A single-frequency test for one-parameter models of the linear thermo-visco-elastic response of glass-forming liquids.

N. L. Ellegaard, T. Christensen, N. B. Olsen, and J. C. Dyre

Department of Mathematics and Physics (IMFUFA),
Roskilde University, P.O.Box 260, DK-4000 Roskilde, Denmark

Abstract

A master equation description of the inherent dynamics is used to calculate the frequency-dependent linear thermo-visco-elastic response functions of a glass-forming liquid. From the imaginary parts of the isobaric specific heat, isothermal bulk modulus, and isobaric thermal expansion coefficient, we define a quantity $\Lambda_{TP}(\omega)$ with the property that $\Lambda_{TP}(\omega) = 1$ is equivalent to having a one-parameter description of the linear thermo-visco-elastic response. This provides an alternative to the well-known criterion based on the Prigogine-Defay ratio.
Several articles have examined if it is possible to give a one parameter description of the thermodynamic relaxation processes of viscous liquids [1, 2, 3, 4, 5, 6, 7]. The so called Prigogine-Defay ratio [1, 2, 3, 4] tests for a one parameter description by comparing the responses of the liquid state with the responses of a glassy state. This approach is problematic because the responses of the glassy state depend on the history of the glass. In other words the original Prigogine-Defay ratio is not a state function. Later tests compare the equilibrium (zero frequency) responses of a liquid to the instantaneous (infinite frequency) responses of the same liquid [5, 6]. In principle this should lead to a test quantity which is a state function. However instantaneous responses are very difficult to measure, as one has to deal with experimental problems which are related to heat flow and thermal stresses in the sample.

In the following we propose a new test which allows testing for a one parameter hypothesis by measuring the imaginary parts of three complex response functions at a single frequency. This way we can completely avoid the measuring of an instantaneous response. We examine a harmonic linear perturbation of a thermoelastic system with temperature $T_0$, pressure $p_0$, entropy $S_0$, and volume $V_0$. Writing $p = p_0 + Re(\delta \tilde{p} e^{i\omega t})$ and $T = T_0 + Re(\delta \tilde{T} e^{i\omega t})$ the oscillation of $V$ and $S$ is described by $V = V_0 + Re(\delta \tilde{V} e^{i\omega t})$ and $S = S_0 + Re(\delta \tilde{S} e^{i\omega t})$. The complex coefficients $\delta \tilde{p}$, $\delta \tilde{V}$, $\delta \tilde{S}$, and $\delta \tilde{T}$ are related by a matrix of complex, frequency dependent response functions.

$$
\begin{pmatrix}
\delta \tilde{S} \\
\delta \tilde{V}
\end{pmatrix}
= 
\begin{pmatrix}
\frac{V_0}{T_0} c_p(\omega) & V_0 \alpha_p(\omega) \\
V_0 \alpha_p(\omega) & V_0 \kappa_T(\omega)
\end{pmatrix}
\begin{pmatrix}
\delta \tilde{T} \\
-\delta \tilde{p}
\end{pmatrix}
$$

(1)

Here $c_p(\omega)$ denotes the isobaric specific heat capacity per volume, $\alpha_p(\omega)$ denotes isobaric thermal expansion coefficient, whereas $\kappa_T(\omega)$ denotes the isothermal bulk compressibility. The matrix is symmetric due to an Onsager relation, which will be proven in the course of this article.

**MARKOVIAN INHERENT DYNAMICS**

We shall base the following calculation on the so called energy landscape picture of the thermodynamics of a viscous liquid [8]. We assume that at a sufficiently low temperature a small molecular system spends most of its time vibrating around a minimum of the potential energy landscape.
energy function. Furthermore, we assume that the rate of transitions is so low that a system achieves vibrational equilibrium between two transitions. An ensemble of such systems is well described by a vector of probabilities \( P = (P_1, P_2, ..., P_N) \) where \( P_n \) denotes the fraction of the ensemble which is vibrating around the energy minimum \( n \). For a large system the rate of transitions is proportional to the system size, and therefore we cannot expect a large system to achieve vibrational equilibrium between each transition. However assuming that a transition from one potential minimum to another minimum is a localized event, leads to an assertion of local vibrational equilibrium.

