_0(0); t] \, d\mathbf{r}_0 \, d\mathbf{p}_0 . \qquad (7.35)$$

The evaluation of the $\mathbf{B}(t)$ matrix is somewhat lengthy but straightforward. Thus we will omit the derivation and pass directly to the results. These are

$$\tfrac{1}{2}m[\Omega_0^{(+)}]^2\overline{\rho_0(t) \cdot \rho_0(t)} = \tfrac{3}{2}\epsilon_0(T)\left\{1 - 2[\Omega_0^{(+)}]^2\left[\chi^{(-)}(t)\chi^{(+)}(t) + \dot{\chi}^{(-)}(t)\int_t^\infty \chi^{(+)}(\tau)d\tau\right] + [\dot{\chi}^{(-)}(t)]^2 + [\Omega_0^{(+)}]^2[\chi^{(-)}(t)]^2\right\} , \qquad (7.36a)$$

$$\overline{\rho_0(t) \cdot \pi_0(t)} = 3\epsilon_0(T)\left\{[\dot{\chi}^{(-)}(t)\chi^{(-)}(t) - \dot{\chi}^{(+)}(t)\chi^{(-)}(t)] - \ddot{\chi}^{(-)}(t)\int_t^\infty \chi^{(+)}(\tau)d\tau + [\Omega_0^{(+)}]^2\dot{\chi}^{(-)}(t)\ddot{\chi}^{(-)}(t)\right\} , \qquad (7.36b)$$

$$\overline{\pi_0(t) \cdot \pi_0(t)} = \tfrac{3}{2}\epsilon_0(T)\left\{1 + 2[\ddot{\chi}^{(-)}(t)\chi^{(+)}(t) - \dot{\chi}^{(-)}(t)\dot{\chi}^{(+)}(t)] + [\dot{\chi}^{(+)}(t)]^2 + [\Omega_0^{(+)}]^2[\ddot{\chi}^{(-)}(t)]^2\right\} . \qquad (7.36c)$$

Equations (7.33)–(7.36) describe the dynamics of the atom given that the rigorous equivalent chain heatbath is modeled by a Gaussian mechanical system. [There is one restriction in that Eq. (7.33) describes the dynamics given that the initial conditions of the atom are $\mathbf{r}_0, \mathbf{p}_0$. In fact, these initial conditions must be distributed in accordance with the uncertainty principle. Thus, Eq. (7.33) must be convoluted with, say, a Wigner space Glauber[23] packet to obtain the actual time-dependent atomic *wdf*.] Finally, we note that as $t \to \infty$, we have that

$f[\mathbf{r}_0, \mathbf{p}_0; \mathbf{r}_0(0), \mathbf{p}_0(0); t]$ properly reduces to the equilibrium distribution function $f_{ca}^{(0)}[\mathbf{r}_0, \mathbf{p}_0]$ given in Eq. (7.22). This result follows from Eq. (7.29) and Eqs. (7.32)–(7.36) and the fact that $\lim_{t \to \infty} \dot{\chi}^{(\pm)}(t) = 0$.

ACKNOWLEDGMENTS

APPENDIX A: PROOF OF EQS. (6.1)

We next derive the statistical relations Eqs. (6.1). We begin with Eq. (3.10) which in integrated form reads

$$\int_0^\infty \rho^{(+)}(\omega)\,d\omega$$

$$= \frac{3}{2}\frac{1}{(\langle p_0^2\rangle/2m)}\int_0^\infty \rho^{(-)}(\omega)\epsilon(\omega)\,d\omega \ . \tag{A1}$$

Using Eqs. (3.9c) and (6.2) shows that Eq. (A1) is equivalent to the first of the statistical relations Eqs. (6.1a). Integrating Eq. (3.5), evaluating the resulting expression for $\chi^{(+)}(t)$ at $t = 0$, and using $\chi^{(+)}(0) = 0$ yield the second statistical relation Eq. (6.1b). Finally, Eqs. (3.5) and (3.8b) yield the relation

$$\frac{\langle \hat{\mathbf{r}}_0(t)\cdot\hat{\mathbf{r}}_0\rangle_+}{\langle \hat{r}_0^2\rangle} = \tfrac{1}{2}m\frac{\langle \hat{\mathbf{r}}_0(t)\cdot\hat{\mathbf{r}}_0\rangle_+}{(\langle p_0^2\rangle/2m)} = \int_0^\infty \cos\omega t\,\rho^{(+)}(\omega)\,d\omega \ . \tag{A2}$$

Integrating Eq. (A2) twice with respect to time and evaluating the result at $t = 0$ then yields

$$\tfrac{1}{2}m\langle \hat{r}_0^2\rangle_+ = \frac{\langle p_0^2\rangle}{2m}\int_0^\infty \omega^{-2}\rho^{(+)}(\omega)\,d\omega \ . \tag{A3}$$

Simplifying Eq. (A3) using Eq. (6.1a) and Eq. (6.3) yields the third statistical relation Eq. (6.1c).

