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Statistical description of history-dependent creep constitutive equations for viscoelastic media

Lu Meng* and Soon-Bok Lee†

Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, Science Town, Taejon, 305-701, Korea

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In this paper a nonequilibrium statistical ensemble theory is used to describe viscoelastic creep behaviors. By using the history-dependent distribution function and taking stress as a controllable kinetics argument, a stress ensemble is introduced for obtaining the corresponding thermodynamics functionals such as entropy, enthalpy and the Gibbs free energy, etc. With consideration of the dissipation constraint to materials with memory, the creep stress-strain relation can be automatically obtained through the compatible conditions among thermodynamic functionals. Moreover, when higher-order Fourier transform components of stress are further considered as controllable arguments, the wavelength-dependent stress-strain relations characterized by the Fourier components of strain can also be obtained within the framework of the thermodynamics theory with memory. Discussion of linearly dissipative systems in which a dissipation-fluctuation mechanism is involved gives an explicit physical interpretation to the viscoelastic creep function by the time correlation function of the Hamiltonian and other relevant quantities. Besides, all the results obtained are shown to be self-consistent when simplified to an equilibrium or a local equilibrium state.

I. INTRODUCTION

Macroscopic creep properties of different materials arise from distinct microscopic physical behaviors, and a lot of work has been done, on or above the atomistic scale, to study the creep mechanisms by using varieties of kinetics or statistical mechanics approaches. For example, for viscous creep of polymers one can use the generalized Langevin kinetics equation as a starting point, and through its solution (usually in numeric forms) obtain the viscous coefficients for the rate type of creep constitutive equations. This kinetics method has been widely used in theoretical studies as well as in engineering practices, and has achieved a great deal of fruitful results for dilute polymeric liquids and, in many cases, for polymeric melts or other dense liquids.[1–3] Another typical creep phenomenon that can be frequently seen is the viscoplastic flow of metals subject to external loading at elevated temperatures. This kind of creep, whose mechanism is different from that of polymers, is mainly due to the movement of defects within crystals, and can be well explained by dislocation theories.[4] Both kinetics approaches and dislocation theories have made tremendous successes in explaining the creep properties within their interests, and also provide us a better understanding for other classes of creep problems in some way. Based on the previous knowledge, the present paper attempts to develop a statistical description for history-dependent creep constitutive equations of viscoelastic solids, whose mechanism, as is known, cannot be conveniently modeled in terms of the Langevin kinetic equation, nor properly described by dislocation theories.

We start to deal with our problem from the nonequilibrium statistical ensemble theory developed by McLennen[5–7] and Zubarev.[8,9] With the history-dependent distribution function available, we can construct the nonequilibrium thermodynamics functionals via the microscopic information on the atomistic scale, and therefore realize a transition from a concrete system to a continuum medium in a manner similar to the Gibbsian statistical ensemble method. Since in continuum mechanics strain is often required to be a response instead of a controllable kinetics argument, a stress ensemble has to be herein introduced. The stress ensemble concept, to the best of our knowledge, was first systematically proposed in Ref. 10 for the description of elastic properties of solids at an equilibrium state. Here, we use and generalize the concept to deal with history-dependent creep behaviors in irreversible processes. From the distribution function established for the stress ensemble, the internal energy, the entropy, and the Gibbs free energy can be expressed in history-dependent functionals. As a matter of fact, these thermodynamic expressions, together with the stress-strain relation obtained from the thermodynamic constraint, form a description for our problem, namely, give us the constitutive equations required for thermo-viscoelastic creep.

Unlike what was done in some earlier works (see, e.g., Refs. 5–8 and 11) for formal descriptions of viscous coefficients of fluids in transport processes, the procedure we follow is first to construct the nonequilibrium and nonlocal Gibbs free energy based on the understanding to the entropy and the nonequilibrium Massieu-Planck functional. Then we further discuss the Gibbs free energy with a modern thermodynamics theory. As history-dependent creep behaviors are always coupled with an intrinsically dissipative characterization of systems, the thermodynamics approach for materials with memory is needed in irreversible processes.[12,13] Applying the Coleman-Noll method and imposing dissipation inequality to the Gibbs free energy, the global average and wavelength-dependent nonlocal stress-strain relation as well as the entropy expression are automatically obtained or satisfied. The restriction imposed by the second thermodynamics law upon thermodynamic functionals also results in the necessary requirements which constitutive relations must obey, and therefore reveals an innate connection among the Gibbs energy, the entropy, and the strain response. This connection enables one to guarantee the compatibility among these thermodynamic functions, without which the constitutive equations would be of little theoretical significance. Thus it is shown that along with such a procedure one is able to construct the required self-consistent nonequilibrium thermodynamic functionals and, in this way, to establish a physical representation from the atomistic point of view for the viscoelastic creep behaviors related to microscopic relaxation processes.

The basic concepts and assumptions are first elaborated and proposed in Sec. II. The nonequilibrium distribution function proposed in Refs. 7–9 is listed in Sec. III and is recast into an alternative form that is applicable to a stress ensemble. In Sec. IV we construct the Gibbs free energy expression and other relevant ones on the basis of the distribution function, and in Sec. V a discussion is carried out to the constraint of the Clausius-Duhem dissipation inequality on thermodynamics functionals. Simplification of some limiting cases is given in Sec. VI, which includes an analytical result of creep function based on a simplified model in a linearly dissipative process.

II. PHYSICAL BACKGROUND AND ASSUMPTIONS

We take a representative element as the sample under consideration. This element occupies a finite volume V and contains a large number of microparticles (say, molecules or atoms). Consequently, it can be treated as a statistical system even though it might be viewed as a continuum point on a larger macroscopic scale (note that the terminology a *volume element* and a *statistical system* are alternatively used throughout, yet they express the same meaning). Furthermore, in contrast with the conventional assumption in equilibrium statistical mechanics that a system under study is in a spatially uniform state, the system herein studied is undergoing a process which is spatially nonuniform and, actually, relatively transient. This indicates that the stress (or strain) and temperature distributions over the system are nonuniform, and their higher-order time-dependent Fourier components should be also regarded as the ensemble arguments for a general consideration. Needless to say, all those limitations and assumptions proposed in Ref. 10 regarding the interactions between the system and its environment as well as the interactions among subdivisions are needed, yet we give no repeat of them for brevity. Besides, another additional restriction to the space nonuniformity and the motion of atoms is proposed here as our first assumption.

(i) The local strain and local stress can be defined within each subdivision. Moreover, from the current strain and its previous history the stress can be completely determined, and, conversely, the strain can also be determined from the current stress and its entire history prior to the current time t.

This assumption ensures that the description of strain and stress is meaningful, and also implies that our following discussion should be confined to solids since for liquids, as is believed, it makes no sense for one to define a strain other than a strain rate or a velocity gradient field. This characteristic of liquids is due to the fact that the state of liquids is independent of their initial reference configurations except their volumetric term.

As what we are concerned with in the context is the viscoelastic behavior other than properties associated to plasticity of viscoplasticity of materials, we only focus our attention to the process of deformation in which no movement of dislocations or other impurities is involved. This limitation leads to our second assumption.

(ii) The global or local macroscopic mean deformation of the representative element contains no plasticity contribution due to either that external thermodynamical loading is not sufficiently large to make dislocations, if any, be activated or that, for example, in case of perfect crystals, there exist no defects within the system.

With that assumption one no longer needs to take into account how to make the generalized coordinates of dislocations enter the Hamiltonian of the system, as is done in Ref. 14. The third assumption is as follows.

(iii) For the system under study there exist at least two different time characteristic scales, denoted by T_M and T_m, respectively. The former is corresponding to the macroscopically averaged motion, and the latter to the microscopically thermal vibration of microparticles. It is supposed that $T_M \gg T_m$.

The comparison of various kinds of time scale permits one to perform many mathematical and physical manipulations for simplifying the problem.

