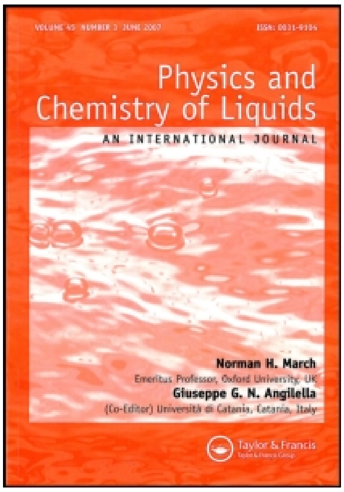

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Intermediate Scattering Function and Atomic Transport in Liquid Metals

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Abstract—It is stressed that theories that relate the intermediate scattering function $F(qt)$ to its self part $F_s(qt)$ may imply a relationship between the sound wave attenuation coefficient Γ and the diffusion constant D. The consequences of several recent theories of liquids are examined from this point of view. An approximate relation $\Gamma = M\rho D/S(o)$ is thereby proposed, where M is the atomic mass, ρ the number density and $S(o)$ is the long wavelength limit of the structure factor.

1. Introduction

For monatomic simple liquids the intermediate scattering function is defined as

$$F(qt) = \langle \rho_{\mathbf{q}}(t)\rho_{-\mathbf{q}}(0)\rangle \tag{1.1}$$

where $\rho_{\mathbf{q}}$ is a density fluctuation given by $\rho_{\mathbf{q}} = \sum_i^N e^{i\mathbf{q}\cdot\mathbf{r}_i}$, and the averaging is to be taken with respect to the equilibrium distribution function. The $\mathbf{r}_i$'s denote the atomic positions.

Although neutron scattering experiments provide much detailed information about the Fourier transform of $F(qt)$, there is no microscopic theory which would describe it even qualitatively correctly in terms of fundamental quantities like the interatomic potential. Therefore, often, an understanding of the intermediate scattering function is sought in terms of its self part defined as

$$F_s(qt) = \langle e^{i\mathbf{q}\cdot[\mathbf{r}(t)-\mathbf{r}(0)]}\rangle \tag{1.2}$$

where $\mathbf{r}(t)$ is the position vector of a randomly selected atom at the time t.

What lends impetus to such an approach is the fact that in a neutron scattering experiment, $S(q\omega)$, the Fourier transform of $F(qt)$, and $S_s(q\omega)$, the Fourier transform of $F_s(qt)$, are measured independently. They are, respectively, proportional to the coherent and incoherent scattering cross-section that a neutron when scattered by the liquid changes its momentum by $\hbar\mathbf{q}$ and its energy by $\hbar\omega$. Consequently, a theoretical relation between $F(qt)$ and $F_s(qt)$ is amenable to experimental verification.

The first example of the kind of relation sought was given by Vineyard (1958) in the form

$$F(qt) = S(q)\, F_s(qt) \tag{1.3}$$

where $S(q)$ is the liquid structure factor. Table 1 gives the various relations predicted by more recent theories. To facilitate comparison they are expressed in terms of the Laplace transforms:

$$\hat{F}(qp) = \int_0^\infty dt\, e^{-pt}\, F(qt) \tag{1.4}$$

$$\hat{F}_s(qp) = \int_0^\infty dt\, e^{-pt}\, F_s(qt) \tag{1.5}$$

It is the purpose of this paper to examine the implications of these relations for atomic transport.

2. Intermediate Scattering Functions and Transport Coefficients

The Fourier transform of the intermediate scattering functions $F(qt)$ and $F_s(qt)$ are related to the sound attenuation coefficient Γ‡ and the diffusion constant D by the following Kubo relations

$$D = \pi \underset{\omega\to 0}{\mathrm{Lt}}\ \underset{q\to 0}{\mathrm{Lt}}\ \frac{\omega^2}{q^2} S_s(q\omega) \tag{2.1}$$

$$\Gamma = \pi M^2 \rho\beta \underset{\omega\to 0}{\mathrm{Lt}}\ \underset{q\to 0}{\mathrm{Lt}}\ \frac{\omega^4}{q^4} S(q\omega) = \tfrac{4}{3}\eta + \zeta \tag{2.2}$$

where η and ζ are the shear and bulk viscosities respectively, ρ is the average number density of the fluid and $\beta = (k_B T)^{-1}$.

