# On a Theorem of Irreversible Thermodynamics. II*

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The fluctuation-dissipation theorem, which relates the equilibrium fluctuations to the admittance of a thermodynamic linear dissipative system, is generalized for more than a single extensive parameter. The real part of the admittance is shown to be symmetric, supplying thereby an extension of the reciprocity theorem of Onsager. The analysis is macroscopic and thermodynamic in nature, and is carried out for adiabatic constraints as well as for microcanonical constraints.

## 1. INTRODUCTION

THIS paper is a sequel to an earlier paper of the same title,[1] to be referred to as "I," and is the thermodynamic counterpart of the preceding statistical paper.[2]

In "I" we established the relations

$$\langle\xi^2\rangle=-\frac{2}{\pi}k\int d\omega\sigma_S(\omega)\omega^{-2}, \tag{1.1}$$

and

$$\langle\xi^2\rangle=\frac{2}{\pi}kT\int d\omega\sigma_U(\omega)\omega^{-2}, \tag{1.2}$$

where $\langle\xi^2\rangle$ is the mean square fluctuation of an extensive parameter in the frequency interval determined by the range of integration, and where $\sigma_S(\omega)$ and $\sigma_U(\omega)$ are conductances which characterize the irreversible response of the system to an applied force. The first of the above equations applies to systems in which all extensive parameters other than the one of interest are held constant, whereas the second equation applies to systems similarly constrained except that the constraint on the energy is replaced by the condition of adiabatic insulation. In this paper we shall generalize these results to the case in which several extensive parameters are permitted to fluctuate spontaneously, and in which the several associated forces act on the system to induce an irreversible composite process. The analysis parallels the quantum statistical analysis of the preceding paper and augments it by the consideration of adiabatic constraints. The symmetry of the real part of the admittance matrix is established by thermodynamic reasoning, but that of the imaginary part does not follow from our thermodynamic analysis.

## 2. THE METHOD

As in "I" the proof of the fluctuation-dissipation theorem (here established for multiple extensive variables) is based on the Wiener-Khinchin formula,

$$G_{ij}(\omega)=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\tau\langle\xi_i(t)\xi_j(t+\tau)\rangle e^{-i\omega\tau}, \tag{2.1}$$

which reduces the problem of determining the spectral density matrix $G_{ij}(\omega)$ to that of determining the autocorrelation matrix $\langle\xi_i(t)\xi_j(t+\tau)\rangle$. This latter quantity may be written as

$$\langle\xi_i(t)\xi_j(t+\tau)\rangle=\int d\xi_0'\cdots\int d\xi_r'\xi_i'W_1(\xi_0'\cdots\xi_r')\times\langle\tau,\xi_0'\cdots\xi_r'|\xi_j\rangle, \tag{2.2}$$

where $W_1(\xi_0'\cdots\xi_r')d\xi_0'\cdots d\xi_r'$ is the probability of finding $\xi_0\cdots\xi_r$ in the range $d\xi_0'\cdots d\xi_r'$, and $\langle\tau,\xi_0'\cdots\xi_k'|\xi_j\rangle$ is the expectation value of $\xi_j$ at a time $\tau$ after the variables $\xi_0\cdots\xi_r$ had the value $\xi_0'\cdots\xi_r'$. Thus random variable theory provides us with the spectral density of the equilibrium fluctuations if we know the two quantities $W_1(\xi_0\cdots\xi_r)$ and $\langle\tau,\xi_0'\cdots\xi_r'|\xi_j\rangle$. Now $W_1(\xi_0\cdots\xi_r)$ is the familiar distribution function of statistical thermodynamics, so that the calculation of $\langle\tau,\xi_0'\cdots\xi_r'|\xi_j\rangle$ is the crux of the derivation. But the mean decay curve $\langle\tau,\xi_0'\cdots\xi_r'|\xi_j\rangle$ of a spontaneous extensive parameter fluctuation is identical to the observed curve of macroscopic drift into equilibrium. The latter curve, finally, may be expressed in terms of the admittance matrix describing such irreversible processes. Thus the conditional mean $\langle\tau,\xi_0'\cdots\xi_r'|\xi_j\rangle$ can be written in terms of the admittance matrix so that Eqs. (2.1) and (2.2) yield the desired relation between $G_{ij}(\omega)$ and $Y_{ij}(\omega)$.

