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ARTICLES

Theory of stress fluctuations

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The current status of the theory of stress fluctuations is marked by two circumstances: no currently available formulas are valid for a metallic system, and a series of contradictory formulas remains unresolved. Here we derive formulas for shear- and isotropic-stress energy fluctuations, in the primary statistical mechanics ensembles. These formulas are valid for a classical monatomic system representing a metal or nonmetal, in cubic crystal, amorphous solid, or liquid phases. Current contradictions in fluctuation formulas are resolved through the following observations. First, the expansion of a dynamical variable $\mathcal{A}$ in terms of the fluctuations explicit in a given ensemble distribution, for example $\delta\mathcal{A}=a\,\delta\mathcal{N}+b\,\delta\mathcal{H}$ in the grand canonical ensemble, is correct if and only if $\delta\mathcal{A}$ is a function only of $\delta\mathcal{N}$ and $\delta\mathcal{H}$. The common use of this expansion has produced incorrect fluctuation formulas. Second, the thermodynamic fluctuations of Landau and Lifshitz do not correspond to statistical mechanics fluctuations, and the two types of fluctuations have essentially different values.

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I. INTRODUCTION

We have recently developed an accurate and comprehensive theory of the motion of atoms in a monatomic liquid [1–6]. Equilibrium thermodynamic properties have been calculated from the partition function [1,2], and nonequilibrium properties have been modeled with increasing accuracy, including the glass transition [3], and the velocity autocorrelation function [4–6]. We have now turned our attention to the stress autocorrelation functions, whose integrals yield the liquid viscosity coefficients [7,8]. The first step in analyzing such functions is to evaluate them at zero time, where they become simply stress fluctuations. Regarding stress fluctuations, the literature reveals two important circumstances: (a) because of the volume dependences in the potential energy governing the motion of ions in a metal, no currently available formulas are valid for a metal, and (b) for pressure fluctuations, a number of conflicting formulas have been presented, and the contradictions are currently unresolved. The purpose of this paper is to derive stress fluctuation formulas for a classical monatomic solid or liquid metal, and to resolve the current contradictions regarding the theory of pressure fluctuations.

Statistical mechanics is based on averaging, according to a statistical probability distribution, the dynamical properties of a mechanical system. Here, fluctuations measure the widths of the distribution in various phase-space directions. These fluctuations are important when they appear in a theoretical derivation of a given material property, as when stress fluctuations appear in the liquid viscosity theory [7,8]. Since each statistical ensemble has its unique statistical distribution, the fluctuations are strongly ensemble dependent. To compare different theoretical results, it will be necessary to account for the ensemble differences of order 1 in stress fluctuations. On the other hand, in the present work we can ignore the ensemble differences of order N^{-1} which appear in both mean values and fluctuations. In Sec. II, formulas are derived in classical statistical mechanics for fluctuations of shear and isotropic components of the stress energy tensor, for a monatomic system in solid or liquid phase, and in various ensembles of interest. These formulas are compared in Sec. III with previous statistical mechanics results.

A different formulation of fluctuations, presented by Landau and Lifshitz [9,10], has come to be known as ‘‘thermodynamic fluctuations.’’ To understand the meaning of thermodynamic fluctuations, and to see how they differ *essentially* from statistical mechanics fluctuations, it is helpful to make a logically simple reconstruction of the derivation of Landau and Lifshitz. This is done in Sec. III, and the reasons for inconsistencies in pressure fluctuation formulas become obvious. Our conclusions are summarized in Sec. IV.

II. STRESS FLUCTUATION FORMULAS

A. The system

The system is composed of N similar atoms in a volume V, metal or nonmetal, in solid or liquid phase. The position and velocity of ion K are $\mathbf{r}_K$ and $\mathbf{v}_K$, respectively, for $K=1,\cdots,N$, and the Hamiltonian is

$$\mathcal{H}=\tfrac{1}{2}m\Sigma_K\mathbf{v}_K^2+\Phi(\{\mathbf{r}_K\}). \tag{1}$$

The potential energy is expressed in the form based on electronic structure theory

$$\Phi=\Omega(V)+\tfrac{1}{2}\Sigma'_{KL}\varphi(|\mathbf{r}_K-\mathbf{r}_L|;V), \tag{2}$$

where $\Omega(V)$ is the major binding potential, $\varphi(r;V)$ is the effective ion–ion potential, and irreducible n-ion potentials for $n\geqslant 3$ are neglected. The volume dependences in Φ are crucial for a metal. The motion of the ions is treated as classical and, since we are interested in thermodynamic quantities, the system center of mass is fixed.