III. NONEQUILIBRIUM DISTRIBUTION FUNCTION FOR STRESS ENSEMBLE

In order to describe the viscoelastic creep behavior by virtue of statistical physics approaches, a nonequilibrium distribution function exhibiting the dissipatively irreversible behavior and the memory characterization of the system is needed. According to the nonequilibrium statistical ensemble theory (see Refs. 5–9 for details), the distribution function of nonconservative systems subjected to external reservoirs obeys the following governing equation:

$$\frac{\partial f}{\partial t}+\{f,H\}+\sum_{\alpha}\frac{\partial f F_{\alpha}}{\partial p_{\alpha}}=0, \quad \alpha=1,2,\ldots,3N, \tag{1}$$

where f denotes the distribution function, N is the atom number in the system, $\{\ \}$ indicates the classical Poisson bracket, and H represents the Hamiltonian of the system expressed by

$$H=\sum_{i}^{N}\frac{|\mathbf{p}_i|^2}{2m_i}+\Phi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N), \tag{2}$$

in which $\Phi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)$ follows the interaction potential among atoms of the system. In the above equation and expression, F_{α} $(\alpha=1,2,\ldots,3N)$ denote the interaction between the system and its external environment, $\mathbf{x}_i$ is the rectangular Cartesian coordinate of the ith atom, m_i is its mass, and $\mathbf{p}_i$ the corresponding momentum.

By considering such a statistical ensemble of which systems exchange energies and momentum but no particles with external reservoirs, and no chemical reactions take place in the process, the external forces F_α ($\alpha=1,2,3,\ldots,3N$) can be taken as

$$\sum_\alpha \frac{\partial F_\alpha}{\partial p_\alpha}=-\int_{\partial v}\beta(\mathbf{x},t)[\mathbf{j}_H(\mathbf{x})-\mathbf{v}(\mathbf{x},t)\cdot\boldsymbol{\sigma}(x)]\cdot d\mathbf{a}, \quad (3)$$

where ∂v is the current surface of the volume element and $d\mathbf{a}$ denotes the area element, $\mathbf{v}(\mathbf{x})$ and $\beta(\mathbf{x})$ are the locally averaged velocity and the local inverse temperature, respectively, $\mathbf{j}_H$ indicates the energy flux density, and $\boldsymbol{\sigma}$ the momen-tum flux density (Cauchy stress tensor in the current configuration). $H(\mathbf{x})$ is the density of the Hamiltonian per unit volume, and the solution of the distribution function satisfying Eq. (1) can be reduced to[7]

$$f(t)=Q^{-1}(t)f_l(t)\exp[D(t)], \quad (4)$$

where

$$D(t)=\int_v\int_{-\infty}^{t}\Bigg\{\mathbf{j}_H(\mathbf{x},t-\tau)\cdot\nabla\beta(\mathbf{x},t-\tau)+H(\mathbf{x},t-\tau)\frac{\partial\beta(\mathbf{x},\tau)}{\partial t}-\boldsymbol{\sigma}(\mathbf{x},t-\tau):\nabla\Big[\beta(\mathbf{x},\tau)\mathbf{v}(\mathbf{x},\tau)\Big]$$

$$-\beta(\mathbf{x},\tau)\mathbf{p}(\mathbf{x},t-\tau)\cdot\frac{\partial\mathbf{v}(\mathbf{x},\tau)}{\partial t}\Bigg\}d\tau\, dv \quad (5)$$

and

$$f_l(t)=\exp\left\{-\int_v\beta(\mathbf{x},t)[H(\mathbf{x})-\mathbf{v}(\mathbf{x})\cdot\mathbf{p}(\mathbf{x})]dv\right\},\quad Q(t)=\int_\Gamma f_l(t)\exp[D(t)]d\Gamma. \quad (6)$$

Here, Γ represents the phase space. Integration of $\mathbf{j}_H(\mathbf{x})$, $\boldsymbol{\sigma}(\mathbf{x})$, and $H(\mathbf{x})$ over the regime V gives the corresponding energy flux vector $\mathbf{j}_H$, the momentum flux tensor $\boldsymbol{\sigma}$, and the Hamiltonian of the system, i.e.,

$$\int_V \mathbf{j}_H(\mathbf{x},t)dv=\mathbf{j}_H(t),$$

$$\int_V \boldsymbol{\sigma}(\mathbf{x},t)dv=\boldsymbol{\sigma}(t), \quad (7)$$

$$\int_V H(\mathbf{x},t)dv=H(t).$$

Here, the physical quantities $\mathbf{j}_H$, $\boldsymbol{\sigma}$, and H as well as their corresponding densities per unit volume are denoted by the same symbols for simplicity, yet the latter are emphatically specified by explicitly introducing a spatial variable $\mathbf{x}$ or $\mathbf{X}$ to display them being position dependent in the current or initial reference configuration. The summation convention on repeated indices is applied throughout, otherwise a specification would be given.

Because of what we are concerned with is the macroscopic behavior of the system, we decompose

$$x_\alpha=\langle x_\alpha\rangle+q_\alpha^*,\quad p_\alpha=\langle p_\alpha\rangle+p_\alpha^*\quad(\alpha=1,2,3,\ldots,3N), \quad (8)$$

where the brackets $\langle\ \rangle$ denotes an averaging operation over $f(t)$, $\langle x_\alpha\rangle$ and $\langle p_\alpha\rangle$ are the ensemble mean coordinate and momentum of the αth atom, respectively, and q_α^* and p_α^* indicate the coordinate and momentum of the thermal vibration superimposed on $\langle x_\alpha\rangle$ and $\langle p_\alpha\rangle$, respectively. Obviously,

$$\langle q_\alpha^*\rangle\equiv 0,\quad \langle p_\alpha^*\rangle\equiv 0\quad(\alpha=1,2,\ldots,3N). \quad (9)$$

Let

$$\Delta\langle\mathbf{x}_j(k)\rangle=\langle\mathbf{x}_j\rangle-\langle\mathbf{x}_k\rangle \quad (10)$$

be the current mean difference vector between the two atoms labeled respectively by j and k after deformation, and let

$$\Delta\langle\mathbf{X}_J(K)\rangle=\langle\mathbf{X}_J\rangle-\langle\mathbf{X}_K\rangle \quad (11)$$

be the initial mean difference vector of the same two atoms before deformation. Introducing a deformation gradient tensor $\mathbf{a}$, one has

$$\Delta\langle\mathbf{x}_i(k)\rangle=\mathbf{a}\cdot\Delta\langle\mathbf{X}_J(K)\rangle. \quad (12)$$

The material stain can be defined as

$$\mathbf{E}=\tfrac{1}{2}(\mathbf{a}^T\mathbf{a}-\mathbf{I}), \quad (13)$$

where $\mathbf{I}$ is the unit tensor. Equations (8)–(13) allow one to make the strain tensor enter the Hamiltonian and establish a strain ensemble

$$H=H(q^*,p^*;\{a_{iJ}\};\mathfrak{R})\ \text{ or }\ H=H(q^*,p^*;\{E_{IJ}\};\mathfrak{R}). \quad (14)$$

Here, $\mathfrak{R}$ denotes an initial configuration associated with initial arrangements of $\{\mathbf{X}_J\}$ ($J=1,2,\ldots,N$) . The coordinates and momenta of atoms in the system are collectively labeled as (q,p) or (q^*,p^*) herein and hereafter. Although all the thermodynamics expressions as well as the Hamiltonian in essence depend on the reference configuration $\mathfrak{R}$, in the following discussion the argument $\mathfrak{R}$ will be omitted for convenience and is taken as understood.