In what follows it will be useful to define the spectral functions

$$z(\omega) = \underset{q\to 0}{\mathrm{Lt}}\ \frac{\omega^2}{q^2} S_s(q\omega) \tag{2.3}$$

$$s(\omega) = \underset{q\to 0}{\mathrm{Lt}}\ \frac{\omega^4}{q^4} S(q\omega) \tag{2.4}$$

‡ Γ as used here is simply $\frac{4}{3}\eta + \zeta$, as in (2.2), and therefore is strictly only proportional to the sound wave attenuation.

TABLE 1.

Theories	Relations between $\hat{F}$ and $\hat{F}_s$	Relations between z and s
Vineyard (1958)	$\hat{F}(qp) = S(q)\,\hat{F}_s(qp)$	—
Effective mass approximation	$\hat{F}(qp) = S(q)\,\hat{F}_s\left(\frac{q}{\sqrt{S(q)}}, p\right)$	—
Kerr (1968)	$\hat{F}(qp) = \frac{S(q)\,\hat{F}_s(qp)}{1 + c(q)[p\hat{F}_s(qp) - 1]}$ ‡	—
The "phonon" theory	——— ,, ———	$s(\omega) = \frac{1}{\beta M S(0)} z(\omega)$
Hubbard and Beeby (1969)	$\hat{F}(qp) = \frac{S(q)}{p} + \left[\left(\frac{q^2}{2\pi M\beta p}\frac{\partial}{\partial p}\hat{F}_s(qp)\right)\Big/\left(1 - \omega_q^2\frac{\partial \hat{F}_s(qp)}{\partial p}\right)\right]$ §	$s(\omega) = \frac{1}{\beta M}\left[z(\omega) - \frac{1}{2}\omega\frac{\partial z(\omega)}{\partial \omega}\right]$

‡ The direct correlation function $c(q)$ is defined as $[S(q) - 1]/S(q)$.

§ The Hubbard–Beeby dispersion relation is given by $\omega_q^2 = \frac{\rho}{M}\int \frac{\partial^2\phi}{\partial z^2} g(r)[1 - \cos qz]\, d\mathbf{r}$.

and to note that while their values at $\omega = 0$ are determined by the corresponding transport coefficients i.e.:

$$D = \pi \operatorname*{Lt}_{\omega \to 0} z(\omega) \tag{2.5}$$

$$\Gamma = \pi M^2 \rho \beta \operatorname*{Lt}_{\omega \to 0} s(\omega), \tag{2.6}$$

their integrals are given by sum rules which $S(q\omega)$ and $S_s(q\omega)$ must satisfy, as follows:

$$\int_{-\infty}^{\infty} d\omega \, z(\omega) = \int_{-\infty}^{\infty} d\omega \operatorname*{Lt}_{q \to 0} \frac{\omega^2}{q^2} S_s(q\omega) = \operatorname*{Lt}_{q \to 0} \int_{-\infty}^{\infty} d\omega \, \frac{w^2}{q^2} S_s(q\omega) = \frac{1}{\beta M} \tag{2.7}$$

$$\begin{aligned} \int_{-\infty}^{\infty} d\omega \, s(\omega) &= \int_{-\infty}^{\infty} d\omega \operatorname*{Lt}_{q \to 0} \frac{\omega^4}{q^4} S(q\omega) = \operatorname*{Lt}_{q \to 0} \int_{-\infty}^{\infty} d\omega \, \frac{\omega^4}{q^4} S(q\omega) \\ &= \frac{1}{\beta M} \left[\frac{3}{\beta M} + \int d\mathbf{r} \, \frac{\partial^2 \phi}{\partial x^2} g(r) \left(\frac{1 - \cos \mathbf{q} \cdot \mathbf{r}}{q^2} \right)_{q=0} \right]. \end{aligned} \tag{2.8}$$

The quantities entering the fourth moment are the pair potential $\phi(r)$ and the radial distribution function $g(r)$. The fact that one may interchange the operations of taking the limit with respect to q and integrating with respect to the frequency ω is not at all obvious. However, this is discussed in some detail in Appendix 1.