We have derived formulas in the canonical ensemble for the stresses and elastic constants of the above system [11]. These formulas have been used to calculate elastic constants as function of temperature for bcc sodium [12], and for hcp magnesium [13]. Here we will solve these formulas for stress fluctuations in terms of elastic constants. Volume and distance derivatives of φ are abbreviated as follows:

$$\begin{aligned}\varphi^* &= V(\partial\varphi/\partial V),\\ \varphi^{**} &= V^2(\partial^2\varphi/\partial V^2),\\ \varphi' &= r(\partial\varphi/\partial r),\\ \varphi'' &= r^2(\partial^2\varphi/\partial r^2),\\ \varphi'^* &= rV(\partial^2\varphi/\partial V\partial r).\end{aligned} \tag{3}$$

The volume derivatives Ω^* and Ω^{**} are similar. Cartesian components of $\mathbf{r}$ are written in the form $\hat{r}_i = r_i/|\mathbf{r}|$, and the following tensors are defined:

$$\begin{aligned}\phi_{ij} &= \varphi^*\delta_{ij} + \varphi'\hat{r}_i\hat{r}_j,\\ \varphi_{ijkl} &= (\varphi^{**}+\varphi^*)\delta_{ij}\delta_{kl} - \varphi^*(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) + \phi'^*(\delta_{ij}\hat{r}_k\hat{r}_l\\ &\quad + \delta_{kl}\hat{r}_i\hat{r}_j) + (\varphi''-\varphi')\hat{r}_i\hat{r}_j\hat{r}_k\hat{r}_l.\end{aligned} \tag{4}$$

We use the shorthand notation $\Sigma\varphi$ for the sum $\frac{1}{2}\Sigma'_{KL}\varphi_{KL}$ which appears in Eq. (2), and $\langle\cdots\rangle$ represents a canonical ensemble average. Then the stresses τ_{ij}, and the isothermal elastic constants C^T_{ijkl}, are given by [11]

$$\begin{aligned}V\tau_{ij} &= (\Omega^* - NkT)\delta_{ij} + \langle\Sigma\varphi_{ij}\rangle,\\ VC^T_{ijkl} &= (\Omega^{**}+\Omega^*)\delta_{ij}\delta_{kl} + (NkT-\Omega^*)(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})\\ &\quad + \beta[\langle\Sigma\phi_{ij}\rangle\langle\Sigma\varphi_{kl}\rangle - \langle\Sigma\varphi_{ij}\Sigma\varphi_{kl}\rangle] + \langle\Sigma\varphi_{ijkl}\rangle,\end{aligned} \tag{5}$$

where T is temperature and $\beta = 1/kT$.

Two limitations will be imposed to simplify the presentation without losing any essential features of the theory. First, the applied stress is isotropic pressure P, which means the shear stresses τ_{ij} for $i \neq j$ vanish, and

$$\tau_{ij} = -P\delta_{ij}. \tag{6}$$

From Eq. (5) it follows

$$PV = -\Omega^* + NkT - \langle\Sigma(\phi^* + \tfrac{1}{3}\varphi')\rangle. \tag{7}$$

Second, the system will have cubic or isotropic symmetry, so the Cartesian directions *x*,*y*,*z* are equivalent. In other words the system will be a cubic crystal, an amorphous solid, or a liquid.

B. Derivation of stress fluctuations

The microscopic stress energy tensor σ_{ij}, a dynamical variable, is defined by

$$\begin{aligned}\sigma_{ij} &= -\Omega^*\delta_{ij} + m\Sigma_K v_{Ki}v_{Kj} - \tfrac{1}{2}\Sigma'_{KL}(\phi^*_{KL}\delta_{ij}\\ &\quad + \hat{r}_{KLi}\hat{r}_{KLj}\phi'_{KL}),\end{aligned} \tag{8}$$

and satisfies, by virtue of the system symmetry and Eq. (7),

$$\langle\sigma_{ij}\rangle = PV\delta_{ij}. \tag{9}$$

With the abbreviations Eqs. (3) and (4), the shear components are written

$$\sigma_{xy} = m\Sigma v_x v_y - \Sigma\varphi_{xy}. \tag{10}$$

In view of Eq. (9), $\langle\sigma_{xy}\rangle = 0$. To calculate the fluctuation $\langle(\sigma_{xy})^2\rangle$, we use the canonical ensemble averages, for systems with cubic or isotropic symmetry,