Substitution of Eqs. (8)–(13) into Eq. (4) and Eq. (5) leads to

$$\begin{aligned} f(t) &= Q^{-1}(t) f_I(t) \exp[D(t)] \\ &= Q^{-1}(t) \exp\left\{ -\int_v \beta(\mathbf{x},t) \left[H^*(\mathbf{x},t) + \frac{1}{2}\rho(\mathbf{x},t) v_i^2(\mathbf{x},t) \right] dv \right\} \\ &\quad \times \exp\left\{ \int_V \int_{-\infty}^{t} \mathbf{j}'_H(\mathbf{x},t-\tau)\cdot\nabla\beta(\mathbf{x},\tau) + H'(\mathbf{x},t-\tau)\frac{\partial\beta(\mathbf{x},\tau)}{\partial\tau} \right. \\ &\quad \left. -\beta(\mathbf{x},\tau)\boldsymbol{\sigma}'(\mathbf{x},t-\tau):\nabla\mathbf{v}(\mathbf{x},\tau) - \beta(\mathbf{x},\tau)\mathbf{p}'(\mathbf{x},t-\tau)\cdot\frac{\partial\mathbf{v}(\mathbf{x},\tau)}{\partial\tau} \right\} d\tau\, dv, \end{aligned} \tag{15}$$

where

$$\mathbf{j}'_H = \mathbf{j}^*_H + H^*\mathbf{v} - \tfrac{1}{2}\rho\mathbf{v}^2\mathbf{v} - \mathbf{v}^2\mathbf{p}^* - \boldsymbol{\sigma}'\cdot\mathbf{v}, \tag{16}$$

$$H' = H^* - \tfrac{1}{2}\rho\mathbf{v}^2, \tag{17}$$

$$H^* = \frac{1}{2}\sum_\alpha \frac{|p^*_\alpha|^2}{m_\alpha} + \Phi(q^*;\{\mathbf{a}\}), \tag{18}$$

$$\mathbf{p}' = \mathbf{p}^* + \rho\mathbf{v}, \tag{19}$$

$$\boldsymbol{\sigma}' = \boldsymbol{\sigma}^* + \tfrac{1}{2}\rho\mathbf{v}^T\otimes\mathbf{v} + \tfrac{1}{2}\rho\mathbf{v}\otimes\mathbf{v}^T + \mathbf{v}^T\otimes\mathbf{p}^* + \mathbf{p}^*\otimes\mathbf{v}, \tag{20}$$

$$(i,j=1,2,3).$$

All the physical quantities asterisked follow that they are defined in the moving coordinates performed by a Galilean transformation with a locally averaged velocity $\mathbf{v}(\mathbf{x})$. Note that the Hamiltonian H implicitly depends on the time t via the argument $\mathbf{a}$ on the macroscopic time scale T_M.

To establish a stress ensemble, one has to make the stress enter the Hamiltonian as a controllable argument. From Eq. (14), for equilibrium states a transformation between a strain ensemble and a stress ensemble can be obtained by (cf. Refs. 10 and 17 for details)

$$\mathbf{T}^m = \frac{1}{V}\frac{\partial H^*(q^*,p^*;\{\mathbf{a}\})}{\partial\mathbf{a}} \quad\text{or}\quad \Sigma^m = \frac{1}{V}\frac{\partial H^*(q^*,p^*;\{\mathbf{E}\})}{\partial\mathbf{E}}, \tag{21}$$

where $\mathbf{T}^m$ and Σ^m are, respectively, the first and second Piola-Kirchhoff stress in microscopic phase space, V is the initial volume of the element in its reference configuration. As is shown in Ref. 14, a relation between the current microscopic phase stress and the current strain still exists as

$$\mathbf{T}^m(q^*,p^*;\{\mathbf{a}\};t) = \frac{\partial H^*(q^*,p^*;\{\mathbf{a}\};t)}{\partial\mathbf{a}} \Leftrightarrow \mathbf{T}^{*m}(t) \tag{22}$$

in nonequilibrium states and irreversible processes. Thus an inverse of Eq. (22) formally gives

$$\mathbf{a}^m(t) = \mathbf{a}^m(q^*,p^*;\{\mathbf{T}\};t) \quad\text{or}\quad \mathbf{E} = \mathbf{E}^m(q^*,p^*;\{\Sigma\}). \tag{23}$$

The superscript m in Eqs. (21)–(23) indicates that the strain is a microscopic fluctuation quantity if the stress $\mathbf{T}$ or Σ is regarded as a fixed one, since we cannot fix the strain and stress at the same time in a statistical system. If we let $\mathbf{E}^{m(r)}$ $(r=0,\pm1,\pm2,\ldots)$ be the phase function of $\mathbf{E}^{(r)}$ $(r=0,\pm1,\pm2,\ldots)$, their phase average function is then designated by

$$\mathbf{E}^{(r)} = \langle\mathbf{E}^{m(r)}\rangle. \tag{24}$$

As a result of the above relationship and with consideration of the basic assumption listed in Sec. II, we can use the augmented system concept[10] to construct our stress ensemble. In fact, one can imagine that the stress ensemble is based on a system consisting of the original atomic system described by coordinates and momenta (q^*,p^*), plus the kinematics parameters or generalized kinematics arguments like $\mathbf{a}$, which are regarded as additional coordinates or degrees of freedom of the augmented system. The Hamiltonian, denoted by $H^*_\sigma(q^*,p^*;\{\mathbf{E}^m\};\ \{\Sigma\};t) \Leftrightarrow H^*_\sigma(t)$, of the augmented system takes the following form in terms of the Legendre transform:

$$\begin{aligned} H^*_\sigma(q^*,p^*;\{\mathbf{E}^m\};\{\Sigma\};t) &= H^*(q^*p^*;\{\mathbf{E}^m\};t) \\ &\quad - V\mathbf{E}^m(t):[\Sigma(t) - \Sigma'(0)] \end{aligned} \tag{25}$$

for a uniform system, and

$$\begin{aligned} H^*_\sigma(q^*,p^*;\{\mathbf{E}^m\},\{\Sigma\};\mathbf{X},t) &= H^*(q^*,p^*;\{\mathbf{E}^m\};\mathbf{X},t) \\ &\quad - \mathbf{E}^m(\mathbf{X},t);[\Sigma(\mathbf{X},t) \\ &\quad - \Sigma'(\mathbf{X},0)] \end{aligned} \tag{26}$$

for a nonuniform system, provided Eqs. (25) and (26) can be defined, either directly, or by some process of analytic continuous. Note that the stresses Σ and Σ' are corresponding to σ and σ', respectively, but the former are defined in the reference configuration.

Since H^* and H^*_σ are alternate Hamiltonian for the description of the same system interaction with the environments, the ensemble should be of the same form (cf. Ref. 10 for details) in both cases. Thus the distribution function of the corresponding stress ensemble takes

$$f_\sigma(t) = Q_\sigma^{-1}(t) f_{I\sigma}(t) \exp[D_\sigma(t)], \tag{27}$$

where

$$f_{I\sigma}(t)=\exp\left\{-\int_V \beta(\mathbf{X},t)\left[H_\sigma^*(\mathbf{X},t)+\frac{1}{2}\rho_R(\mathbf{X},t)\mathbf{v}^2(\mathbf{X},t)\right]dV\right\}, \tag{28}$$

$$D_\sigma(t)=\int_V\int_{-\infty}^{t}\left\{\mathbf{j}'_{H\sigma}(\mathbf{X},t-\tau)\cdot\nabla\beta(\mathbf{X},\tau)+[H'_\sigma(\mathbf{X},t-\tau)+\Sigma'(\mathbf{X},t-\tau):\mathbf{E}^m(\mathbf{X},\tau)]\right.$$
$$\left.\times\frac{\partial\beta(\mathbf{X},\tau)}{\partial\tau}+\beta(\mathbf{X},\tau)\mathbf{E}^m(\mathbf{X},\tau):\frac{\partial\Sigma'(\mathbf{X},t-\tau)}{\partial\tau}-\beta(\mathbf{X},\tau)\mathbf{p}'(\mathbf{X},\tau)\cdot\frac{\partial\mathbf{v}(\mathbf{X},\tau)}{\partial\tau}\right\}d\tau\,dV, \tag{29}$$

$$Q_\sigma(t)=\int_{\Gamma^*}f_{I\sigma}(t)\exp[D_\sigma(t)]d\Gamma^*. \tag{30}$$

Here, $\mathbf{j}'_{H\sigma}$ and H'_σ correspond to j'_H and H' with H_σ^* in place of H^* in Eqs. (16) and (17), respectively. Γ^* in Eq. (30) represents the augmented phase space, and an integration over it follows:

$$\int_{\Gamma^*}f\,d\Gamma^*=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}f\,dq_1^*\cdots dq_{3N}^*dp_1^*\cdots dp_{3N}^*dE_{11}^*dE_{12}^m\cdots dE_{33}^m. \tag{31}$$

In deriving Eqs. (27)–(30) we have shifted the volume integration from the current configuration to its reference configuration, and for it the local conservation laws have to be utilized. Besides, the relation $\int_v \boldsymbol{\sigma}:\nabla\mathbf{v}\,dv=\int_V\Sigma:\dot{\mathbf{E}}\,dV$ has been directly employed.