During derivation of the connection between $\langle\tau,\xi_0'\cdots\xi_r'|\xi_j\rangle$ and $Y_{ij}$, recourse is made to the principle of microscopic reversibility, whereby $\langle\tau,\xi_0'\cdots\xi_r'|\xi_j\rangle$ appears as an even function of $\tau$. By this means we then derive the symmetry of the real part of the matrix $Y_{ij}$, obtaining a set of generalized reciprocity relations.

The derivation outlined is carried out for systems under two distinct types of constraints. In the first type, all of the extensive parameters are either rigidly fixed (microcanonical) or free to vary (these "canonical" variables being those of which the fluctuations are studied). In the second type of constraint, the micro-

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[1] H. B. Callen and R. F. Greene, Phys. Rev. 86, 702 (1952).

[2] Callen, Barasch, and Jackson, preceding paper, Phys. Rev. 88, 1382 (1952).

canonical constraint on the energy is relaxed and replaced by the condition of adiabatic insulation. For this latter type of system it is necessary to augment the derivation by the construction of a theory of fluctuations of several extensive parameters under adiabatic constraint; this theory is given in Appendix A.

### 3. THE ADMITTANCE OF THERMODYNAMIC SYSTEMS

In this section we recall briefly the thermodynamic definition of the admittance function which characterizes the response of the system to an applied force and the analytic properties of this admittance function. We state these definitions and analytic properties appropriately to a system with several driven parameters.

We frame our thermodynamic analysis in the "entropy language," in which the entropy $S$ is taken as the dependent function of the equilibrium values of the energy $X_0$ and the various other extensive parameters:

$$S=S(X_0, X_1, \cdots, X_r). \tag{3.1}$$

The intensive parameters in the entropy language are

$$F_k\equiv \partial S/\partial X_k, \quad k=0, 1, \cdots, r. \tag{3.2}$$

Here $F_0$ is the inverse temperature, and the other $F_k$ are simply $-1/T$ times the corresponding intensive parameters, in the more conventional energy language.

The instantaneous deviation of an extensive parameter $x_j$ from its equilibrium value $X_j$ is denoted by $\xi_j$:

$$\xi_j\equiv x_j-X_j. \tag{3.3}$$

The intensive forces which enter into the succeeding analysis are the intensive parameters of the driving reservoir with which the system is presumed to be in interaction. This reservoir is assumed to have characteristic relaxation times small compared to the reciprocal of any of the frequencies of interest, so that it is always in quasi-static equilibrium.

Let $\beta_i(\omega)$ be the Fourier amplitude of the $i$th driving force

$$f_i(t)=F_i+\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} d\omega\beta_i(\omega)e^{i\omega t}, \tag{3.4}$$

and let $\alpha_j(\omega)$ be the Fourier amplitude of the $j$th extensive parameter

$$x_j(t)=X_j+\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} d\omega\alpha_j(\omega)e^{i\omega t}. \tag{3.5}$$

For sufficiently small amplitudes $\alpha_j$ and $\beta_i$ will be linearly related, thus defining the admittance matrix $Y_{ji}(\omega)$:

$$i\omega\alpha_j(\omega)=\sum_{i=0}^{r} Y_{ji}(\omega)\beta_i(\omega). \tag{3.6}$$

The condition that a constant applied force leads to constant values of the extensive parameters gives, as in "I,"

$$Y_{ji}(\omega)=i\omega\partial X_j/\partial F_i+O(\omega^2), \tag{3.7}$$

where the partial derivative is to be taken with all the other intensive parameters held constant.

The causal relationship between the applied forces and the induced response has its analytic statement in the further requirement that the matrix elements $Y_{ji}(\omega)$ have no poles in the lower half of the $\omega$-plane.

### 4. THE CONDITIONAL EXPECTATION VALUE

Having formulated a thermodynamic definition of the admittance function, we proceed with the plan outlined in Sec. II: We must calculate $\langle\tau, \xi_0'\cdots\xi_r'|\xi_j\rangle$, the expectation value of $\xi_j$ at a time $\tau$ after the set $\xi_0\cdots\xi_r$ had exactly the value $\xi_0'\cdots\xi_r'$.