In the following we examine a linear experiment in which we control the intensive variables \( T \) and \( p \) and calculate the resulting change of the extensive variables \( S \) and \( V \). Here \( S \) denotes the ensemble entropy whereas \( V \) denotes the ensemble average of the volume.

\[
S = - \sum_m P_m \left( \frac{\partial G_m}{\partial T} + k_B \ln P_m \right)
\]

\[
V = \sum_m P_m \frac{\partial G_m}{\partial p}
\]

\( G_n(T, p) \) denotes the vibrational Gibbs energy of a single minimum, whereas the Gibbs energy of an ensemble is given by

\[
G(T, p, P) = \sum_n P_n (G_n(T, p) + k_B T \ln P_n).
\]

We introduce the notation \( X = (T, -p) \) and \( Q = (S, V) \), and note that the following equation is fulfilled for all choices of \( P \)

\[
Q_\alpha = -\frac{\partial G}{\partial X_\alpha}, \quad \alpha = 1, 2.
\]

The equilibrium distribution is easily found by minimizing \( G \) under the constraint \( \sum_m P_m = 1 \),

\[
P^{eq}_n(T, p) = \exp\left(-\frac{G_n - G}{k_B T}\right).
\]

For a linearly perturbed system, the rate of entropy change, \( \dot{S} \), is related to the heat flow, \( J_q \), by the relation \( J_q = T \dot{S} \). Thus the rate of change of the energy is given by \( \dot{U} = T \dot{S} - p \dot{V} \). We insert in the relation \( \dot{G} = U - T S + p V \) to get

\[
\dot{G} = -S \dot{T} + V \dot{p} = -\sum_\alpha Q_\alpha \dot{X}_\alpha.
\]
When the thermal energy per degree of freedom is low compared to the height of an energy barrier, the transitions between minima are well described as a Markov process, and the dynamics of $P_m$ is described by a master equation

$$\dot{P}_n = \sum_m W_{nm} P_m$$

The rate matrix $W$ depends on $T$ and $p$, and the equilibrium distribution $P_m^{eq}$ fulfills $\sum_m W_{nm} P_m^{eq} = 0$. We proceed to examine linear perturbations around a reference state $X^0 = (T^0, -p^0)$. Furthermore we introduce $W_{nm}^0 = W_{nm}(T_0, p_0)$ and $P_m^0 = P_m^{eq}(T_0, p_0)$. We let $\delta$ denote perturbations around the reference state to get

$$\delta \dot{P}_n = \sum_m W_{nm}^0 \delta P_m + \delta W_{nm} P_m^0.$$ 

We note that $\delta(\sum_m W_{nm} P_m^{eq}) = 0$. This leads to $\sum_m \delta W_{nm} P_m^0 = -\sum_m W_{nm}^0 \delta P_m^{eq}$. We insert to get

$$\delta \dot{P}_n = \sum_m W_{nm}^0 (\delta P_m - \delta P_m^{eq}). \quad (8)$$

A little algebra and the use of (6) leads to [22]

$$\frac{\partial \ln P_m^{eq}}{\partial X_\beta} = \frac{1}{k_B T_0} \left( \frac{\partial Q_\beta}{\partial P_m} Q_\beta + \delta_1 k_B \right). \quad (9)$$

We insert in (8) and remember $\sum_m W_{nm}^0 P_m^0 = 0$ to get

$$\delta \dot{P}_n = \sum_m W_{nm}^0 \left( \delta P_m - \sum_\beta \frac{1}{k_B T_0} P_m^0 \frac{\partial Q_\beta}{\partial P_m} \delta X_\beta \right). \quad (10)$$

The steady state fulfills

$$\sum_n (W_{ln}^0 - i\omega \delta_{ln}) \delta \tilde{P}_n = \sum_{m, \beta} \frac{1}{k_B T_0} W_{lm}^0 P_m^0 \frac{\partial Q_\beta}{\partial P_m} \delta \tilde{X}_\beta. \quad (11)$$

Here $\delta \tilde{P}_n$ and $\delta \tilde{X}_\beta$ denote complex amplitudes. For $\omega > 0$ we can simplify (11) by defining

$$A_{nm}(\omega) = \frac{1}{k_B T_0} \sum_l (W^0 - i\omega I)^{-1}_{nl} W_{lm}^0 P_m^0. \quad (12)$$