If we use the deformation gradient **a** instead of the strain **E** to enter the Hamiltonian, the augmented phase integration over six-dimensional **E** should be replaced by a nine-dimensional integration over **a**. However, the requirement of invariance of H with respect to a rigid rotation of the deformed body implies that the parameters **a** appear in combinations that are correspondingly invariant, such as the material strain components **E**; thus we usually regard $H(t)\Leftrightarrow H(q^*,p^*;\{\mathbf{E}\})$. Correspondingly, for the stress ensemble we take $H_\sigma^*(t)\Leftrightarrow H_\sigma^*(q^*,p^*;\{\Sigma\})$ instead of $H_\sigma^*(t)\Leftrightarrow H_\sigma^*(q^*,p^*;\{\mathbf{T}\})$ by using the stress Σ to replace the stress **T**.

IV. NONEQUILIBRIUM THERMODYNAMIC FUNCTIONALS

From the nonequilibrium distribution function $f_\sigma(t)$, one can directly define the entropy that exhibits both the nonequilibrium state of the system and the irreversible dissipative process which the system is undergoing. In fact, in Refs. 6–8 the entropy is defined as

$$S(t)=-\langle\ln f_L(t)\rangle. \tag{32}$$

Then, the entropy is equivalently transformed into

$$S(t)=-\langle\ln f_{L\sigma}(t)\rangle \tag{33}$$

for the stress ensemble. Here,

$$f_{L\sigma}(t)=Q_\sigma^{-1}(t)f_{I\sigma}(t). \tag{34}$$

Motivated by the definition of (33) and the definition of the Gibbs free energy

$$G=e-TS-\int_V\Sigma:\mathbf{E}\,dV, \tag{35}$$

where $T=[k\beta]^{-1}$ is the absolute temperature and $e=\langle H^*(t)\rangle$ is the internal energy of the system, one then has

$$G(t)=\langle H_\sigma^*(t)\rangle-\beta^{(0)}(t)\ln Q_\sigma(t)-\beta^{(0)-1}(t)$$
$$\times\int_V\beta(\mathbf{X},T)[\langle H_\sigma^*(\mathbf{X},t)\rangle+\tfrac{1}{2}\rho_R(\mathbf{X})\mathbf{v}^2(\mathbf{X},t)]dV, \tag{36}$$

where

$$\beta^{(0)}(t)=\frac{1}{V}\int_V\beta(\mathbf{X},t)dV \tag{37}$$

is the volume mean inverse temperature, and ρ_R is the initial density. Here, the Legendre transform is again assumed to be valid for Eq. (35).

The history-dependent functional $\ln Q_\sigma(t)$ is the generalized Massieu-Planck thermodynamic functional for a stress ensemble. It will be shown later that the Gibbs free energy expression described by Eq. (36) offers a correct entropy expression under the restriction of the dissipation law and as one of the necessary requirements of the second thermodynamic law, provide one with the strain stress relation which, in a general case, is of nonlocal form and can be degenerated into a local one in limiting cases.

V. DISSIPATION INEQUALITY

The Clausius-Duhem dissipation inequality is

$$-\int_V\rho_R(\dot{G}+\dot{T}S)dV+\int_V\left(\dot{\Sigma}:\mathbf{E}-\frac{1}{T}\mathbf{h}\cdot\mathbf{g}\right)dV\geqslant 0, \tag{38}$$

where **h** is the heat flux vector and **g** is the temperature gradient.

Substitution of Eq. (36) into Eq. (38) yields

$$\begin{aligned}
&\Big\{-S^{(0)}(t)+k\ \ln Q_{\sigma}(t)-k\int_V \beta(\mathbf{X},t)[\langle H'_{\sigma}(\mathbf{X},0)\rangle+\Sigma'(\mathbf{X},0):\langle\mathbf{E}^m(\mathbf{X},t)\rangle]dV\\
&\quad+k\int_V\beta(\mathbf{X},t)[\langle H^*_{\sigma}(\mathbf{X},t)\rangle+\tfrac{1}{2}\rho_R(\mathbf{X})\mathbf{v}^2(\mathbf{X},t)]dV\Big\}\dot{T}^{(0)}(t)+\left[\langle\mathbf{E}^{m(0)}(t)\rangle+\frac{1}{V}\left\langle\frac{\partial H^*_{\sigma}(t)}{\partial\Sigma^{(0)}}\right\rangle\right]:\dot{\Sigma}^{(0)}(t)\\
&\quad-\sum_{\substack{r=-\infty\\ r\neq 0}}^{+\infty}\left\{S^{(-r)}(t)+k\beta^{(0)-2}(t)\int_V\beta^2(\mathbf{X},t)[\langle H'_{\sigma}(\mathbf{X},0)\rangle+\Sigma'(\mathbf{X},0):\langle\mathbf{E}^m(\mathbf{X},t)\rangle]e^{irx}dV\right\}\dot{T}^{(r)}(t)\\
&\quad+\sum_{\substack{r=-\infty\\ r\neq 0}}^{+\infty}\left[\langle\mathbf{E}^{m(-r)}(t)\rangle+\frac{1}{V}\left\langle\frac{\partial H^*_{\sigma}(t)}{\partial\Sigma^{(r)}}\right\rangle\right]:\dot{\Sigma}^{(r)}(t)-k\int_V\beta(\mathbf{X},t)\{\mathbf{h}(\mathbf{X},t)+\langle\mathbf{j}'_{H\sigma}(\mathbf{X},t)\rangle\}\cdot\nabla\beta(\mathbf{X},t)dV-\Theta_h(t)+\Theta_s(t)\\
&\quad+\beta^{(0)-1}(t)\Gamma_d(t)\geqslant 0,
\end{aligned}\tag{39}$$

where

$$T^{(0)}(t)=\frac{1}{V}\int_v T(\mathbf{X},t)dV=\frac{1}{V}\int_V[k\beta(\mathbf{X},t)]^{-1}dV,\tag{40}$$

$$\Theta_h=\int_V\int_{\Gamma^*}[\Sigma(\mathbf{X},t):\mathbf{E}^m(\mathbf{X},t)+\mathbf{j}'_{H\sigma}(\mathbf{X},t)\cdot\nabla\beta(\mathbf{X},t)]\left[\{f,H^*\}+\sum_{\alpha}\frac{\partial fF_{\alpha}}{\partial p_{\alpha}}\right]d\Gamma^*dV,\tag{41}$$

$$\Theta_s=\int_V\int_{\Gamma^*}H\left[\{f,H^*\}+\sum_{\alpha}\frac{\partial fF_{\alpha}}{\partial p_{\alpha}}\right]d\Gamma^*dV,\tag{42}$$

$$\begin{aligned}
\Gamma_d=\int_V\int_{-\infty}^{t}\Big\langle\frac{\partial}{\partial t}\Big\{&\mathbf{j}_{H\sigma}(\mathbf{X},t-\tau)\cdot\nabla\beta(\mathbf{X},\tau)+[H'_{\sigma}(\mathbf{X},t-\tau)+\Sigma'(\mathbf{X},t-\tau):\mathbf{E}^m(\mathbf{X},\tau)]\frac{\partial\beta(\mathbf{X},\tau)}{\partial\tau}+\beta(\mathbf{X},\tau)\mathbf{E}^m(\mathbf{X},\tau):\frac{\partial\Sigma'(\mathbf{X},t-\tau)}{\partial\tau}\\
&-\beta(\mathbf{X},\tau)\mathbf{p}'(\mathbf{X},\tau,t)\cdot\frac{\partial\mathbf{v}(\mathbf{X},\tau)}{\partial\tau}\Big\}\Big\rangle dV\,d\tau,
\end{aligned}\tag{43}$$

and

$$\begin{gathered}
S^{(r)}(t)=\frac{1}{V}\int_V S(\mathbf{X},t)e^{-irX}dV,\\
\mathbf{E}^{m(r)}(t)=\frac{1}{V}\int_V\mathbf{E}^m(\mathbf{X},t)e^{-irX}dV,\\
\Sigma^{P(r)}(t)=\frac{1}{V}\int_V\Sigma(\mathbf{X},t)e^{-irX}dV,\\
r=\pm1,\pm2,\ldots,
\end{gathered}\tag{44}$$

represent the corresponding Fourier components of $S(\mathbf{X},t)$, $\mathbf{E}(\mathbf{X},t)$, and $\Sigma(\mathbf{X},t)$, respectively. It should be noted that since creep behaviors are often associated with relatively slow processes, the terms related to the mean inertial effects such as $\partial\mathbf{v}/\partial\tau$, etc., can be neglected.