3. Relations between $z(\omega)$ and $s(\omega)$

Clearly, if a theory relates $F(qt)$ to $F_s(qt)$ and this relationship is valid in the hydrodynamic limit (small q, long time) then the implication is that the relaxation of $F_s(qt)$ determines the relaxation of $F(qt)$. Under favorable conditions this might lead to a relation between $z(\omega)$ and $s(\omega)$, and therefore to a relation between Γ and D. Indeed such a relation was suggested by Brown and March (1968). They proposed that for liquid metals near the melting point

$$\Gamma \equiv \tfrac{4}{3}\eta + \zeta \cong \frac{2.8 \, DM\rho}{S(0)}. \tag{3.1}$$

As is well known, for a dilute gas of hard spheres, the shear viscosity η is related to D through

$$\eta \simeq DM\rho. \tag{3.2}$$

If one attempts to calculate $s(\omega)$ by using eq. (2.4) for the various theories listed in Table 1, one finds that the existence of the $q \to 0$ limit constitutes a rather severe test for the theory. This limit exists only for the Hubbard–Beeby theory and the "phonon" theory (see eqns (3.8) and (3.9)). These two give well defined relations between $s(\omega)$ and $z(\omega)$ as shown in the third column of Table 1. Evidently, the first three theories are not applicable in the hydrodynamic limit.

Concerning the conditions under which the Kubo limit exists, we can say that if the q dependence of the fourth moment is given correctly by the theory, the fact that $\int_{-\infty}^{\infty} s(\omega)\, d\omega$ is the fourth moment implies that $s(\omega)$ is everywhere finite. Satisfying the fourth moment is equivalent to conservation of current, which may be seen as follows.

The conservation of current j implies that

$$\dot{\mathbf{j}}_{\mathbf{q}}(t) = i\mathbf{q} \cdot \boldsymbol{\sigma}_q(t) \tag{3.3}$$

where $\boldsymbol{\sigma}_q(t)$ is the stress tensor. Hence

$$\ddot{\rho}_q = i\mathbf{q} \cdot \dot{\mathbf{j}}_q = -\mathbf{q} \cdot \boldsymbol{\sigma}_q(t) \cdot \mathbf{q} \tag{3.4}$$

and consequently

$$\frac{1}{q^4}\frac{\partial^4 F(qt)}{\partial t^4} = \frac{1}{q^4}\langle \ddot{\rho}_q(t)\ddot{\rho}_{-q}(0)\rangle = \frac{1}{q^4}\langle (\mathbf{q} \cdot \boldsymbol{\sigma}_q(t) \cdot \mathbf{q})(\mathbf{q} \cdot \boldsymbol{\sigma}_q(t) \cdot \mathbf{q})\rangle. \tag{3.5}$$

It is now clear that the current conservation equation implies that

$$\operatorname*{Lt}_{q \to 0} \frac{1}{q^4}\frac{\partial^4 F(qt)}{\partial t^4} = \langle \sigma_0^{\mathrm{XX}}(t)\, \sigma_0^{\mathrm{XX}}(0)\rangle \tag{3.6}$$

exists, where σ^{XX} is the diagonal element of the stress tensor in the direction of $\mathbf{q}$. The first three theories in Table 1 may be shown by direct calculation to violate current conservation.