Here $I$ denotes the identity matrix. We substitute (12) into (11) to get

$$\delta \tilde{P}_n = \sum_{m, \beta} A_{nm}(\omega) \frac{\partial Q_\beta}{\partial P_m} \delta \tilde{X}_\beta. \quad (13)$$
This equation describes the dynamics of the ensemble. In order to calculate the response functions, we define 
\[ J_{\alpha\beta}^\infty = -\frac{\partial^2 G}{\partial X_\alpha \partial X_\beta} \] and expand the complex amplitudes \( \delta \tilde{Q}_\alpha \) to the first order to get
\[ \delta \tilde{Q}_\alpha = \sum_n \frac{\partial Q_\alpha}{\partial P_n} \delta \tilde{P}_n + \sum_\beta J_{\alpha\beta}^\infty \delta \tilde{X}_\beta. \] (14)

We insert in (13) to get an expression for the thermoviscoelastic response functions that were introduced in (1). This gives
\[ \delta \tilde{Q}_\alpha = \sum_\beta J_{\alpha\beta}(\omega) \delta \tilde{X}_\beta, \] where
\[ J_{\alpha\beta}(\omega) = J_{\alpha\beta}^\infty + \sum_{m,n} \frac{\partial Q_\alpha}{\partial P_n} A_{nm}(\omega) \frac{\partial Q_\beta}{\partial P_m}. \] (15)

As \( A_{nm}(\infty) = 0 \) we get \( J_{\alpha\beta}(\infty) = J_{\alpha\beta}^\infty \). We can show that \( J_{\alpha\beta}(\omega) \) is symmetric by introducing a symmetric matrix \( Y_{mn} \) with the elements \( Y_{mn} = (P^0_0)^{-\frac{1}{2}} W_{nm} (P^0_n)^{-\frac{1}{2}} \). This gives
\[ A_{nm}(\omega) = \frac{1}{k_B T_0} \sum_l (P^0_n)^{-\frac{1}{2}} (i\omega I + Y)^{-1} Y_{nl} (P^0_m)^{-\frac{1}{2}}. \] (16)

The matrices \( (i\omega I + Y)^{-1} \) and \( Y \) commute so it is easy to show that \( A_{nm}(\omega) \) is symmetric.

We insert in (15) to conclude that the matrix \( J(\omega) \) is also symmetric.

**PRIGOGINE-DEFAY RATIO**

Having calculated the response functions we can insert in the “linear Prigogine-Defay ratio”
\[ \Pi = \frac{(c_p(0) - c_p(\infty))(\kappa T(0) - \kappa T(\infty))}{T_0(\alpha_p(0) - \alpha_p(\infty))^2}. \] (17)

We insert (15) and remember \( A_{nm}(\infty) = 0 \) to get
\[ \Pi = \frac{\left( \sum_{m,n} \frac{\partial S}{\partial P_n} A_{nm}(0) \frac{\partial S}{\partial P_m} \right) \left( \sum_{m,n} \frac{\partial V}{\partial P_n} A_{nm}(0) \frac{\partial V}{\partial P_m} \right)}{\left( \sum_{m,n} \frac{\partial S}{\partial P_n} A_{nm}(0) \frac{\partial V}{\partial P_m} \right)^2}. \] (18)

From the Schwartz inequality to find \( \Pi \geq 1 \). We can describe the special case \( \Pi = 1 \) by noting that null space of \( A_{nm}(\omega) \) is given by null(\( A(\omega) \)) = span\{e\}. Here \( e \) is a vector with elements on the form \( e_n = \frac{1}{N} \). We note that \( \Pi = 1 \) is only fulfilled we can define constants \( \gamma \) and \( c \), so that all the following equation is fulfilled for all \( n \)
\[ \frac{\partial V}{\partial P_n} = \gamma \frac{\partial S}{\partial P_n} + c. \] (19)
This result is similar to earlier treatments of the Prigogine-Defay ratio. As mentioned in the introduction, the Prigogine-Defay ratio is very difficult to measure, and therefore we propose the following ratio which is inspired by \[10, 11\]

\[
\Lambda_T(\omega) = \frac{\frac{1}{T_0} \alpha_p''(\omega) \kappa_T''(\omega)}{(\alpha_p''(\omega))^2}.
\]

We insert (15) to get

\[
\Lambda_T(\omega) = \left( \sum_{m,n} \frac{\partial S}{\partial P_n} A_{nm}''(\omega) \frac{\partial S}{\partial P_m} \right) \left( \sum_{m,n} \frac{\partial V}{\partial P_n} A_{nm}''(\omega) \frac{\partial V}{\partial P_m} \right) \left( \sum_{m,n} \frac{\partial S}{\partial P_n} A_{nm}''(\omega) \frac{\partial V}{\partial P_m} \right)^2
\]