$$\begin{aligned}\langle(\Sigma m v_x v_y)^2\rangle &= N(kT)^2,\\ \langle(\Sigma m v_x v_y)(\Sigma\phi_{xy})\rangle &= 0,\end{aligned} \tag{11}$$

and we solve for $\langle(\Sigma\varphi_{xy})^2\rangle$ from the elastic constant $C^T_{xyxy} = C^T_{44}$. The result is

$$\beta\langle(\sigma_{xy})^2\rangle = NkT - VB^T_{44} + \tfrac{1}{15}\langle\Sigma(\varphi''+4\varphi')\rangle, \tag{12}$$

where $B^T_{44} = C^T_{44} - P$ [14]. The average on the right side can be transformed to an integral over the pair distribution $g(r)$, from the general relation

$$\frac{1}{2}\Sigma'_{KL}f(r_{KL}) = 2\pi\rho N\int_0^\infty f(r)g(r)r^2\,dr, \tag{13}$$

where $\rho = N/V$. The final result for the shear stress fluctuation is

$$\begin{aligned}\beta\langle(\sigma_{xy})^2\rangle &= NkT - VB^T_{44} + \frac{2\pi}{15}N\rho\int_0^\infty[\varphi''(r)\\ &\quad + 4\varphi'(r)]g(r)r^2\,dr.\end{aligned} \tag{14}$$

For an amorphous solid, $B^T_{44} = \frac{1}{2}(B^T_{11} - B^T_{12})$, while $B^T_{44} = 0$ for a liquid.

The dynamical variable representing the isotropic stress energy is $\mathcal{Q}$,

$$\mathcal{Q} = \tfrac{1}{3}\Sigma_i\sigma_{ii}. \tag{15}$$

From Eq. (8) for σ_{ij} we have

$$\mathcal{Q} = -\Omega^* + \tfrac{2}{3}\mathcal{K} - \mathcal{W}, \tag{16}$$

where $\mathcal{K}$ is the kinetic energy in the center of mass system

$$\mathcal{K} = \tfrac{1}{2}m\Sigma v^2, \tag{17}$$

and $\mathcal{W}$ is the generalized virial

$$\mathcal{W} = \tfrac{1}{3}\Sigma_i\Sigma\varphi_{ii}. \tag{18}$$

Note that Ω^* in Eq. (16) does not contribute to fluctuations in $\mathcal{Q}$. Defining the fluctuation variable as $\delta\mathcal{A} = \mathcal{A} - \langle\mathcal{A}\rangle$, we find

$$\delta\mathcal{Q}=\mathcal{Q}-PV=\tfrac{2}{3}\,\delta\mathcal{K}-\delta\mathcal{W},$$

$$\delta\mathcal{K}=\mathcal{K}-\tfrac{3}{2}NkT, \tag{19}$$

$$\delta\mathcal{W}=\mathcal{W}-\langle\Sigma(\varphi^{*}+\tfrac{1}{3}\varphi')\rangle.$$

From this point we need to distinguish averages of a given fluctuation which differ in relative order 1 in different ensembles. Averages in the canonical ensemble are denoted $\langle\cdots\rangle_C$, and we have

$$\langle\delta\mathcal{K}^2\rangle_C=\tfrac{3}{2}N(kT)^2,$$

$$\langle\delta\mathcal{K}\delta\mathcal{W}\rangle_C=0, \tag{20}$$

so that the fluctuation in $\mathcal{Q}$ becomes

$$\langle\delta\mathcal{Q}^2\rangle_C=\tfrac{2}{3}N(kT)^2+\langle\delta\mathcal{W}^2\rangle_C. \tag{21}$$

Finally we can write Eq. (5) for the combination of elastic constants

$$VB_T=\tfrac{1}{3}V(B_{11}^T+2B_{12}^T)=\tfrac{1}{3}V(C_{11}^T+2C_{12}^T+P), \tag{22}$$

and we can solve this for $\langle\delta\mathcal{W}^2\rangle_C$ to obtain

$$\beta\langle\delta\mathcal{Q}^2\rangle_C=\Omega^{**}-VB_T+\tfrac{5}{3}NkT+\frac{2\pi}{9}N\rho\int_0^\infty[9\varphi^{**}(r)+6\varphi'^{*}(r)+\varphi''(r)-2\varphi'(r)]g(r)r^2\,dr. \tag{23}$$

This is our closed-form expression for isotropic stress energy fluctuations in the canonical ensemble.