For a reason explained in "I" we may equate $\langle\tau, \xi_0'\cdots\xi_r'|\xi_j\rangle$ to the decay function which describes the macroscopic behavior of $\xi_j$ after the microcanonical constraint $\xi_0\cdots\xi_r=\xi_0'\cdots\xi_r'$ is lifted. This decay function is simple to get. Rather than impose a constraint which is to be lifted at $t=0$, we may instead impose an appropriately chosen set of "forces" which is, again, to be lifted at $t=0$. This set of forces, of course, is chosen so as to induce the same initial macroscopic state as would the constraints it replaces. That is, we consider that until $t=0$ the system is in equilibrium with a set of applied forces $F_i+\delta F_i$ of such magnitude as to produce values $X_i+\xi_i'$ of the set of $x_i$. At time $t=0$ the applied forces are suddenly changed to $F_0, F_1, \cdots, F_r$, and the macroscopically observed value of $\xi_j$ at time $t=\tau$ is $\langle\tau, \xi_0'\cdots\xi_r'|\xi_j\rangle$. The problem is now in a form suitable for analysis in terms of the admittance function. The applied forces are

$$\delta f_i=\begin{cases}\displaystyle\sum_{k=0}^{r}\frac{\partial F_i}{\partial X_k}\xi_k', & t<0,\\ 0, & t\geqslant 0,\end{cases} \tag{4.1}$$

or

$$\delta f_i=\frac{1}{(2\pi)^{\frac{1}{2}}}\sum_{k=0}^{r}\frac{\partial F_i}{\partial X_k}\xi_k'\int_{-\infty}^{\infty}d\omega \times\left[\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\delta(\omega)+\frac{i}{\omega(2\pi)^{\frac{1}{2}}}\right]e^{i\omega\tau}. \tag{4.2}$$

For this improper integral we take the Cauchy principle value. The response to this applied force is, according to Eq. (3.6),

$$\xi_j(t)=\frac{1}{(2\pi)^{\frac{1}{2}}}\sum_{i,k=0}^{r}\frac{\partial F_i}{\partial X_k}\xi_k'\int_{-\infty}^{\infty}d\omega Y_{ij}(\omega)/i\omega \times\left[\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\delta(\omega)+\frac{i}{\omega(2\pi)^{\frac{1}{2}}}\right]e^{i\omega\tau}. \tag{4.3}$$

Equation (3.7) now gives

$$\xi_j(\tau)=\tfrac{1}{2}\xi_j'+\frac{1}{2\pi}\sum_{i,k}\xi_k'\frac{\partial F_i}{\partial X_k}\int_{-\infty}^{\infty}d\omega Y_{ij}(\omega)\omega^{-2}e^{i\omega\tau}. \quad (4.4)$$

This formula is correct for $\tau>0$, but to find $\xi_j(\tau)$ for negative $\tau$ we must invoke the principle of microscopic reversibility. We here assume that the extensive parameters are even functions of the particle momenta and that there are no magnetic or Coriolis fields; the more general cases follow through precisely as in the previous paper[2] in this journal. Then the principle of microscopic reversibility insures that $\xi_j(\tau)$ is an even function of $\tau$, whence

$$\langle\tau,\,\xi_0'\cdots\xi_r'\,|\,\xi_j\rangle=\frac{1}{2\pi}\sum_{i,k}\xi_k'\frac{\partial F_i}{\partial X_k}\int_{-\infty}^{\infty}d\omega\omega^{-2}\times[Y_{ij}(\omega)+Y_{ij}^*(\omega)]e^{i\omega\tau}. \quad (4.5)$$

## 5. THE SPECTRAL DENSITY OF THE SPONTANEOUS FLUCTUATIONS

Having now computed the quantity $\langle\tau,\,\xi_0'\cdots\xi_r'\,|\,\xi_j\rangle$, we may find the correlation moment $\langle\xi_i(t)\xi_j(t+\tau)\rangle$ by Eq. (2.2), and thence the spectral density $G_{ij}(\omega)$ by Eq. (2.1). Thus

$$\langle\xi_i(t)\xi_j(t+\tau)\rangle=\frac{1}{2\pi}\sum_{l,k}\frac{\partial F_l}{\partial X_k}\langle\xi_i\xi_k\rangle\int_{-\infty}^{\infty}d\omega\omega^{-2}\times[Y_{lj}(\omega)+Y_{lj}^*(\omega)]e^{i\omega\tau}, \quad (5.1)$$

and

$$G_{ij}(\omega)=\frac{1}{(2\pi)^{\frac{1}{2}}}\sum_{l,k}\frac{\partial F_l}{\partial X_k}\langle\xi_i\xi_k\rangle\omega^{-2}[Y_{lj}(\omega)+Y_{lj}^*(\omega)]. \quad (5.2)$$