From the Schwartz inequality we find that \( \Lambda_T(\omega) \geq 1 \), for all \( \omega \in ]0, \infty[ \). In order to analyze the reverse relation we note that \( \text{null}(A''(\omega)) = \text{span}\{e\} \). This tells us for all \( \omega \in ]0, \infty[ \) that \( \Lambda_T(\omega) = 1 \) is equivalent to (19) and thus \( \Lambda_T(\omega) = 1 \) is equivalent to \( \Pi = 1 \). We can get a better understanding of the implications of (19) if we approximate \( G_n \) by a Taylor expansion in \( T \) to get \( G_n = H_n - TS_{vib}^n \). This approach is essentially equivalent to a series of recent articles on thermodynamics of the energy landscape \[12, 13, 14\]. A little calculation yields \[25\]

\[
\frac{\partial S}{\partial P_n} = \frac{H_n - G - k_B T_0}{T_0}.
\]

We insert in (19) to get

\[
\frac{\partial V}{\partial P_n} = \gamma \frac{H_n}{T_0} + \left( c - \gamma \frac{G + k_B T_0}{T_0} \right)
\]

This formula shows that if \( \Pi = 1 \) and if \( G_n = H_n - TS_{vib}^n \), then the equilibrium fluctuations of inherent enthalpy are directly correlated to the fluctuations of inherent volume.

**SINGLE PARAMETER MODEL**

In the following we will describe a simple formalism that makes it easy to perform calculations on a model fulfilling \( \Pi = 1 \). This calculation is inspired by the circuit model formalism for thermodynamics \[15, 16, 17, 18\]. Inspired by Goldstein and La Nave et. al. we introduce the following parameter \[12, 19\]

\[
\delta \varepsilon = \frac{\partial S}{\partial P_n} \delta P_n = \gamma^{-1} \frac{\partial V}{\partial P_m} \delta P_m.
\]
We combine (22) with (14) to find that in a linear experiment the instantaneous values of $S$ and $V$ are functions of $T, p$ and $\delta \varepsilon$.

\[
\delta S = \delta \varepsilon + J_{11}^\infty \delta T - J_{21}^\infty \delta p \\
\delta V = \gamma \delta \varepsilon + J_{12}^\infty \delta T - J_{22}^\infty \delta p 
\]

(23)

This model is different from the order parameter models introduced by Meixner and Prigogine, as it allows for $\delta \varepsilon$ to have non exponential relaxation $[1, 10]$. In the following we will show that the dynamics of this system can be described as the flow of Gibbs energy between the two reservoirs 1 and 2 with the Gibbs energy densities $G_1$ and $G_2$. These reservoirs will be chosen so that the total Gibbs energy $G$ is given by

\[
G = G_1 + G_2 
\]

(24)

We define the function $G_1$ to be the loss Gibbs energy during an isostructural process leading the system, from a state $(T, p, \bar{P})$ to the state $(T_0, p_0, \bar{P})$.

\[
G_1 = \int_{T_0, p, \bar{P}}^{T, p, \bar{P}} V \, dp^* - \int_{T_0, p, \bar{P}}^{T, p, \bar{P}} S \, dT^* 
\]

(25)

We insert (23) and $J_{12}^\infty = J_{21}^\infty$ to find $G_1$ is a function of $\delta T, \delta p$ and $\delta \varepsilon$. Furthermore we get the following second order expansion.

\[
G_1(\delta T, \delta p, \delta \varepsilon) = V_0 \delta p - S_0 \delta T + \frac{1}{2} \begin{pmatrix} \delta T \\ -\delta p \\ \delta \varepsilon \end{pmatrix}^T \begin{pmatrix} J_{11}^\infty & J_{12}^\infty & 1 \\ J_{21}^\infty & J_{22}^\infty & \gamma \\ 1 & \gamma & 0 \end{pmatrix} \begin{pmatrix} \delta T \\ -\delta p \\ \delta \varepsilon \end{pmatrix} 
\]

We would like to derive an equation of conservation of Gibbs energy for reservoir 1. Therefore we define $\psi = -\frac{\partial G_1}{\partial \varepsilon}$ and note from (25) that $S = -\frac{\partial G_1}{\partial T}$ and $V = \frac{\partial G_1}{\partial p}$ to get

\[
\dot{G}_1 = -ST + V \dot{p} - \psi \dot{\varepsilon}. 
\]

(26)

A similar equation for reservoir 2 follows from (7), (24) and (26)

\[
\dot{G}_2 = \dot{G} - \dot{G}_1 = \psi \dot{\varepsilon} 
\]