APPENDIX B: PROOF OF EQ. (7.7)

To prove Eq. (7.7), we begin by relating the operator product $\hat{A}[\hat{\mathbf{r}},\hat{\mathbf{p}}]\hat{B}[\hat{\mathbf{r}},\hat{\mathbf{p}}]$ to the Wigner equivalents of $\hat{A}$ and $\hat{B}$, $A[\mathbf{r},\mathbf{p}]$ and $B[\mathbf{r},\mathbf{p}]$. This may be accomplished using Eqs. (7.4b) and (7.5) which yields

$$\hat{A}[\hat{\mathbf{r}},\hat{\mathbf{p}}]\hat{B}[\hat{\mathbf{r}},\hat{\mathbf{p}}] = \int d\mathbf{r}'\,d\mathbf{p}'\int d\mathbf{r}''\,d\mathbf{p}''$$

$$\times A[\mathbf{r}',\mathbf{p}']B[\mathbf{r}'',\mathbf{p}'']\hat{D}_{\mathbf{r}',\mathbf{p}';\mathbf{r}'',\mathbf{p}''}[\hat{\mathbf{r}},\hat{\mathbf{p}}] \ , \tag{B1}$$

where we define the operator $\hat{D}_{\mathbf{r}',\mathbf{p}';\mathbf{r}'',\mathbf{p}''}$ by

$$\hat{D}_{\mathbf{r}',\mathbf{p}';\mathbf{r}'',\mathbf{p}''}[\hat{\mathbf{r}},\hat{\mathbf{p}}] = \Delta[\mathbf{p}'-\hat{\mathbf{p}},\mathbf{r}'-\hat{\mathbf{r}}]\Delta[\mathbf{p}''-\hat{\mathbf{p}},\mathbf{r}''-\hat{\mathbf{r}}] \ . \tag{B2}$$

According to Eq. (7.4a), the Wigner equivalent of $\hat{A}\hat{B}$, $AB[\mathbf{r},\mathbf{p}]$ may be found by multiplying both sides of Eq. (B1) by $\Delta[\mathbf{p}-\hat{\mathbf{p}},\mathbf{r}-\hat{\mathbf{r}}]$ and integrating over $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$. This yields

$$AB[\mathbf{r},\mathbf{p}] = \int d\mathbf{r}'\,d\mathbf{p}'\int d\mathbf{r}''\,d\mathbf{p}''$$

$$\times A[\mathbf{r}',\mathbf{p}']B[\mathbf{r}'',\mathbf{p}'']D_{\mathbf{r}',\mathbf{p}';\mathbf{r}'',\mathbf{p}''}[\mathbf{r},\mathbf{p}] \ , \tag{B3}$$

where $D_{\mathbf{r}',\mathbf{p}';\mathbf{r}'',\mathbf{p}''}[\mathbf{r},\mathbf{p}]$ is the Wigner equivalent of $\hat{D}_{\mathbf{r}',\mathbf{p}';\mathbf{r}'',\mathbf{p}''}[\hat{\mathbf{r}},\hat{\mathbf{p}}]$, i.e.,

$$D_{\mathbf{r}',\mathbf{p}';\mathbf{r}'',\mathbf{p}''}[\mathbf{r},\mathbf{p}] = \int_{\mathrm{op}} d\hat{\mathbf{r}}\,d\hat{\mathbf{p}}\,\hat{D}_{\mathbf{r}',\mathbf{p}';\mathbf{r}'',\mathbf{p}''}[\hat{\mathbf{r}},\hat{\mathbf{p}}]\Delta[\mathbf{p}-\hat{\mathbf{p}},\mathbf{r}-\hat{\mathbf{r}}] \tag{B4}$$

Using Eq. (B2) and the definition of the Δ function, the quantum trace indicated by Eq. (B4) may be explicitly evaluated to yield

$$D_{\mathbf{r}',\mathbf{p}';\mathbf{r}'',\mathbf{p}''}[\mathbf{r},\mathbf{p}] = \left(\frac{2}{\hbar}\right)^{3(N+1)}$$

$$\times \exp\left\{\frac{2i}{\hbar}[\mathbf{p}\cdot(\mathbf{r}''-\mathbf{r}') - \mathbf{p}''\cdot(\mathbf{r}-\mathbf{r}') - \mathbf{p}'\cdot(\mathbf{r}''-\mathbf{r}')]\right\} \ . \tag{B5}$$