C. Transformation between ensembles

We work with three ensembles: (a) grand canonical (GC), in which the energy $\mathcal{H}$ fluctuates about its mean value U, and the particle number $\mathcal{N}$ fluctuates about its mean value N; (b) canonical ensemble (C), in which $\mathcal{H}$ fluctuates about the same mean U, and $\mathcal{N}$ is fixed at N; and (c) microcanonical (MC), in which $\mathcal{H}$ is fixed at U and $\mathcal{N}$ is fixed at N. Since we are considering all ensembles to represent a system with fixed center of mass, the microcanonical ensemble here is equivalent to the molecular dynamics ensemble [15–18].

The theory relating mean fluctuations between ensembles was presented by Lebowitz, Percus, and Verlet [15], and their Eq. (2.11) gives the following relations:

$$\langle\delta\mathcal{A}^2\rangle_{\mathrm{MC}}=\langle\delta\mathcal{A}^2\rangle_C-\langle\delta\mathcal{H}^2\rangle_C\left[\left(\frac{\partial\langle\mathcal{A}\rangle}{\partial U}\right)_V\right]^2, \tag{24}$$

$$\begin{aligned}\langle\delta\mathcal{A}^2\rangle_{\mathrm{MC}}={}&\langle\delta\mathcal{A}^2\rangle_{\mathrm{GC}}-\langle\delta\mathcal{N}^2\rangle_{\mathrm{GC}}\left[\left(\frac{\partial\langle\mathcal{A}\rangle}{\partial N}\right)_{U,V}\right]^2\\&-2\langle\delta\mathcal{N}\delta\mathcal{H}\rangle_{\mathrm{GC}}\left(\frac{\partial\langle\mathcal{A}\rangle}{\partial N}\right)_{U,V}\left(\frac{\partial\langle\mathcal{A}\rangle}{\partial U}\right)_{N,V}\\&-\langle\delta\mathcal{H}^2\rangle_{\mathrm{GC}}\left[\left(\frac{\partial\langle\mathcal{A}\rangle}{\partial U}\right)_{N,V}\right]^2.\end{aligned} \tag{25}$$

The extensive variable fluctuations in these formulas are calculated directly form the ensemble statistical distributions, and the textbook results are

$$\begin{aligned}\langle\delta\mathcal{H}^2\rangle_C&=kT^2C_V,\\\langle\delta\mathcal{H}^2\rangle_{\mathrm{GC}}&=kT^2C_V+\frac{kTD^2}{VB_T},\\\langle\delta\mathcal{N}\delta\mathcal{H}\rangle_{\mathrm{GC}}&=\frac{NkTD}{VB_T},\\\langle\delta\mathcal{N}^2\rangle_{\mathrm{GC}}&=\frac{N^2kT}{VB_T},\end{aligned} \tag{26}$$

where $D=U+PV-\alpha TVB_T$, and C_V is the specific heat at constant volume, B_T is the isothermal bulk modulus, and α is the volumetric thermal expansion coefficient. Notice that the right sides of Eq. (26) are all of order N.

Let us first apply Eqs. (24) and (25) to the shear stress energy σ_{xy}. Since $\langle\sigma_{xy}\rangle=0$, the ensemble corrections vanish, and the expression given in Eq. (14) for the fluctuation $\langle(\sigma_{xy})^2\rangle$ is correct in all ensembles.

When Eqs. (24) and (25) are applied to the isotropic stress energy $\mathcal{Q}$, since $\langle\mathcal{Q}\rangle=PV$ and V is constant, the thermodynamic derivatives are given by

$$\begin{aligned}V\left.\frac{\partial P}{\partial U}\right)_{N,V}&=\frac{\alpha VB_T}{C_V}=\gamma,\\V\left.\frac{\partial P}{\partial N}\right)_{U,V}&=\frac{VB_T-\gamma D}{N},\end{aligned} \tag{27}$$

where γ is defined by the first equation, and is the thermodynamic Grüneisen parameter. Evaluation of Eq. (24) gives the microcanonical–canonical relation

$$\langle\delta\mathcal{Q}^2\rangle_{\mathrm{MC}}=\langle\delta\mathcal{Q}^2\rangle_C-kT^2\gamma^2C_V. \tag{28}$$