On account of the fact that the inequality of Eq. (38) must hold for all the admissible thermodynamic processes with respect to arbitrary $\dot{\Sigma}^{(0)}(t)$ and $\dot{\beta}^{(0)}(t)$ on the time scale T_M, the coefficients of $\dot{\Sigma}^{(0)}(t)$ and $\dot{\beta}^{(0)}(t)$ in Eq. (39) should vanish.[12,13] Thus one has

$$S^{(0)}(t)=k\ \ln Q_{\sigma}(t)-k\int_V\beta(\mathbf{X},t)[\langle H'_{\sigma}(\mathbf{X},0)\rangle+\Sigma'(\mathbf{X},0):\langle\mathbf{E}^m(\mathbf{X},t)\rangle]dV+k\int_V\beta(\mathbf{X},t)[\langle H^*_{\sigma}(\mathbf{X},t)\rangle+\tfrac{1}{2}\beta(\mathbf{X},t)\mathbf{v}^2(\mathbf{X},t)]dV\tag{45}$$

and

$$\langle\mathbf{E}^{m(0)}(t)\rangle=-\frac{1}{V}\left\langle\frac{\partial H(t)}{\partial\Sigma^{(0)}}\right\rangle,\tag{46}$$

with the Claussius-Duhem inequality being reduced to

$$-\sum_{\substack{r=-\infty\\ r\neq 0}}^{+\infty}\left\{S^{(-r)}(t)+k\beta^{(0)-2}(t)\int_V\beta^2(\mathbf{X},t)[\langle H'_\sigma(\mathbf{X},0)\rangle+\Sigma'(\mathbf{X},0):\langle\mathbf{E}^m(\mathbf{X},t)\rangle]e^{irX}dV\right\}\dot{T}^{(r)}(t)$$

$$+\sum_{\substack{r=-\infty\\ r\neq 0}}^{+\infty}\left[\langle\mathbf{E}^{m(-r)}(t)\rangle-\left\langle\frac{\partial H^*_\sigma(t)}{\partial\Sigma^{(r)}}\right\rangle\right]:\dot{\Sigma}^{(r)}(t)$$

$$-k\int_V\beta(\mathbf{X},t)\{\mathbf{h}(\mathbf{X},t)+\langle\mathbf{j}'_{H\sigma}(\mathbf{X},t)\rangle\}\cdot\nabla\beta(\mathbf{X},t)dV-\Theta_h(t)+\Theta_s(t)+\beta^{(0)-1}(t)\Gamma_d(t)\geqslant 0. \quad (47)$$

Note that the second term on the right side of Eq. (45) describes the contribution caused by the initial entropy; thus, by letting

$$\langle H'_\sigma(\mathbf{X},0)\rangle=0,\quad \langle\Sigma'(\mathbf{X},0)\rangle=0, \quad (48)$$

one is then left with

$$S^{(0)}(t)=k\ \ln Q_\sigma(t)+k\int_V\beta(X,t)[\langle H^*_\sigma(\mathbf{X},t)\rangle+\tfrac{1}{2}\rho_R(\mathbf{X})\mathbf{v}^2(\mathbf{X},t)]dV, \quad (49)$$

which can be readily shown to be completely identical with the definition of (33) and finally shifted to the entropy expression (32).

Equations (46) and (47) bring about the relations for the global entropy and the average stress-strain equation. Generally, these relations are history dependent and nonlocal. The requirements of Eq. (46) being local with respect to the volume element and being determined merely by the global average arguments $\beta^{(0)}$ and $\mathbf{E}^{(0)}$ imply that all those boundary-dependent integrals in Eq. (28) should be rapidly convergent over the space V. Furthermore, if the higher-order Fourier components of $\Sigma(\mathbf{X},t)$ and $\beta(\mathbf{X},t)$ are taken as controllable arguments, following the same procedure performed for the inequality (39), we can obtain those wavelength-dependent relations

$$S^{(-r)}(t)=k\beta^{(0)-2}(t)\int_V\beta^2(\mathbf{X},t)[\langle H'_\sigma(\mathbf{X},0)\rangle+\Sigma'(\mathbf{X},0):\langle\mathbf{E}^m(\mathbf{X},t)\rangle]e^{irx}dV, \quad (50)$$

$$\langle\mathbf{E}^{m(-r)}(t)\rangle=-\frac{1}{V}\left\langle\frac{\partial H^*_\sigma(t)}{\partial\Sigma^{(4)}}\right\rangle\quad (r=\pm 1,\pm 2,\ldots). \quad (51)$$

From Eq. (51) we have

$$\mathbf{E}^{m(-r)}=-\frac{1}{V}\frac{\partial H^*_\sigma(t)}{\partial\Sigma^{(r)}}\quad (r=0,\pm 1,\pm 2,\ldots), \quad (52)$$

which indicates that there exists a conjugate relation, as that in equilibrium, between the strain and the stress via H^*_σ in irreversible processes. Note that Eqs. (46), (51), and (52) are obtained with the assistance of the modern thermodynamics concepts for materials with memory.

VI. DISCUSSION

Let $\beta(\mathbf{X},t)=\text{const}$, $\Sigma(\mathbf{X},t)=\Sigma(t)$ being independent of spatial location. Thus, for a linearly dissipative system one can assume that the derivation of the system from an (local) equilibrium state is small and the dissipation is much smaller than unity, i.e.,

$$D_\sigma(t)\ll 1. \quad (53)$$

Then, one can expand $f_\sigma(t)$ with respect to $D_\sigma(t)$ and obtain

$$f_\sigma(t)=[1-D_\sigma(t)-\langle D_\sigma(t)\rangle_L]f_{L\sigma}(t)+o[D_\sigma(t)]. \quad (54)$$

Substituting Eq. (54) into Eq. (46) and ignoring higher-order terms of $D_\sigma(t)$, one arrives at

$$\mathbf{E}(t)=-\frac{1}{V}\int_{\Gamma^*}[1-D_\sigma(t)-\langle D_\sigma(t)\rangle_L]f_{L\sigma}(t)\frac{\partial H^*_\sigma(t)}{\partial\Sigma}d\Gamma^*$$

$$=-\frac{1}{V}\left\langle\frac{\partial H^t_\sigma(t)}{\partial\Sigma}\right\rangle_L+\frac{1}{V}\int_{-\infty}^{t}\left[\left\langle\frac{\partial H^*_\sigma}{\partial\Sigma}\frac{\partial H^*_\sigma(t)}{\partial\Sigma}\frac{\partial\Sigma'(t-\tau)}{\partial\tau}\right\rangle_L-\left\langle\frac{\partial H^*_\sigma(\tau)}{\partial\Sigma}\frac{\partial\Sigma'(t-\tau)}{\partial\tau}\right\rangle_L\left\langle\frac{\partial H^*_\sigma(t)}{\partial\Sigma}\right\rangle_L\right]d\tau. \quad (55)$$

Using the same assumption in Refs. 15 and 16 that the relations of Eq. (9) still hold over the locally averaging operation $\langle\ \rangle_L$, namely,

$$\langle q^*_\alpha\rangle_L\equiv 0,\quad \langle p^*_\alpha\rangle_L\equiv 0\quad (\alpha=1,2,\ldots,3N), \quad (56)$$

one has

$$\frac{\partial \Sigma'}{\partial \tau} = \frac{\partial \Sigma}{\partial \tau} \tag{57}$$

after the inertial terms for the mean rigid movement of the system are neglected. Within this approximation one can use Σ to replace Σ' in Eq. (55). Thus we have

$$\begin{aligned}\mathbf{E}(t) &= -\frac{1}{V}\int_{\Gamma^*}[1-D_\sigma(t)-\langle D_\sigma(t)\rangle_L]f_{L\sigma}(t)\frac{\partial H_\sigma^*(t)}{\partial \Sigma}d\Gamma^* \\ &= -\frac{1}{V}\left\langle\frac{\partial H_\sigma^*(t)}{\partial \Sigma}\right\rangle_L + \frac{1}{V}\int_0^t\left[\left\langle\frac{\partial H_\sigma^*(t-\tau)}{\partial \Sigma}\,\frac{\partial H_\sigma^*(t)}{\partial \Sigma}\right\rangle_L - \left\langle\frac{\partial H_\sigma^*(t-\tau)}{\partial \Sigma}\right\rangle_L\left\langle\frac{\partial H_\sigma^*(t)}{\partial \Sigma}\right\rangle_L\right]:\frac{\partial \Sigma(\tau)}{\partial \tau}d\tau. \end{aligned} \tag{58}$$

Here, we have used the assumption that the external loading commences at $t=0$ so that $\Sigma(t)=\mathbf{0}$ for $t<0$ and that $\Sigma(t-\tau)\equiv\mathbf{0}$ for $\tau>t$.