It may be noted that, as a result of the above discussion, we may write

$$s(\omega) = \int_{-\infty}^{\infty} dt\, e^{-i\omega t}\, \langle \sigma_0^{\mathrm{XX}}(t)\, \sigma_0^{\mathrm{XX}}(0)\rangle, \tag{3.7}$$

a relation given earlier by Schofield.

3.1 "Phonon" theory

Though the Kerr theory fails to conserve current, it is interesting to notice that it is simply related to "phonon" theory for which we can find a plausible "Kubo limit". If we take this theory to be defined by the elementary relations

$$F(qt) = S(q) \cos \omega_q t \; : \; \omega_q^2 = \frac{q^2}{\beta M S(q)} \tag{3.8}$$

and

$$F_s(qt) = \cos \left[\frac{qt}{(\beta M)^{\frac{1}{2}}}\right], \tag{3.9}$$

then taking the Laplace transform of (3.9) and inserting this into the third entry in Table 1 brings back the Laplace transform of relation (3.8). Thus the Kerr theory relates F and F_s given by (3.8) and (3.9) exactly.

While, from the fourth moment given by Kerr, it is clear that the Kubo limit does not exist, we can use the explicit forms (3.8) and (3.9) to show, after a short calculation, that

$$s(\omega) = \frac{1}{\beta M S(0)} z(\omega). \tag{3.10}$$

From (3.10), (2.5) and (2.6), we clearly regain a relation of the form (3.1). However, the use of "phonon" theory in this way requires qualification. This theory determines $s(\omega)$ and $z(\omega)$ separately and the relation (3.10) could conceivably result from their pathological delta function form. Obviously, in "phonon" theory, the sound waves are not damped. However, the argument strongly suggests that there may well be a relation between F and F_s, intimately related to Kerr's theory, with a Kubo limit.

3.2 Hubbard–Beeby theory

We turn next to consider the predictions of the Hubbard–Beeby theory. Although the authors point out that their theory becomes inaccurate in the hydrodynamic regime, the Kubo limit in fact exists, and as shown in Appendix 2, the result we obtain relating the spectral functions is

$$s(\omega) = \frac{1}{\beta M}\left[z(\omega) - \tfrac{1}{2}\omega \frac{\partial z(\omega)}{\partial \omega}\right] \tag{3.11}$$

Hence the sound wave attenuation is given by

$$\Gamma = DM\rho \tag{3.12}$$

which is like (3.1), but without the structure factor $S(o)$. Comparison with the dilute gas of hard spheres theory given by (3.2) shows extreme similarity. While the similar forms of (3.1) and (3.12) are reassuring, nevertheless the difference due to the factor $1/S(0)$ is quantitatively very significant. For liquid metals near the melting point, $1/S(0)$ is in the range 30–100 and the presence of $(1/S(0))$ is essential in the relation between Γ and D for even order of magnitude agreement with experiment (cf. Table 3 of Brown and March).

The Hubbard–Beeby theory, bearing some relation to the random phase approximation, clearly does not take sufficient account of the short range order that exists in a dense metallic fluid. It predicts too small damping in the hydrodynamic limit.

3.3 Effective mass theory

It is interesting to note that the somewhat ad hoc procedure of replacing $F_s(qt)$ by $F_s(q/\sqrt{S(q)}, t)$ in the relation

$$\hat{F}(qp) = \frac{S(q)}{p} + \left\{\left[\frac{q^2}{2\pi M\beta p}\frac{\partial}{\partial p}\hat{F}_s(qp)\right]\Big/\left[1-\omega_q^2\frac{\partial}{\partial p}\hat{F}_s(qp)\right]\right\} \tag{3.13}$$

leads to the result

$$s(\omega) = \frac{1}{\beta M S(0)}\left[z(\omega) - \tfrac{1}{2}\omega\frac{\partial z(\omega)}{\partial\omega}\right], \tag{3.14}$$

which implies a result like (3.1). Such a replacement has been used by Skold to improve upon the Vineyard approximation. The result is the effective mass theory listed in Table 1. Ideally, one would seek a justification by summing up more terms in the expansion for the response function in the Hubbard–Beeby theory. However, we have already stressed that the presence of the factor $(1/S(0))$ in (3.1) is essential for order of magnitude agreement with experiment. Clearly, neutron measurements on both the spectral functions would be of considerable importance in showing the way in which (3.14) will need refinement.