The fluctuation moment $\langle\xi_i\xi_k\rangle$ is well known from conventional thermodynamic fluctuation theory for systems with canonical and microcanonical constraints. In fact, we have

$$\sum_k\frac{\partial F_l}{\partial X_k}\langle\xi_i\xi_k\rangle=-k\delta_{il}. \quad (5.3)$$

Restricting ourselves temporarily to systems with canonical and microcanonical constraints (the adiabatic constraint will be considered in the next section), we thus find

$$G_{ij}(\omega)=-\left(\frac{2}{\pi}\right)^{\frac{1}{2}}k\omega^{-2}\sigma_{Sij}(\omega), \quad (5.4)$$

where the conductance matrix $\sigma_{Sij}$ is the real part of the admittance matrix

$$\sigma_{Sij}=\tfrac{1}{2}[Y_{ij}(\omega)+Y_{ij}^*(\omega)]. \quad (5.5)$$

By the definition of the spectral density, we now have our generalization of the fluctuation-dissipation theorem

$$\langle\xi_i\xi_j\rangle=-\frac{2}{\pi}k\int_{-\infty}^{\infty}d\omega\omega^{-2}\sigma_{Sij}(\omega). \quad (5.6)$$

## 6. SPECTRAL DENSITY UNDER ADIABATIC CONSTRAINT

In the previous section we have found the form of the fluctuation-dissipation theorem appropriate to a system with several extensive parameters canonically constrained and with all other extensive parameters microcanonically constrained. We now wish to consider the case in which the constraint on the energy is replaced by the condition that the system is adiabatically insulated; that is, no heat flow is possible through the boundary of the system. For such a system it is most convenient to employ the energy language, based on the fundamental relation

$$X_0=X_0(S,X_1,\cdots,X_r), \quad (6.1)$$

with the intensive parameters defined by

$$P_k\equiv\partial X_0/\partial X_k)_{S,\,X_1,\ldots,\,X_r}. \quad (6.2)$$

Under the adiabatic constraint the first-order entropy change is zero during a fluctuation, and the energy change is simply

$$\delta x_0=\sum_1^r P_k\delta x_k. \quad (6.3)$$

The forces are now taken as the energy language intensive parameters of the driving reservoir,

$$p_i(t)=P_i+\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\omega\beta_i(\omega)e^{i\omega t}, \quad (6.4)$$

and the admittance function now has the dimensions of $\omega x/p$ rather than of $\omega x/f$. As a function of $\omega$ we again have the condition

$$Y_{ji}(\omega)=i\omega\partial X_j/\partial P_i)_S+O(\omega^2), \quad (6.5)$$

and the partial derivative is now to be taken with all other intensive parameters (except $P_i$ and $T$) and with the entropy constant.

We then find, in analogy with (5.2), that the spectral density matrix is

$$G_{ij}(\omega)=\frac{1}{(2\pi)^{\frac{1}{2}}}\sum_{k,l}\frac{\partial P_i}{\partial X_k}\langle\xi_k\xi_l\rangle\omega^{-2}[Y_{lj}(\omega)+Y_{lj}^*(\omega)], \quad (6.6)$$

or

$$G_{ij}(\omega)=\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\sum_{k,l}\frac{\partial P_i}{\partial X_k}\langle\xi_k\xi_l\rangle\omega^{-2}\sigma_{Ulj}, \quad (6.7)$$

where

$$\sigma_{Ulj}=\tfrac{1}{2}[Y_{lj}(\omega)+Y_{lj}^*(\omega)]. \quad (6.8)$$

The subscript $U$ is now written explicitly to indicate that $\sigma_U$ is the real part of the energy language admittance.