As a result of Eqs. (56) and (57) a physical interpretation can be given to the linear thermo-viscoelastic creep function

$$\mathbf{E}(t)=\mathbf{E}^e(t)+\int_0^t \mathbf{\Omega}[t,\tau;\{\Sigma\}]:\frac{\partial \Sigma(\tau)}{\partial \tau}d\tau. \tag{59}$$

Evidently,

$$\mathbf{E}^e(t) = -\frac{1}{V}\left\langle\frac{\partial H_\sigma^*(t)}{\partial \Sigma}\right\rangle_L \tag{60}$$

indicates the instantaneously elastic effect, and

$$\mathbf{\Omega}[t,\tau;\{\Sigma\}]=\frac{1}{V}\left[\left\langle\frac{\partial H_\sigma^*(t-\tau)}{\partial \Sigma}\,\frac{\partial H_\sigma^*(t)}{\partial \Sigma}\right\rangle_L - \left\langle\frac{\partial H_\sigma^*(t-\tau)}{\partial \Sigma}\right\rangle_L\left\langle\frac{\partial H_\sigma^*(t)}{\partial \Sigma}\right\rangle_L\right] \tag{61}$$

is the creep function. Equation (61) reveals an interesting result that the viscoelastic creep, like stress relaxation, also originated from fluctuations. Equation (61) can be viewed as a special case of the fluctuation-dissipation theorem which has been used in linearly dissipative thermodynamics processes. Note that the time correlation function in Eq. (61) is somewhat different from the results that appeared in some previous literature (cf. Ref. 18), as the averaging operation is not over an equilibrium distribution function but attributed to a local equilibrium state. In addition, the expression for $\mathbf{\Omega}$ is self-contained, namely, it is only associated with the Hamiltonian and its derivatives with respect to stress components.

The averaging operation in Eq. (61) is with respect to the current coordinates and momenta of the system, yet there exist mechanical quantities containing the past histories. Hence a numeric kinetics computation usually is necessary. It is possible, however, for one to obtain some analytical results under approximate assumptions.

Consider a system consisting of one-dimensional damped oscillators (under the assumption that there are two different characteristic time scales). Suppose that the Hamiltonian can be expanded into the quadratic form in the reference configuration, namely,

$$H_\sigma^* = \frac{1}{2m}p_\alpha^* p_\alpha^* + A_{ij}(\Sigma)q_i^* q_j^* \quad (i,j,=1,2,3,\ldots,N), \tag{62}$$

where

$$A_{ij}=\frac{\partial^2 H_\sigma^*}{\partial q_i^* \partial q_j^*} \tag{63}$$

only depends on Σ and thereby varies with time relatively slowly, and q_i^* in Eqs. (62) and (63) are specified by Eq. (8). It is supposed here that q_i^* $(i=1,2,3,\ldots,N)$ are considerably greater than their mean fluctuation $\langle q_i^{*2}\rangle^{1/2}$. Thus Eq. (61) can be written as

$$\begin{aligned}\Omega(\tau,t) &= Q_{L\sigma}^{-1}(t)\int_{\Gamma^*}e^{-\beta(t)H_\sigma^*(t)}\frac{\partial H_\sigma^*(t)}{\partial \Sigma}\,\frac{\partial H_\sigma^*(t-\tau)}{\partial \Sigma}d\Gamma^* \\ &= Q_{L\sigma}^{-1}(t)\int_{\Gamma_{\delta p}^*}e^{-(1/2m)\beta(t)p_\alpha^*(t)p_\alpha^*(t)}d\Gamma_p^*\int_{\Gamma_q^*}e^{-(1/2)\beta(t)A_{ij}(t)q_i^*(t)q_j^*(t)}C_{ij}(t)C_{kl}^t(t)q_i^*(t)q_j^*(t)q_k^{*t}(t)q_l^{*t}(t)d\Gamma_q^*\end{aligned} \tag{64}$$

in which

$$C_{ij}(t)=\frac{\partial^3 H_\sigma^*}{\partial \Sigma\, \partial q_i^* \partial q_j^*},\quad C_{kl}^t(t)\equiv C_{kl}(t-\tau),\quad q_i^{*t}(t)\equiv q_i^*(t-\tau)\quad (i,j,k,l=1,2,3,\ldots,N). \tag{65}$$

On the basis of the assumption that there exist two different time scales in the system as stated previously, if supposing that the particles' motion is proportionally damped, an analytical form of $\Omega(t,\tau)$ can be obtained (cf. Appendix for details). In fact, beginning with

$$M_{ij}q_j^*(t)+\lambda_{ij}q_j^*(t)+A_{ij}q_j^*(t)=0 \quad (i,j=1,2,3,\ldots,N) \tag{66}$$

and

$$\lambda_{ij}=\gamma_1(\beta)M_{ij}+\gamma_2(\beta)A_{ij}, \tag{67}$$

where $M_{ij}=m\delta_{ij}$, λ_{ij}, and A_{ij} are known as mass matrix, damp matrix, and stiffness matrix, respectively, γ_1 and γ_2 are damping coefficients, which could be obtained for friction solids on the basis of some empirical and theoretical models, we can finally arrive at

$$\Omega(t,\tau)=\sum_{u,v}\left[\Lambda_{uv}^{(1)}(t,\tau)+\Lambda_{uv}^{(2)}(t,\tau)\right]\exp\left(-\frac{t-\tau}{\tau_{uv}}\right), \tag{68}$$

where

$$\Lambda_{uv}^{(1)}(t,\tau)=\Omega_{L\sigma}^{-1}(t)\Xi_{mnrs}(t,\tau)\mu_{ru}^t(t)\mu_{sv}^t(t)\int_{\Gamma_p^*}e^{-[\beta(t)/2m]p_\alpha^*(t)p_\alpha^*(t)}d\Gamma_p^*\int_{\Gamma_x^*}e^{-\beta(t)D_{nn}(t)x_n(t)x_n(t)}x_m(t)x_n(t)$$
$$\times\left[g_{m'}^t(t)g_{n'}^t(t)x_{m'}(t)x_{n'}(t)+h_{k'}^t(t)h_{l'}^t(t)p_{k'}^*(t)p_{l'}^*(t)\right]|J|d\Gamma_x^* \tag{69}$$

and

$$\Lambda_{uv}^{(2)}(t,\tau)=Q_{L\sigma}^{-2}\Xi_{mnrs}(t,\tau)\mu_{ru}^t(t)\mu_{sv}^t(t)g_{m'}^t(t)g_{n'}^t(t)\int_{\Gamma_p^*}e^{-[\beta(t)/2m]p_\alpha^*(t)p_\alpha^*(t)}d\Gamma_p^*\int_{\Gamma_x^*}e^{-\beta(t)D_{nn}(t)x_n(t)x_n(t)}x_m(t)x_n(t)|J|d\Gamma_x^*$$
$$\times\int_{\Gamma_p^*}e^{-[\beta(t)/2m]p_\alpha^*(t)p_\alpha^*(t)}d\Gamma_p^*\int_{\Gamma_X^*}e^{-\beta(t)D_{nn}(t)x_n(t)x_n(t)}x_{m'}(t)x_{n'}(t)|J|d\Gamma_x^*\,. \tag{70}$$

In (68) $\tau_{uv}=(\xi_u\omega_u+\xi_v\omega_v)^{-1}$ $(u,v=1,2,3,\ldots,N)$ denote the retardation times (no summation is made on u and v here).

In the above expressions, $\{x_n\}$ are the coordinates defined by

$$q_i^*(t)=a_{ij}(t)x_j(t) \tag{71}$$

and μ_{ij} is a matrix which transforms x_i into a principal coordinate. And, $\xi_i=\frac{1}{2}[\gamma_1(\beta)+\gamma_2(\beta)\omega_i^2]\omega_i^{-1}$, where ω_i $(i=1,2,3,\ldots,N)$ are the natural frequencies of the corresponding conservative system of Eq. (66), $|J|$ is the Jacobean from $\{q^*\}$ space to $\{x\}$ space, and $\Xi_{mnrs}(t,\tau)$, $g_i^t(t)$, and $h_i^t(t)$ are functions of time and Σ but independent of $\{p^*,q^*\}$ and defined in the Appendix.