(27)

Most of the literature on network thermodynamics is expressed in terms of energy flows, and in order to stay consistent with this literature we define reservoir energies $U_1 = G_1 + ST - pV$, 


\( U_2 = G_2 \) to get
\[
U = U_1 + U_2 \\
\dot{U}_1 = T \dot{S} - p \dot{V} - \psi \dot{\varepsilon} \\
\dot{U}_2 = \psi \dot{\varepsilon}
\] (28)

These formulas describe the dynamics of the liquid as energy flow between two reservoirs. We proceed to find equations for the dynamics of each reservoir. The dynamics of the first reservoir follows from (25). We use the definitions of \( S, V \) and \( \psi \) and examine a harmonic perturbation to get
\[
\begin{pmatrix}
\delta \tilde{S} \\
\delta \tilde{V} \\
-\delta \tilde{\psi}
\end{pmatrix}
= 
\begin{pmatrix}
J_{11}^\infty & J_{12}^\infty & 1 \\
J_{21}^\infty & J_{22}^\infty & \gamma \\
-1 & -\gamma & 0
\end{pmatrix}
\begin{pmatrix}
\delta \tilde{T} \\
\delta \tilde{p} \\
\delta \varepsilon
\end{pmatrix}
\] (29)

The partial antisymmetry of this matrix reflects the fact that \(-p, T \) and \(-\psi \) are generalized forces on reservoir 2, whereas \( V, S \) and \( \varepsilon \) are generalized charges. In order to describe the second reservoir, we need a relation between \( \delta \tilde{\psi} \) and \( \delta \tilde{\varepsilon} \). We use (11), (12) and (13) to get
\[
\delta \tilde{\varepsilon} = a(\omega) \delta \tilde{\psi}
\] where
\[
a(\omega) = \sum_{m,n} \frac{\partial S}{\partial P_n} A_{nm}(\omega) \frac{\partial S}{\partial P_m}.
\] (30)

Finally we insert \( \delta \tilde{\varepsilon} = a(\omega) \delta \tilde{\psi} \) in (29) to find a simple expressions for the three complex response functions that we defined in (1):
\[
\frac{V_0}{T_0} \alpha_p(\omega) = J_{11}^\infty + a(\omega) \\
V_0 \alpha_{p}(\omega) = J_{12}^\infty + \gamma a(\omega) \\
V_0 \kappa_T(\omega) = J_{22}^\infty + \gamma^2 a(\omega)
\]

* Electronic address: gnalle@ruc.dk

[1] I. Prigogine and R. Defay, Chemical Thermodynamics (Longman, 1954).
[2] R. O. Davies and G. O. Jones, Proc. Roy. Soc. A (London) 217, 26 (1952).
[3] R. O. Davies and G. O. Jones, Adv. Phys. 2, 370 (1953).
[4] R. Roe, J. Appl. Phys 48 (1977).
[5] C. T. Moynihan and P. K. Gupta, J. Non-cryst Solids. 29, 143 (1978).
[6] C. T. Moynihan and A. V. Lesikar, Ann. N.Y. Acad. Sci. 371, 151 (1981).
[7] T. N. Nieuwenhuizen, Phys. Rev. Lett. 79, 1317 (1997).
[8] M. Goldstein, J. Chem. Phys. 51, 3728 (1969).
[9] N. G. V. Kampen, *Stochastical Processes in Physics and Chemistry* (North Holland, 1981).
[10] J. Meixner and H. G. Reik, in *Handbuch der Physik* (Springer, 1959).
[11] A. V. Lesikar and C. T. Moynihan, J. Chem. Phys. 72, 6422 (1980).
[12] E. L. Nave, S. Mossa, and F. Sciortino, Phys. Rev. Lett. 88, 225701 (2002).
[13] M. S. Shell, P. G. Debenedetti, E. L. Nave, and F. Sciortino, J. Chem. Phys. 118, S1085 (2003).
[14] E. L. Nave, S. Mossa, F. Sciortino, and P. Tartaglia, J. Phys. Condens. Matter 15, S1085 (2003).
[15] G. F. Oster, A. S. Perelson, and A. Kathalsky, Quarterly reviews of biophysics 6, 1 (1973).
[16] L. Peusner, *Studies in network Thermodynamics*, vol. 5 of *Studies in modern thermodynamics* (Elsevier, USA, 1986), first presented as a phd thesis at MIT.
[17] L. Peusner, in *Nonequlibrium theory and extremum principles*, edited by S. Sieniutycz and P. Salamon (Taylor and Francis, 1990), vol. 3 of *Advances in thermodynamics*, chap. 2.
[18] D. C. Mikulecky, *Applications of network thermodynamics to problems in biomecidical engineering* (New York university press, 1993).
[19] M. Goldstein, J. Chem. Phys. 39, 3369 (1963).