One other aspect of the theories discussed here needs comment. Within the philosophy of relating F to F_s, we should use the exact frequency spectrum $z(\omega)$ in (3.11) and (3.14). This satisfies the relation

$$\int_{-\infty}^{\infty} z(\omega)\,d\omega = \frac{1}{\beta M}. \tag{3.15}$$

Hence we obtain from (3.14) the result

$$\int_{-\infty}^{\infty} s(\omega)\,d\omega = \frac{3}{\beta^2 M^2 S(0)} \tag{3.16}$$

On the other hand, the Hubbard–Beeby result (3.11) gives this formula, with $S(0) = 1$. This is curious, because the Hubbard–Beeby form for $S(q\omega)$ satisfies the fourth moment relation

$$\int_{-\infty}^{\infty} \omega^4 S(q\omega)\, d\omega = \frac{3q^4}{M^2\beta^2} + \frac{q^2\rho}{M^2\beta}\int \frac{\partial^2\phi}{\partial z^2}\, g(r)\,[1-\cos qz]\, d\mathbf{r} \qquad (3.17)$$

exactly.

The difference in the Hubbard–Beeby theory between the fourth moment relation and the area under the frequency function $s(\omega)$ appears to come from the inevitable degree of internal inconsistency in the theory, which leads to different answers depending on the order of the limits $q \to 0$, $t \to 0$. The two limits are the same in the exact theory, according to the arguments given in Appendix 1.

If we use "phonon" theory to evaluate the fourth moment, we find as $q \to 0$,

$$\int_{-\infty}^{\infty} \frac{\omega^4}{q^4} S(q\omega)\, d\omega \sim \frac{1}{\beta^2 M^2 S(0)}\,. \qquad (3.18)$$

This appears to work reasonably well for liquid metals near the melting point and the effective mass theory result (3.16) gives a better approximation to this than the Hubbard–Beeby theory by a factor of the order of 10.

4. Summary

(1) Approximate theories relating F and F_s ought to satisfy current conservation to ensure reasonable behaviour in the hydrodynamic limit.

(2) The main consequences of the approximate theories relating F and F_s appear to be:

(*a*) Equation (3.10) at $\omega = 0$ relating the sound attenuation and diffusion. To bring theory and experiment into even semi-quantitative agreement, the presence of $S(0)$ is essential in liquid metals.

(*b*) Equation (3.14) relating the frequency functions $s(\omega)$ and $z(\omega)$. Experimental information as to the way in which such a relation should be refined is badly needed.

(*c*) From the measured transport coefficients, it seems clear that either the present functional relations are too simple, or that explicit introduction of at least the three-particle correlation function into the theory is required.

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Appendix 1

In this Appendix, we show that

$$\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dt \operatorname*{Lt}_{q\to 0} \frac{1}{q^4} \frac{\partial^4 F(qt)}{\partial t^4} e^{i\omega t} = \operatorname*{Lt}_{q\to 0} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dt \frac{1}{q^4} \frac{\partial^4 F(qt)}{\partial t^4} e^{i\omega t} \tag{A1.1}$$

in an exact theory. Clearly the right-hand-side of this expression is the $q \to 0$ limit of the fourth moment relation. The left-hand-side is equal to $\int_{-\infty}^{\infty} s(\omega)\, d\omega$ if the $q \to 0$ limit is interchangeable with the time integration. We see no reason with physical situations why this should not be possible, though we cannot prove the result rigorously. (The theory of Hubbard and Beeby has a structure that does not allow us to make such an interchange).