Equation (68) gives the spectra of viscoelastic creep function described by (58), from which a relation between the macroscopic retardation times and the relaxation properties of microparticles is explicitly demonstrated. Especially, the integration of the expressions (69) and (70) can be calculated analytically, but we do not give them here for brevity. A detailed analysis to $\Lambda_{uv}^{(1)}$ and $\Lambda_{uv}^{(2)}$ shows that they are dependent on the square of the temperature.

VII. CONCLUDING REMARKS

Unlike the deriving of viscous coefficients of fluids in terms of statistical mechanics approaches, the determination of creep function of solids cannot start from such an idea that is the identification of the microscopic conservative equation for momentum with the analogous one, say, the Navier-Stokes equation, from continuum mechanism which contains viscosity as an empirical transport coefficient. Instead, we establish the description of the viscoelastic creep function from the thermodynamic functionals based on a nonequilibrium stress ensemble, in which the local temperature and stresses as well as their histories are taken as kinetic controllable arguments. In fact, based on a nonequilibrium stress ensemble established, the nonlinear creep stress-strain relations given by Eqs. (46) and (51) are obtained as one of the necessary requirements of dissipation restriction to the thermodynamic functional in arbitrarily irreversible processes. Principally, once the kinetics behaviors of microparticles in the system are known, the creep function can be obtained from the expressions of Eqs. (46) and (51).

Under the condition of linear dissipative processes, the expression of Eq. (46) can be reduced to a simpler case. The creep function is then related to the way in which spontaneous fluctuations regress in a local equilibrium system. A one-dimensional analytical results of creep function for this case is obtained under some approximations, through which one is able to get some insight into the connection of the viscoelastic creep to the internal relaxation of microparticles. More realistic models are being considered in our succeeding work.

In addition, our attention has been confined to the situation to which the classical statistical mechanics applies, since creep problems frequently occur at relatively high temperatures. Under this condition, quantum effects are usually not important. In fact, through an analogy of the classical theory, a quantum description for our problem could also be available.

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APPENDIX

Proof of the derivation for (68) is as follows.

The creep function for a linearly dissipative process is as follows [cf. Eq. (61) in the context]:

$$\Omega(t,\tau)=\left\langle \frac{\partial H_\sigma^*(t)}{\partial\Sigma}\frac{\partial H_\sigma^*(t-\tau)}{\partial\Sigma}\right\rangle_L - \left\langle \frac{\partial H_\sigma^*(t)}{\partial\Sigma}\right\rangle_L \left\langle \frac{\partial H_\sigma^*(t-\tau)}{\partial\Sigma}\right\rangle_L \equiv \Omega^{(1)}(t,\tau)-\Omega^{(2)}(t,\tau), \tag{A1}$$

where the averaging operation is over the local equilibrium for a stress ensemble, e.g.,

$$\Omega^{(1)}(t,\tau)=Q_{L\sigma}^{-1}(T)\int_{\Gamma^*} e^{-\beta(t)H_\sigma^*(t)} \times\frac{\partial H_\sigma^*(t)}{\partial\Sigma}\frac{\partial H_\sigma^*(t-\tau)}{\partial\Sigma}d\Gamma^*, \tag{A2}$$

in which

$$Q_{L\sigma}(t)=\int_{\Gamma^*} e^{-\beta(t)H_\sigma^*(t)}d\Gamma^*. \tag{A3}$$

Note that the Hamiltonian H_σ^* can be decomposed into two parts,

$$H_\sigma^*=K(p^*)+V_\sigma(q^*;\Sigma) = \frac{1}{2m}p_\alpha^* p_\alpha^*+V_\sigma(q^*;\Sigma) \quad (\alpha=1,2,3,\ldots,N), \tag{A4}$$

where $V_\sigma(q^*;\Sigma)$ denotes the potential term depending only on the coordinates and current stress Σ. Here and hereafter the summation convention over repeated indices is used and a specification would be given otherwise. Expanding H_σ^* into the quadratic form with respect to the coordinates q_i^*, we have

$$H_\sigma^*(t)=\frac{1}{2m}p_\alpha^*(t)p_\alpha^*(t)+A_{ij}(\sigma)q_i^*(t)q_j^*(t) \quad (i,j,\alpha=1,2,3,\ldots,N), \tag{A5}$$

where

$$A_{ij}=\frac{\partial^2 V_\sigma}{\partial q_i^*\partial q_j^*}. \tag{A6}$$

Thus Eq. (A2) is reduced to

$$\Omega^{(1)}(t,\tau)=Q_{L\sigma}^{-1}(t)\int_{\Gamma^*} e^{-\beta(t)[(1/2m)p_\alpha^*(t)p_\alpha^*(t)+(1/2)A_{ij}q_i^*(t)q_j^*(t)]}C_{ij}(t)C_{kl}^t(t)q_i^*(t)q_j^{*t}(t)q_k^{*t}(t)q_l^{*t}d\Gamma^*, \tag{A7}$$

where

$$C_{ij}(t)=\frac{\partial A_{ij}}{\partial\Sigma},\quad C_{ij}^t(t)\equiv C_{ij}(t-\tau),\quad q_i^{*t}\equiv q_i^*(t-\tau). \tag{A8}$$

For convenience of calculation we use a coordinates transform to make the term $\frac{1}{2}A_{ij}q_iq_j$ be of a standard quadratic form, i.e., by letting

$$q_i^*(t)=a_{ij}(t)x_j(t), \tag{A9}$$

we have

$$\tfrac{1}{2}A_{ij}q_i^*q_j^*=D_{nn}x_nx_n, \tag{A10}$$

while a_{ij} satisfying

$$\tfrac{1}{2}A_{mn}a_{im}a_{jn}=D_{nn}\delta_{ij} \tag{A11}$$

in which δ_{ij} is the Kronecker delta. Thus Eq. (A7) becomes

$$\Omega^{(1)}(t,\tau)=Q_{L\sigma}^{-1}(t)\Xi_{mnrs}(t,\tau)\int_{\Gamma^*} e^{-\beta(t)[(1/2m)p_\alpha^*(t)p_\alpha^*(t)+D_{nn}x_n(t)x_n(t)]}x_m(t)x_n(t)x_r^t(t)x_s^t(t)|J|d\Gamma^*, \tag{A12}$$

where

$$\Xi_{mnrs}(t,\tau)=C_{ij}(t)C^{t}_{kl}(t)a_{im}(t)a_{jn}(t)a^{t}_{kr}(t)a^{t}_{ls}(t).$$

Here, $|J|$ is the transform from the space of $\{q\}$ to that of $\{x\}$.

To calculate Eq. (A12) the kinetics behaviors of particles are needed. In a nonconservative system the motion of particles is governed by

$$\dot{p}_i(t)=-\frac{\partial H(t)}{\partial q_i}+f_i \quad (i=1,2,3,\ldots,N), \tag{A13}$$

where f_i denotes the external force exerted on the ith particle, and it depends upon the momenta of the system and the arguments of the environment.

Since we have assumed in the context that there exist two different characteristic time scales between the macroscopically averaged movement and the thermal motion of microparticles around it, namely,

$$\dot{q}^{*}_i(t)\gg\frac{d}{dt}\langle q_i(t)\rangle, \quad \dot{p}^{*}_i\gg\frac{d}{dt}\langle p_i(t)\rangle, \tag{A14}$$

we approximately have

$$\dot{p}^{*}_i(t)=-\frac{\partial H^{*}(t)}{\partial q^{*}_i}+f_i\equiv-\frac{\partial H^{*}_{\sigma}(t)}{\partial q^{*}_i}+f_i. \tag{A15}$$

By substituting Eq. (A5) into Eq. (A15) and assuming that

$$f_i=-\lambda_{ij}(\beta)\dot{q}^{*}_j \tag{A16}$$

we have

$$m\delta_{ij}\ddot{q}^{*}_i+\lambda_{ij}\dot{q}^{*}_i+A_{ij}q^{*}_i=0 \quad (i,j=1,2,3,\ldots,N). \tag{A17}$$

Using the linear transform of Eq. (A9), Eq. (A17) can be reduced to

$$\tilde{m}_{ik}\ddot{x}_k+\tilde{\lambda}_{ik}\dot{x}_k+\tilde{A}_{ik}x_k=0 \quad (i,k=1,2,3,\ldots,N), \tag{A18}$$

where

$$\tilde{m}_{ik}=m\delta_{ij}a_{jk}, \quad \tilde{\lambda}_{ik}=\lambda_{ij}a_{jk}, \quad \tilde{A}_{ik}=A_{ij}a_{jk}. \tag{A19}$$

In deriving Eq. (A18) from Eqs. (A17) and (A9), we have tacitly used the assumption that the coefficient matrices are time dependent via the argument $\Sigma(t)$ and their varying with time is much slower than that of the thermal motion of particles, such that the coefficients can be dealt with being frozen as the first-order approximation.