In Appendix A we calculate the fluctuation moment $\langle\xi_k\xi_l\rangle$ under adiabatic constraints as

$$\langle\xi_k\xi_l\rangle = kT\partial X_k/\partial P_l)_S. \quad (6.9)$$

This gives the fluctuation-dissipation theorem for adiabatic constraints:

$$\langle\xi_k\xi_l\rangle = \frac{2}{\pi}kT\int_0^\infty d\omega\omega^{-2}\sigma_{Ukl}(\omega). \quad (6.10)$$

### 7. RECIPROCITY RELATIONS

We now show that the conductance matrix is symmetric under our assumptions of vanishing magnetic field and parameters even in the particle momenta. This symmetry is a generalization of the reciprocity theorem of Onsager.

For simplicity we consider canonical and microcanonical constraints, although the theorem follows identically for the adiabatic constraint. We have

$$G_{ij}(\omega) = -(2/\pi)^{\frac{1}{2}}k\omega^{-2}\sigma_{Sij}(\omega), \quad (7.1)$$

and

$$G_{ij}(\omega) = \frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^\infty d\omega\langle\xi_i(t)\xi_j(t+\tau)\rangle e^{-i\omega\tau}. \quad (7.2)$$

Now, according to the principle of microscopic reversibility we have[3]

$$\langle\xi_i(t)\xi_j(t+\tau)\rangle = \langle\xi_i(t)\xi_j(t-\tau)\rangle, \quad (7.3)$$

and as we are dealing with a stationary random process we can substitute $t+\tau$ for $t$ in the right-hand member, yielding

$$\langle\xi_i(t)\xi_j(t+\tau)\rangle = \langle\xi_j(t)\xi_i(t+\tau)\rangle. \quad (7.4)$$

With Eqs. (7.1) and (7.2) this immediately yields the reciprocity theorem

$$\sigma_{Sij}(\omega) = \sigma_{Sji}(\omega). \quad (7.5)$$

Similarly, for adiabatic constraints,

$$\sigma_{Uij}(\omega) = \sigma_{Uji}(\omega). \quad (7.6)$$

### APPENDIX A. FLUCTUATIONS UNDER AN ADIABATIC CONSTRAINT

Let us consider the thermodynamic fluctuations of a system canonical with respect to several extensive parameters $x_1, x_2, \cdots, x_r$ and under an adiabatic constraint.

The probability of a fluctuation to instantaneous values $x_0, x_1, \cdots, x_r$ is[4]

$$W(x_0,\cdots,x_r) = \Omega_0 \times\exp\left\{\left[s-S+\sum_{k=1}^r P_k\delta x_k - \frac{1}{T}\delta x_0\right]\Big/ k\right\}, \quad (A.1)$$

where

$$\delta x_k = x_k - X_k = \xi_k, \quad (A.2)$$

and

$$s = S(x_0, x_1, \cdots, x_r). \quad (A.3)$$

Now under an adiabatic constraint,

$$\delta x_0 = \sum_{k=1}^r P_k\delta x_k. \quad (A.4)$$

If we delete from our ensemble those states inconsistent with (A.4) the probability (A.1) becomes

$$W_S = \Omega_0\exp\{[s-S]/k\}. \quad (A.5)$$

But now

$$s-S = \frac{\partial s}{\partial x_0}\delta x_0 + \sum_{k=1}^r \frac{\partial s}{\partial x_k}\delta x_k + \tfrac{1}{2}\left[\sum_{k,l=1}^r \frac{\partial^2 s}{\partial x_k\partial x_l}\delta x_k\delta x_l + 2\sum_{k=1}^r \frac{\partial^2 s}{\partial x_0\partial x_k}\delta x_k\delta x_0 + \frac{\partial^2 s}{\partial x_0^2}(\delta x_0)^2\right]+\cdots, \quad (A.6)$$

which becomes, using (A.4),

$$s-S = \tfrac{1}{2}\sum_{k,l=1}^r \delta x_k\delta x_l\left[\frac{\partial^2 s}{\partial x_k\partial x_l} + 2P_l\frac{\partial^2 s}{\partial x_0\partial x_k} + P_kP_l\frac{\partial^2 s}{\partial x_0^2}\right], \quad (A.7)$$

dropping the higher order terms. (These various derivatives are, of course, to be evaluated at the "point" $x_k = X_k$.) Now in general, for any quantity

$$\delta(\ ) = \frac{\partial}{\partial x_0}(\ )\delta x_0 + \sum_{k=1}^r \frac{\partial}{\partial x_k}(\ )\delta x_k;$$

so under the constraint (A.4), which we denote by a subscript $s$,

$$\frac{\partial}{\partial x_l}(\ )_S = P_l\frac{\partial}{\partial x_0}(\ ) + \frac{\partial}{\partial x_l}(\ ). \quad (A.8)$$