The intermediate scattering function $F(qt)$ which satisfies

$$\frac{1}{q^4} \frac{\partial^4 F(qt)}{\partial t^4} = \frac{1}{q^4} \langle \ddot{\rho}_{\mathbf{q}}(t) \ddot{\rho}_{-\mathbf{q}}(0) \rangle \tag{A1.2}$$

yields, on carrying out the differentiations

$$\begin{aligned} \frac{1}{q^4} \frac{\partial^4 F(qt)}{\partial t^4} = {} & \frac{1}{q^4} \left\langle \sum_{ij} \left(\frac{\mathbf{p}_i(t) \cdot \mathbf{q}}{M} \right) \left(\frac{\mathbf{p}_j(0) \cdot \mathbf{q}}{M} \right) e^{i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0)} \right\rangle \\ & + \frac{i}{q^4} \left\langle \sum_{ij} \left(\frac{\mathbf{p}_i(t) \cdot \mathbf{q}}{M} \right) \left(\frac{\mathbf{q} \cdot \mathbf{F}_j(0)}{M} \right) e^{i\mathbf{q} \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(0))} \right\rangle \\ & - \frac{i}{q^4} \left\langle \sum_{ij} \left(\frac{\mathbf{p}_j(0) \cdot \mathbf{q}}{M} \right) \left(\frac{\mathbf{q} \cdot \mathbf{F}_i(t)}{M} \right) e^{i\mathbf{q} \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(0))} \right\rangle \\ & + \frac{1}{q^4} \left\langle \sum_{ij} \left(\frac{\mathbf{F}_i(t) \cdot \mathbf{q}}{M} \right) \left(\frac{\mathbf{F}_j(0) \cdot \mathbf{q}}{M} \right) e^{i\mathbf{q} \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(0))} \right\rangle \end{aligned} \tag{A1.3}$$

If one now passes to the limit $t\to 0$, then the averages may be evaluated exactly and the result is

$$\frac{1}{q^4}\frac{\partial^4 F(qt)}{\partial t^4}\bigg|_{t=0} = \frac{1}{q^4}\left[\frac{3q^4}{\beta^2 M^2} + \frac{q^4}{\beta^2 M^2}\Big(S(q)-1\Big) - \frac{q^4}{\beta^2 M^2}\Big(S(q)-1\Big)\right]$$
$$- \frac{q^4}{\beta^2 M^2}\Big(S(q)-1\Big) + \frac{q^4}{\beta^2 M^2}\Big(S(q)-1\Big)$$
$$+ \frac{q^4}{\beta M^2}\int d\mathbf{r}\, g(r)\frac{\partial^2\phi(r)}{\partial x^2}\left[\frac{1-\cos\mathbf{q}\,.\,\mathbf{r}}{q^2}\right]. \qquad \text{(A1.4)}$$

It is now a simple matter to take the $q\to 0$ limit, and the right-hand-side of (2.8) is obtained.

To take the $q\to 0$ limit first, we assume that the right-hand-side of (A1.3) can be expanded in powers of q. Then we find

$$\frac{1}{q^4}\frac{\partial^4 F(qt)}{\partial t^4} = \frac{1}{q^4}\left\langle\sum_{ij}\left(\frac{\mathbf{p}_i(t)\,.\,\mathbf{q}}{M}\right)^2\left(\frac{\mathbf{p}_j(o)\,.\,\mathbf{q}}{M}\right)^2\right\rangle$$
$$- \frac{1}{q^4}\left\langle\sum_{ij}\left(\frac{\mathbf{p}_i(t)\,.\,\mathbf{q}}{M}\right)^2\left(\frac{\mathbf{q}\,.\,\mathbf{F}_j(o)}{M}\right)\Big[\mathbf{q}\,.\,(\mathbf{r}_i(t)-\mathbf{r}_j(o))\Big]\right\rangle$$
$$+ \frac{1}{q^4}\left\langle\sum_{ij}\left(\frac{\mathbf{p}_j(o)\,.\,\mathbf{q}}{M}\right)^2\left(\frac{\mathbf{q}\,.\,\mathbf{F}_i(t)}{M}\right)\Big[\mathbf{q}\,.\,(\mathbf{r}_i(t)-\mathbf{r}_j(o))\Big]\right\rangle$$
$$- \frac{1}{2q^2}\left\langle\sum_{ij}\left(\frac{\mathbf{q}\,.\,\mathbf{F}_i(t)}{M}\right)\left(\frac{\mathbf{q}.\,\mathbf{F}_j(o)}{M}\right)\Big[\mathbf{q}\,.\,(\mathbf{r}_i(t)-\mathbf{r}_j(o))\Big]^2\right\rangle \qquad \text{(A1.5)}$$