The relation \( \partial G / \partial P_n = \text{const} \) leads to \( G_n + k_B T \ln P_n^\text{eq} + k_B T = \text{const} \). Insert in (4) to find \( G_n + k_B T \ln P_n^\text{eq} = G \), and isolate \( P_n^\text{eq} \) to get the desired result.

We define the enthalpy from the Gibbs energy \( H(T, p, P) = G - T \partial G / \partial T \). Inserting (4) we find that \( H \) corresponds to the average vibrational entropy \( H(T, p, P) = \sum_n P_n (G_n - T \partial G_m / \partial T) \).

We define \( \delta q = \delta H - V \delta p = \delta H - \partial G / \partial p \delta p \). A little calculation yields \( \delta q = -T \partial^2 G / \partial T \partial p \delta p - T \partial^2 G / \partial T \partial P_n \delta P_n = T \delta S \).

First note \( \partial \ln P_n^\text{eq} / \partial (-p) = -1 / k_B T_0 \frac{\partial G_m - G}{\partial (-p)} = 1 / k_B T_0 \left( \frac{\partial V}{\partial P_n} - V \right) \). Then note \( \partial \ln P_n^\text{eq} / \partial T = -1 / k_B T \left( \frac{\partial G_m - G}{\partial T} - \frac{G_m - G}{T} \right) = -1 / k_B T \left( \frac{\partial G_m - G}{\partial T} + k_B \ln P_n^\text{eq} \right) = 1 / k_B T \left( \frac{\partial S}{\partial P_n} - S + k_B \right) \).

The symmetry of \( Y \) follows from detailed balance \( W_{mn} P_n^\text{eq} = W_{nm} P_m^\text{eq} \).

From the definition of equilibrium we get \( \sum_n W_{nm}^0 P_n^0 = 0 \). This gives \( \sum_n A_{nm}(\omega) = 0 \). The remaining eigenvalues are all positive and real \([9]\). We can find the spectrum by performing
an orthogonal diagonalization of \( Y \) to get \( Y_{lm} = \sum_k S_l(k) \lambda_k S_{mk} \). We insert in (16) to find
\[
A_{mn}(\omega) = \frac{1}{k_B T_0} \sum_k (P_m^0)^{1/2} S_{mk} \lambda_k S_{nk} (P_n^0)^{1/2}
\]

[25] From (5) we get \( \frac{\partial S}{\partial \rho_n} = -\frac{\partial^2 G}{\partial \rho_n \partial T} = -\frac{\partial G_{\rho}}{\partial T} - k_B (1 + \ln \rho_n) \). Applying this formula to the equilibrium ensemble (1), we get \( \frac{\partial S}{\partial \rho_n} = \frac{\partial G_{\rho}}{\partial T} + \frac{G_{\rho} - G - k_B T}{T} = \frac{H_{\rho} - G - k_B T}{T} \)

[26] From (24) we get \( \delta \tilde{\psi} = \delta \tilde{T} - \gamma \delta \tilde{p} \). Use (14) to get \( \frac{\partial S}{\partial \rho_n} \delta \tilde{\psi} = \frac{\partial S}{\partial \rho_n} \delta \tilde{T} - \gamma \frac{\partial S}{\partial \rho_n} \delta \tilde{p} = \frac{\partial S}{\partial \rho_n} \delta \tilde{T} - \frac{\partial V}{\partial \rho_n} \delta \tilde{p} - c \delta \tilde{p} = \sum_{\alpha} \frac{\partial Q_{\alpha}}{\partial \rho_n} \delta \tilde{X}_{\alpha} - c \delta \tilde{p} \). We insert in (13) and remember \( \sum_m A_{nm}(\omega) = 0 \) to get \( \delta \tilde{P}_n = \sum_m A_{nm}(\omega) \frac{\partial S}{\partial \rho_m} \delta \tilde{\psi} \). Finally insert (22) to get \( \delta \tilde{\varepsilon} = \sum_{m,n} \frac{\partial S}{\partial \rho_n} A_{mn}(\omega) \frac{\partial S}{\partial \rho_m} \delta \tilde{\psi} \)