We may apply (A.8) to a re-expressed form of (A.7):

$$\begin{aligned} s-S &= \tfrac{1}{2}\sum_{k,l}\delta x_k\delta x_l\left[\frac{\partial}{\partial x_l}\left(-\frac{P_k}{T}\right) + 2P_l\frac{\partial}{\partial x_0}\left(-\frac{P_k}{T}\right) + P_kP_l\frac{\partial}{\partial x_0}\left(\frac{1}{T}\right)\right] \\ &= \tfrac{1}{2}\sum_{k,l}\delta x_k\delta x_l\left[\frac{\partial}{\partial x_l}\left(-\frac{P_k}{T}\right)_S + P_l\frac{\partial}{\partial x_0}\left(-\frac{P_k}{T}\right) + P_kP_l\frac{\partial}{\partial x_0}\left(\frac{1}{T}\right)\right]. \end{aligned} \quad (A.9)$$

Now if we put

$$P_l\frac{\partial}{\partial x_0}\left(-\frac{P_k}{T}\right) = P_l\frac{\partial^2 s}{\partial x_0\partial x_k} = P_l\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right), \quad (A.10)$$

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[3] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

[4] See M. J. Klein and L. Tisza, Phys. Rev. **76**, 1861 (1949).

then (A.9) becomes

$$s-S=\tfrac{1}{2}\sum_{k,l}\delta x_k\delta x_l\left[\frac{\partial}{\partial x_l}\left(-\frac{P_k}{T}\right)_S +P_l\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right)+P_kP_l\frac{\partial}{\partial x_0}\left(\frac{1}{T}\right)\right]. \quad (A.11)$$

Now, using (A.8) again, we find

$$s-S=\tfrac{1}{2}\sum_{k,l=1}^{r}\delta x_k\delta x_l\left[-\frac{1}{T}\frac{\partial P_k}{\partial x_l}\right)_S -P_k\frac{\partial}{\partial x_l}\left(\frac{1}{T}\right)_S+P_l\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right)_S\Bigg]. \quad (A.12)$$

Now the summation of the last two terms in the summand gives zero, so

$$s-S=\frac{-1}{2T}\sum_{k,l=1}^{r}\frac{\partial P_k}{\partial X_l}\bigg)_S\delta x_k\delta x_l. \quad (A.13)$$

We note that

$$\partial P_k/\partial X_l)_S=\partial P_l/\partial X_k)_S\equiv\alpha_{lk}. \quad (A.14)$$

Thus

$$W_S=\Omega_0\exp\left[-\frac{1}{2kT}\sum_{k,l=1}^{r}\frac{\partial P_k}{\partial X_l}\bigg)_S\delta x_k\delta x_l\right]. \quad (A.15)$$

In this expression we must consider that explicit dependence upon $x_0$ has been removed by means of Eq. (A.4). Let us put

$$\pi_l=\frac{1}{kT}\sum_{k=1}^{r}\alpha_{lk}\delta x_k. \quad (A.16)$$

Then

$$\langle\pi_i\delta x_j\rangle=\frac{\int dx_0\cdots\int dx_r\pi_i\delta x_j\exp\left[\frac{-1}{2kT}\sum_{k,l=1}^{r}\alpha_{lk}\delta x_k\delta x_l\right]}{\int dx_0\cdots\int dx_r\exp\left[\frac{-1}{2kT}\sum_{k,l=1}^{r}\alpha_{lk}\delta x_k\delta x_l\right]}$$

$$=\delta_{ij},\ \text{the Kronecker delta.} \quad (A.17)$$

Then (except at critical points) we may insert (A.15)

$$\delta x_k=2kT\textstyle\sum_l\alpha_{kl}^{-1}\pi_l,$$

whence

$$\langle\delta x_i\delta x_k\rangle=2kT\textstyle\sum_l\alpha_{kl}^{-1}\langle\delta x_i\pi_l\rangle$$

$$=2kT\alpha_{ki}^{-1} \quad (A.18)$$

$$=2kT\partial X_i/\partial P_k)_S, \quad (A.19)$$

since $\partial X_i/\partial P_k)_S$ and $\partial P_k/\partial X_i)_S$ are inverse matrices.