where we have not displayed terms like $\left\langle\sum_{ij}\left(\frac{\mathbf{p}_i(t)\,.\,\mathbf{q}}{M}\right)^2\left(\frac{\mathbf{q}\,.\,\mathbf{F}_j(0)}{M}\right)\right\rangle$, which are evidently zero due to the spherical symmetry of the problem.

Though the detailed terms are different, it is straightforward to show from (A1.5) that (A1.1) results.

Appendix 2

To find a relation between $s(\omega)$ and $z(\omega)$ from

$$\hat{F}(qp) = \frac{S(q)}{p} + \left[\left(\frac{q^2}{2\pi M\beta p}\frac{\partial\hat{F}_s(qp)}{\partial p}\right)\Big/\left(1-\omega_q^2\frac{\partial\hat{F}_s(qp)}{\partial \rho}\right)\right], \qquad \text{(A2.1)}$$

we introduce the Laplace transforms

$$\hat{z}(qp) = \int_0^\infty dt\, e^{-pt} \frac{1}{q^2} \frac{\partial^2 F_s(qt)}{\partial t^2} \tag{A2.2}$$

and

$$\hat{s}(qp) = \int_0^\infty dt\, e^{-pt} \frac{1}{q^4} \frac{\partial^4 F(qt)}{\partial t^4}. \tag{A2.3}$$

Clearly

$$z(\omega) = \operatorname*{Lt}_{q\to 0} \operatorname{Re}\{\hat{z}(q, -i\omega)\} \tag{A2.4}$$

and

$$s(\omega) = \operatorname*{Lt}_{q\to 0} \operatorname{Re}\{\hat{s}(q, -i\omega)\}. \tag{A2.5}$$

We may now write $\hat{F}_s(qp)$ and $\hat{F}(qp)$ in terms of $\hat{z}(qp)$ and $\hat{s}(qp)$ by noting that

$$\hat{F}_s(qp) = \frac{1}{p} - \frac{q^2}{p^2}\hat{z}(qp) \tag{A2.6}$$

and

$$\hat{F}(qp) = \frac{S(q)}{p} - \frac{q^2}{p^3\beta M} + \frac{q^4}{p^4}\hat{s}(qp) \tag{A2.7}$$

By substituting these expressions into (A2.3) one obtains

$$\hat{s}(qp) = \frac{p}{\beta M q^2} + \frac{p}{2\pi\beta M q^2}\left[\left\{1 - \frac{2q^2}{p}\hat{z}(qp) + q^2\frac{\partial \hat{z}(qp)}{\partial p}\right\} \Big/ \left\{1 + \frac{\omega_q^2}{p^2}\left(1 - \frac{2q^2}{p}\hat{z}(qp) + q^2\frac{\partial \hat{z}(qp)}{\partial p}\right)\right\}\right]. \tag{A2.8}$$

It is now a matter of simple algebra to calculate $\operatorname*{Lt}_{q\to 0} \operatorname{Re}\hat{s}(q, -i\omega)$, yielding

$$\operatorname*{Lt}_{q\to 0} \operatorname{Re}\hat{s}(q, -i\omega) = \frac{1}{\beta M}\left[z(\omega) - \tfrac{1}{2}\omega\frac{\partial z(\omega)}{\partial \omega}\right] = s(\omega) \tag{A2.9}$$

which is the result we wished to prove.