We have previously related fluctuations in the molecular dynamic and canonical ensembles [17], and calculations there agree with Eq. (28). Evaluation of Eq. (25) gives the microcanonical–grand canonical relation

$$\langle\delta\mathcal{Q}^2\rangle_{\mathrm{MC}}=\langle\delta\mathcal{Q}^2\rangle_{\mathrm{GC}}-kTVB_T-kT^2\gamma^2C_V, \tag{29}$$

and the difference between Eqs. (28) and (29) yields

$$\langle\delta\mathcal{Q}^2\rangle_C=\langle\delta\mathcal{Q}^2\rangle_{\mathrm{GC}}-kTVB_T. \tag{30}$$

III. COMPARISON WITH PREVIOUS RESULTS

A. Statistical mechanics results

An extensive account of linear response in a quantum fluid, specifically of the relation between response to an external perturbation and time dependent correlations in the equilibrium system, was presented by Puff and Gillis [19]. This paper contains formulas for fluctuations among all the hydrodynamic variables in the GC ensemble. We will take the classical limit of their quantum-mechanical expressions, and change their notation to that used here.

From Eqs. (2.47) and (2.48) of Puff and Gillis, after some algebra we find

$$\beta\langle\sigma_{xy}\sigma_{xy}\rangle = NkT + \frac{2\pi}{15}N\rho\int_0^\infty[\varphi''(r)+4\varphi'(r)]g(r)r^2\,dr. \tag{31}$$

This agrees with Eq. (14) for the fluid state, where B_{44}^T vanishes, and noting that the shear stress fluctuation is the same in every ensemble, as shown in Sec. II. From Eqs. (2.47) and (3.1) of Puff and Gillis, again with some algebra, we find

$$\beta\langle\delta\mathcal{Q}\delta\mathcal{Q}\rangle_{\mathrm{GC}} = \frac{5}{3}NkT + \frac{2\pi}{9}N\rho\int_0^\infty[\phi''(r) - 2\phi'(r)]g(r)r^2\,dr. \tag{32}$$

To obtain this from our Eq. (23) for $\langle\delta\mathcal{Q}^2\rangle_C$, we delete from Eq. (23) the explicit volume derivatives Ω^{**}, φ^{**}, and φ'^{*}, since such volume dependence was not considered by Puff and Gillis, and we add the ensemble correction VB_T to the right side of Eq. (23), according to the ensemble relation Eq. (30), and thus recover the Puff and Gillis result Eq. (32). Hence our results for the liquid phase, and with volume-independent potentials, are the same as the classical limit of the equations of Puff and Gillis [19].

In treating pressure fluctuations, Hill [20] made the following calculation in the canonical ensemble. The partition function is $Z=\mathrm{Tr}\,e^{-\beta\mathcal{H}}$, and the pressure is $P=(\partial kT\ln Z/\partial V)_T$, so that

$$P=\frac{1}{Z}\mathrm{Tr}\left[-\frac{\partial\mathcal{H}}{\partial V}e^{-\beta\mathcal{H}}\right]. \tag{33}$$

Associating the microscopic pressure operator $\mathcal{P}$ with $-\partial\mathcal{H}/\partial V$, and differentiating Eq. (33) again with respect to volume gives

$$\langle\delta\mathcal{P}^2\rangle = kT\left[\left(\frac{\partial P}{\partial V}\right)_T - \left\langle\frac{\partial\mathcal{P}}{\partial V}\right\rangle\right], \tag{34}$$

where $\delta\mathcal{P}=\mathcal{P}-P$. The first derivative on the right is simply $-B_T/V$. But the only way to evaluate the second term is to carry out the phase space average of the microscopic operator $\partial\mathcal{P}/\partial V$. Hence Eq. (34) does not help to determine the pressure fluctuations. Hill observed that the second term depends ''in detail on the law of force between the molecules and the walls of the container.'' The same point of view was expressed by Münster [21], and it is certainly correct. But notice that we have in Eq. (23) a closed form expression for pressure fluctuations, through the identification $\delta\mathcal{Q}=V\delta\mathcal{P}$, and this expression is independent of boundary conditions. This situation constitutes an example of the general theorem that stresses for a homogeneous system can be expressed as an integral of forces crossing the surface, or can be transformed to a function evaluated in the interior [22]. Equations (14) and (23) are interior evaluations.