For the case that damping matrix can be treated as

$$\tilde{\lambda}_{ij}=\gamma_1(\beta)\tilde{m}_{ij}+\gamma_2(\beta)\tilde{A}_{ij}, \tag{A20}$$

where $\gamma_1(\beta)$ and $\gamma_2(\beta)$ are "frictional coefficients." Equation (A18) is decoupled in the principal coordinates

$$x_i=\mu_{ij}\eta_j, \tag{A21}$$

where η_j $(i=1,2,3,\ldots,N)$ are the normal coordinates of the corresponding conservative system of Eq. (A18). That is,

$$\ddot{\eta}_i+2\omega_i\xi_i\dot{\eta}_i+\omega_i^2\eta_i=0 \quad (i=1,2,3,\ldots,N), \tag{A22}$$

in which $\xi_i=\frac{1}{2}[\gamma_1(\beta)+\gamma_2(\beta)\omega_i^2]\omega_i^{-1}$, and ω_i are the frequencies of the conservative system corresponding to Eq. (A18) and are determined by

$$\det(-\omega^2 m\delta_{ij}+A_{ij})=0. \tag{A23}$$

The solution of Eq. (A22) subject to the initial conditions $\eta_i(0)=\eta_i^0$ and $\dot{\eta}_i^0$ is

$$\eta_i(t)=e^{-\xi_i\omega_i t}[g_i'(t)\eta_i^0+h_i'(t)\dot{\eta}_i^0], \tag{A24}$$

where

$$g_i'(t)=\cos\sqrt{1-\xi_i^2}\,\omega_i t+\frac{\xi_i}{\sqrt{1-\xi_i^2}}\sin\sqrt{1-\xi_i^2}\,\omega_i t \tag{A25}$$

and

$$h_i'(t)=\frac{1}{\sqrt{1-\xi_i^2}}\sin\sqrt{1-\xi_i^2}\,\omega_i t. \tag{A26}$$

Thus one has

$$\eta_i^t\equiv\eta_i(t-\tau)=e^{-\xi_i\omega_i(t-\tau)}[g_i^t(t)\eta_i(t)+h_i^t(t)\dot{\eta}_i(t)], \tag{A27}$$

where

$$g_i^t(t)\equiv g_i(t-\tau)=\cos\sqrt{1-\xi_i^2}\,\omega_i(t-\tau)-\frac{\xi_i}{\sqrt{1-\xi_i^2}}\sin\sqrt{1-\xi_i^2}\,\omega_i(t-\tau) \tag{A28}$$

and

$$h_i^t(t)\equiv h_i(t-\tau)=-\frac{1}{\sqrt{1-\xi_i^2}}\sin\sqrt{1-\xi_i^2}\,\omega_i(t-\tau). \tag{A29}$$

Note that in the expressions of Eqs. (A21)–(A29), no summation is implemented over the repeated indices.

With consideration of the transforms of Eqs. (A9) and (A21), we have

$$x_r^t(t)x_s^t(t)=\mu_{vu}^t(t)\mu_{sr}^t(t)e^{-(\xi_u\omega_u+\xi_v\omega_v)(t-\tau)}[g_{m'}^t(t)g_{n'}^t(t)x_{m'}(t)x_{n'}(t)+g_{m'}^t(t)h_{l'}^t(t)x_{m'}(t)p_{l'}^*(t)$$
$$+h_{k'}^t(t)g_{n'}^t(t)p_{k'}^*(t)x_{n'}(t)+h_{k'}^t(t)h_{l'}^t(t)p_{k'}^*(t)p_{l'}^*(t)], \tag{A30}$$

where

$$g_{m'}^t(t)=g_u^t(t)\mu_{um'}^{t-1}(t),\quad g_{n'}^t=g_v^t(t)\mu_{vn'}^{t-1}(t),$$

$$h_{k'}^t(t)=\frac{1}{m}h_u^t(t)\mu_{ue}^{t-1}(t)a_{ek'}^{t-1}(t),\quad h_{l'}^t(t)=\frac{1}{m}h_v^t(t)\mu_{vf}^{t-1}(t)a_{f\,l'}^{t-1}(t)\quad (m',n',k',l',u,v,e,f=1,2,3,\ldots,N), \tag{A31}$$

where μ_{ij}^{t-1} $(i,j=1,2,3,\ldots,N)$ is the inverse of μ_{ij}^t. Substitution of Eq. (A31) into Eq. (A12) leads to

$$\Omega^{(1)}(t,\tau)=Q_{L\sigma}^{-2}(t)\Xi_{mnrs}(t,\tau)\int_{\Gamma_p^*}e^{-[\beta(t)/2m]p_\alpha^*(t)p_\alpha^*(t)}d\Gamma_p^*\int_{\Gamma_x^*}e^{-\beta(t)D_{nn}(t)x_n(t)x_n(t)}x_m(t)x_n(t)x_r^t(t)x_s^t(t)$$
$$\times[g_{m'}^t(t)g_{n'}^t(t)x_{m'}(t)x_{n'}(t)+g_{m'}(t)h_{l'}^t(t)x_{m'}(t)p_{l'}^*(t)+h_{k'}^t(t)g_{n'}^t(t)p_{k'}^*(t)x_{n'}(t)+h_{k'}^t(t)h_{l'}^t(t)p_{k'}^*(t)p_{l'}^*(t)]$$
$$\times\exp[-(\xi_u\omega_u+\xi_v\omega_v)(t-\tau)]d\Gamma_x^*. \tag{A32}$$

Similarly, we can have

$$\Omega^{(2)}(t,\tau)=\left\langle\frac{\partial H_\sigma^*(t)}{\partial\Sigma}\right\rangle_L\left\langle\frac{\partial H_\sigma^*(t-\tau)}{\partial\Sigma}\right\rangle_L$$
$$=Q_{L\sigma}^{-2}(t)\Xi_{mnrs}(t,\tau)\int_{\Gamma_p^*}e^{-[\beta(t)/2m]p_\alpha^*(t)p_\alpha^*(t)}d\Gamma_p^*\int_{\Gamma_x^*}e^{-\beta(t)D_{nn}(t)x_n(t)x_n(t)}x_m(t)x_n(t)|J|d\Gamma_p^*$$
$$\times\int_{\Gamma_p^*}e^{-[\beta(t)/2m]p_\alpha(t)p_\alpha(t)}d\Gamma_p^*\int_{\Gamma_x^*}e^{-\beta(t)D_{nn}(t)x_n(t)x_n(t)}\mu_{ru}^t(t)\mu_{vs}^t(t)$$
$$\times[g_{m'}^t(t)g_{n'}^t(t)x_{m'}(t)x_{n'}(t)+g_{m'}^t(t)h_{l'}^t(t)x_{m'}(t)p_{l'}^*(t)$$
$$+h_{k'}^t(t)g_{n'}^t(t)p_k^*(t)x_{n'}(t)+h_{k'}^t(t)h_{l'}^t(t)p_{k'}^*(t)p_{l'}^*(t)]$$
$$\times\exp[-(\xi_u\omega_u+\xi_v\omega_v)(t-\tau)]|J|d\Gamma_x^*. \tag{A33}$$

Calculation of Eqs. (A32) and (A33) and substitution of them into Eq. (A1) give one the final result of Eq. (68) appearing in the context.

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[*] On leave as a visiting scientist from Institute of Solid Mechanics, Beijing University of Aeronautics & Astronautics, Beijing, China.

[†] Author to whom all correspondence should be addressed.

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