Equation (B3) may now be explicitly evaluated using Eq. (B5). To do this we expand $A[\mathbf{r}',\mathbf{p}']$ in a power series about $\mathbf{r}',\mathbf{p}' = \mathbf{r},\mathbf{p}$ and $B[\mathbf{r}'',\mathbf{p}'']$ in a power series about $\mathbf{r}'',\mathbf{p}'' = \mathbf{r},\mathbf{p}$. These series may be written formally as

$$A[\mathbf{r}',\mathbf{p}'] = \exp\left[(\mathbf{p}'-\mathbf{p})\cdot\frac{d}{d\mathbf{p}}\right]$$

$$\times \exp\left[(\mathbf{r}'-\mathbf{r})\cdot\frac{d}{d\mathbf{r}}\right]A[\mathbf{r},\mathbf{p}] \ , \tag{B6a}$$

$$B[\mathbf{r}'',\mathbf{p}''] = \exp\left[(\mathbf{p}''-\mathbf{p})\cdot\frac{d}{d\mathbf{p}}\right]$$

$$\times \exp\left[(\mathbf{r}''-\mathbf{r})\cdot\frac{d}{d\mathbf{r}}\right]B[\mathbf{r},\mathbf{p}] \ . \tag{B6b}$$

Combining Eqs. (B3), (B5), and (B6) and performing the indicated integrations yields Eq. (7.7).

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[15] The symmetrized velocity autocorrelation function $\dot{\chi}^{(+)}(t)$ clearly reduces to the classical correlation function $\chi^{CL}(t)$ in the high temperature limit. The reduction of the antisymmetrized correlation function $\chi^{(-)}(t)$ may be established by using the correspondence between the quantum commutator and the classical Poisson bracket, e.g., $[\mathbf{r}_0(t),\mathbf{p}_0] \to i\hbar\{\mathbf{r}_0(t),\mathbf{p}_0\}_{PB}$, where the Poisson bracket is defined by

$$\{A,B\}_{PB} \equiv \sum_{\lambda=0}^{N+1}\left[\frac{\partial A}{\partial r_\lambda}\cdot\frac{\partial A}{\partial p_\lambda} - \frac{\partial A}{\partial p_\lambda}\cdot\frac{\partial B}{\partial r_\lambda}\right] \ .$$

Thus the classical limit of the commutator $[\mathbf{r}_0(t),\mathbf{p}_0]$ is $i\hbar[\partial\mathbf{r}_0(t)/\partial\mathbf{r}_0]$. Therefore in the classical limit

$$\langle\mathbf{r}_0(t)\cdot\mathbf{r}_0\rangle_- \to \frac{i\hbar}{m}\left\langle\frac{\partial}{\partial\mathbf{r}_0}\cdot\mathbf{r}_0(t)\right\rangle_{CL} \ .$$

Using the virial theorem $\langle \partial A(t)/\partial r_0 \rangle_{CL} = m/k_B T \langle \dot{A}(t)\dot{r}_0 \rangle_{CL}$, one may rewrite the classical limit of $\langle r_0(t) \cdot \dot{r}_0 \rangle_-$ as $\langle r_0(t) \cdot \dot{r}_0 \rangle_- \rightarrow i\hbar/k_B T \langle \dot{r}_0(t) \cdot \dot{r}_0 \rangle_{CL}$. Thus we have shown that $\chi^{(-)}(t) \rightarrow \chi^{CL}(t)$ in the classical limit.

[16]This may be accomplished by expanding the time correlation functions in terms of their individual transition matrix element contributions and then taking a Fourier transform.

[17]Equation (3.10) is a special case of the quantum fluctuation-dissipation theorem. For a more detailed discussion of this theorem, see Ref. 14.

[18]Notice that $\langle \dot{R}_p^{(+)}(t+\tau) \cdot \dot{R}_p^{(+)}(\tau)\rangle_+ \neq \langle \dot{R}_p^{(+)}(t) \cdot \dot{R}_p^{(+)} \rangle_+$, i.e., the process $R_p^{(+)}(t)$ is nonstationary if the averaging process is chosen to be a full canonical average. The process $R_p^{(+)}(t)$ can be rendered stationary if the averaging process is chosen to be a canonical average over equivalent chain phase space coor-

dinates conditional that chain atoms $0, 1, \ldots, p-1$ are clamped at equilibrium. These points are discussed for the case of general averaging processes (inner products) $\langle \rangle$ in Sec. XII of Ref. 3.

[19]The derivation of Eqs. (4.4) and (4.5) and Eqs. (4.8) and (4.9) parallels the derivations of Sec. X of Ref. 3.

[20]The derivation of the formal statistical properties, Eqs. (5.2) and (5.3), parallels that of Appendix D of Ref. 3.

[21]The physical interpretation of the adiabatic frequency and the reason for this nomenclature has been discussed in the papers listed in Ref. 1.

[22]This result may be proven using the same argument employed to prove Eq. (5.13) of Ref. 3.

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