B. An unreliable procedure

A procedure often used to calculate fluctuations is to expand a dynamical variable (or an operator) in terms of the extensive-variable fluctuations which define a given ensemble [23]. For the grand canonical ensemble, for example, one writes

$$\mathcal{A}=\langle\mathcal{A}\rangle+\delta\mathcal{N}\left(\frac{\partial\langle\mathcal{A}\rangle}{\partial N}\right)_{U,V}+\delta\mathcal{H}\left(\frac{\partial\langle\mathcal{A}\rangle}{\partial U}\right)_{N,V}. \tag{35}$$

This equation is correct if and only if the fluctuation $\delta\mathcal{A}$ is a function of $\delta\mathcal{N}$ and $\delta\mathcal{H}$ alone. While this condition fails for $\delta\mathcal{Q}$, we will nevertheless complete the calculation, since it will be helpful in clarifying inconsistencies in fluctuation formulas. For $\delta\mathcal{Q}=\mathcal{Q}-\langle\mathcal{Q}\rangle$, Eq. (35) gives

$$\langle\delta\mathcal{Q}^2\rangle_{\mathrm{GC}}=\langle\delta\mathcal{N}^2\rangle_{\mathrm{GC}}\left[\left(\frac{\partial\langle\mathcal{Q}\rangle}{\partial N}\right)_{U,V}\right]^2+2\langle\delta\mathcal{N}\delta\mathcal{H}\rangle_{\mathrm{GC}}\left(\frac{\partial\langle\mathcal{Q}\rangle}{\partial N}\right)_{U,V}\left(\frac{\partial\langle\mathcal{Q}\rangle}{\partial U}\right)_{N,V}+\langle\delta\mathcal{H}^2\rangle_{\mathrm{GC}}\left[\left(\frac{\partial\langle\mathcal{Q}\rangle}{\partial U}\right)_{N,V}\right]^2. \tag{36}$$

The corresponding canonical ensemble equation is

$$\langle\delta\mathcal{Q}^2\rangle_C=\langle\delta\mathcal{H}^2\rangle_C\left[\left(\frac{\partial\langle\mathcal{Q}\rangle}{\partial U}\right)_V\right]^2. \tag{37}$$

From the fluctuations and thermodynamic relations listed in Eqs. (26) and (27), the evaluation of Eq. (36) gives

$$\langle\delta\mathcal{Q}^2\rangle_{\mathrm{GC}}=VkTB_S, \tag{38}$$

where B_S is the adiabatic bulk modulus. Evaluation of (37) gives

$$\langle\delta\mathcal{Q}^2\rangle_C=VkT(B_S-B_T), \tag{39}$$

where B_T is the isothermal bulk modulus. The ensemble difference, from Eqs. (38) and (39), is

$$\langle\delta\mathcal{Q}^2\rangle_C=\langle\delta\mathcal{Q}^2\rangle_{\mathrm{GC}}-VkTB_T. \tag{40}$$

Although derived from an obviously incorrect theoretical procedure, Eqs. (38)–(40) provide a bewildering array of correct or partially correct results, as we shall now describe.

Puff and Gillis [19] carried out the above calculation for the grand canonical ensemble, observed that the answer Eq. (38) disagrees with their answer, and supposed the reason to be the difference between quantum and classical fluctuations. But this is not the reason, for Eq. (39) disagrees with our classical result Eq. (23). Puff and Gillis observed that Eq. (38) is ''well known and the subject of some controversy,'' that the confusion can be appreciated by noting that Landau and Lifshitz also arrived at Eq. (38), and in the process they used a $\langle\delta\mathcal{H}^2\rangle$ not equal to $\langle\delta\mathcal{H}^2\rangle_{\mathrm{GC}}$. (The Landau and Lifshitz calculation is discussed below.)

Münster [21] also observes that the literature contains ''many contradictory conceptions regarding fluctuations of intensive parameters.'' Münster reports that Eq. (39) has been proposed as an evaluation of the canonical ensemble expression Eq. (34), and states that no ensemble in his experience will give the result Eq. (38). Still, in a 1976 paper devoted to time correlation functions, and addressing stress fluctuations in particular, Eq. (38) for pressure fluctuations is given by Ernst, Hauge, and van Leeuwen [23].

We will now clarify two issues that presumably have helped sustain the mystery surrounding Eq. (35) and its application. First, the results Eqs. (38)–(40) are shown correct for an ideal gas by direct calculation. This is understandable: for an ideal gas $\mathcal{Q}$ is a function only of $\mathcal{H}$, since $\mathcal{Q}=\frac{2}{3}\mathcal{K}$ [see Eq. (16)] and $\mathcal{H}=\mathcal{K}$, hence Eqs. (36) and (37) are correct for an ideal gas. But for a system possessing potential energy, Eqs. (36) and (37) are incorrect. Second, while Eqs. (38) and (39) are generally incorrect, their difference written in Eq. (40) is the same as Eq. (30), hence is indeed correct. How can this be? To answer let us write

$$\begin{aligned}\langle\delta\mathcal{Q}^2\rangle_{\mathrm{GC}}-\langle\delta\mathcal{Q}^2\rangle_{C}=&[\langle\delta\mathcal{Q}^2\rangle_{\mathrm{GC}}-\langle\delta\mathcal{Q}^2\rangle_{\mathrm{MC}}]\\&-[\langle\delta\mathcal{Q}^2\rangle_{C}-\langle\delta\mathcal{Q}^2\rangle_{\mathrm{MC}}].\end{aligned}\tag{41}$$

Now the error in Eqs. (36) and (37) amounts in each case to setting $\langle\delta\mathcal{Q}^2\rangle_{\mathrm{MC}}=0$, as is seen by a comparison with Eqs. (25) and (24), respectively. So the corresponding error on the right of Eq. (41) amounts to incorrectly setting $\langle\delta\mathcal{Q}^2\rangle_{\mathrm{MC}}=0$, but this error cancels to give a correct result for the left side.

C. Thermodynamic fluctuations

For a closed system, Boltzmann observed that the ''index of permutability'' $\ln W$, where W is the number of available microstates, has meaning for all (nonequilibrium) states of the system, and is maximum at equilibrium, where it is related to the equilibrium entropy S through $S=k\ln W$ [24]. To study fluctuations of a closed system among its nonequilibrium states, Einstein [25] used this picture to write an explicit nonequilibrium entropy $\hat{S}=k\ln\hat{W}+\mathrm{const}$, then interpreted $\hat{W}$ as the probability of finding a state with nonequilibrium entropy $\hat{S}$ and wrote

$$\hat{W}\propto e^{k(\hat{S}-S)},\tag{42}$$

where again S is the equilibrium entropy. Einstein characterized the nonequilibrium state by a set of observables $\lambda_1\cdots\lambda_n$, and wrote $\hat{S}=\hat{S}(\lambda_1\cdots\lambda_n)$. This marks the appearance of thermodynamic variables in the probability.

Landau and Lifshitz [9] [10] used Eq. (42) to calculate the probability of fluctuations in an open system. For illustration, they imagined a system composed of a fixed set of molecules in the interior of a fluid. As a function of time, nearly every property of this system fluctuates: the volume, the total energy, the kinetic energy, and so on. These quantities fluctuate about their mean values, which correspond to an equilibrium state of the fluid. To clarify the meaning of the fluctuations derived by Landau and Lifshitz, we will present a derivation equivalent to theirs, but simpler.

For virtual variations of a thermodynamic system away from equilibrium, at constant N, Callen [26] has shown that the minimization property of the internal energy is equivalent to the maximization property of the entropy. Accordingly, we write for the probability $\hat{W}$ of fluctuating to a state with nonequilibrium energy $\hat{U}$,

$$\hat{W}\propto e^{-\beta(\hat{U}-U)}.\tag{43}$$

The use of Eq. (43) gives the same result as Eq. (42), but with simpler algebra. With $\hat{U}=\hat{U}(\hat{V},\hat{S})$, the expansion of $\hat{U}-U$ to second order in the fluctuations $\Delta V=\hat{V}-V$ and $\Delta S=\hat{S}-S$ is

$$\hat{U}-U=\frac{1}{2}\frac{\partial^2U}{\partial V^2}\bigg)_S\Delta V^2+\frac{\partial^2U}{\partial S\partial V}\bigg)_{VS}\Delta V\Delta S+\frac{1}{2}\frac{\partial^2U}{\partial S^2}\bigg)_V\Delta S^2,\tag{44}$$

or

$$\beta(\hat{U}-U)=\frac{B_S}{2VkT}\Delta V^2-\frac{\alpha B_T}{kC_V}\Delta V\Delta S+\frac{1}{2kC_V}\Delta S^2.\tag{45}$$

Hence Eq. (43) gives us a Gaussian probability distribution for the coupled fluctuations ΔV and ΔS. Inverting the matrix of coefficients in Eq. (45) yields [27]

$$\begin{aligned}\langle\Delta V^2\rangle&=\frac{kTV}{B_T},\\ \langle\Delta S^2\rangle&=kC_P,\\ \langle\Delta V\Delta S\rangle&=\alpha kTC_V,\end{aligned}\tag{46}$$

where C_P is the specific heat at constant pressure. At this point Landau and Lifshitz assume that all fluctuations correspond, in the mean, to motion of the system on the thermodynamic equilibrium surface. In other words, the mean fluctuation of every thermodynamic variable follows from its equilibrium relation to V and S, and from the V and S fluctuations in Eq. (46). This completes the formulation of thermodynamic fluctuations.

Let us illustrate by calculating fluctuations involving ΔP. We write

$$\begin{aligned}\Delta P&=\frac{\partial P}{\partial V}\bigg)_S\Delta V+\frac{\partial P}{\partial S}\bigg)_V\Delta S,\\ &=\frac{-B_S}{V}\Delta V+\frac{\alpha TB_T}{C_V}\Delta S.\end{aligned}\tag{47}$$

Combining Eq. (47) with Eq. (46) gives

$$\begin{aligned}\langle\Delta P^2\rangle&=\frac{kTB_S}{V},\\ \langle\Delta P\Delta S\rangle&=0,\\ \langle\Delta P\Delta V\rangle&=-kT.\end{aligned}\tag{48}$$

The value of $\langle\Delta P^2\rangle$ is the famous Landau and Lifshitz result [9] [10], which turns out to be the same as Eq. (38), which was derived from Eq. (36). This equality is accidental. There is no general correspondence between Eqs. (36) or (37) and thermodynamic fluctuations.

The above procedure can be followed to express ΔT in terms of ΔV and ΔS, and fluctuations involving ΔT can be evaluated. All the results of Landau and Lifshitz are recovered in this fashion. We find that, with occasional accidental exception, every thermodynamic fluctuation differs from the same fluctuation in every commonly used statistical distribution. Moreover, in all the customary statistical distributions, either V or P is constant, so that all fluctuations involving ΔV or ΔP will vanish, in contrast to the thermodynamic fluctuations listed in Eqs. (46) and (48).

IV. SUMMARY

We have derived the formulas Eq. (14) for shear stress energy fluctuations, and Eq. (23) for isotropic stress energy fluctuations, in the canonical ensemble. These formulas are valid for a classical monatomic system representing a metal or nonmetal, in cubic crystal, amorphous solid, or liquid phases. The shear stress fluctuations are the same in all ensembles, and the isotropic stress fluctuations may be evaluated in microcanonical or grand canonical ensembles by the relations (28) or (30), respectively. Our results, when limited to the fluid phase, and to volume-independent central potentials, agree with the classical limit of the quantum-mechanical expressions of Puff and Gillis [19]. Our results also provide an interpretation of, and a closed form expression for, the intractable canonical ensemble average $\langle \partial \mathcal{P}/\partial V \rangle = -\langle \partial^2 \mathcal{H}/\partial V^2 \rangle$, encountered by Hill [20] in his analysis of pressure fluctuations.

Regarding a number of inconsistencies in pressure fluctuation formulas, which have persisted for many years in the literature, our analysis in Sec. III has led us to the following conclusions. First, the expansion of a dynamical variable $\mathcal{A}$ in terms of the fluctuations, which are used to define a given ensemble, is correct if and only if $\delta\mathcal{A}$ is a function only of those fluctuations. In the grand canonical ensemble, the expansion takes the form $\delta\mathcal{A} = a\,\delta\mathcal{N} + b\,\delta\mathcal{H}$, as shown in Eq. (36) for $\delta\mathcal{Q}$. This expansion should not be used, except for a system such as the ideal gas where its validity is proven. Second, the thermodynamic fluctuations of Landau and Lifshitz [9,10] correspond to motion of a system on the thermodynamic equilibrium surface, in the vicinity of a point on that surface. The distribution of variables represented by this thermodynamic equilibrium motion does not correspond to the statistical distribution of any known ensemble. When a theory is derived within the framework of statistical mechanics, as for example the linear response theory leading to Green-Kubo formulas, it is not legitimate to replace the statistical mechanics fluctuations with thermodynamic fluctuations.

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