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APPLICATIONS OF THE WIGNER REPRESENTATIONS TO THE THEORY OF SLOW NEUTRON SCATTERING

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ABSTRACT

A Wigner representation is used for expressing the thermal average occurring in the Van Hove formulism for slow neutron scattering from macroscopic systems. For quadratic and lower degree potentials results in closed form may be obtained, and in general, an asymptotic series expansion in powers of $\hbar$ is still possible for the incoherent part of the differential cross section for quasi-classical systems. The lead term of this asymptotic expansion results in an expression relating the cross section to a four dimensional Fourier inversion of the classical space-time distribution $G_s^c(r,t)$ and, hence, to the classical motions of the atoms in the scattering system.

Correction terms of $\mathcal{O}(\hbar^2)$ have been obtained explicitly and found to be small for systems at ordinary temperatures. It is shown that because of the contact nature of the Fermi pseudo-potential the exact classical limit ($\hbar \to 0$) for any system is the ideal-gas result. The derivation involves the application of "Weyl's rule," which is rederived in a manner felt to be slightly more understandable than previous derivations and, in addition, extended to Heisenberg operators. In principle, the results can be extended to all orders of $\hbar^2$. No similar asymptotic expansion appears to exist, however, for the coherent cross section. An alternate approach to the interpretation of slow neutron scattering data, based on the use of a specific model Hamiltonian, is illustrated for the case of a monatomic liquid. The model used, originally proposed by Ookawa, is of the crystalline dislocation type and leads to a sum of gas and oscillator Hamiltonians. The incoherent intermediate and scattering functions were found very conveniently from such Hamiltonian by using the Wigner representation previously introduced. The width of the intermediate scattering function for liquid lead was then compared with other models and available experimental results.

On the basis of the present investigation, suggestions for further work are made.

CHAPTER I

INTRODUCTION

With the advent of neutron reactors, and consequent high neutron fluxes, slow neutron spectroscopy has been able to compare advantageously with X-ray, electron, and infrared spectroscopy in providing information about the dynamical structure of solids, liquids, and molecules.[1]

For light atoms, X-ray diffraction has the fundamental disadvantage of the linear dependence of the scattering amplitude on the atomic number of the scatterer. This is not the case for neutrons which, within a factor of two or three, are scattered equally well by most atoms.[2]

A further disadvantage of X-ray and electron scattering from atoms, relative to neutron scattering, results from the fall-off, with increase in angle of scattering, of the atomic form factor for the former as opposed to the angular independent scattering length for slow neutrons.[3]

Most important, however, is that for X-rays and electrons the energy transfers associated with the scattering process are negligible compared to the energy of the scattered photon or particle, and the method, although quite sensitive to target symmetry, provides no information on the atomic motions.

Conversely, an infrared photon of 0.025 ev has a wavelength of the order of 5×10^5Å, and thus, infrared spectroscopy allows for just enough resolution to see only atomic motions in which a very large number of atoms move together as a group.

Neutrons, because of their large mass, may simultaneously have energies comparable to those characteristic of the various modes of molecular motions as well as de Broglie wavelengths of the order of interatomic spacings. It is in this respect that measurements of the energy spectrum of initially slow monoenergetic neutrons, after scattering by a specimen, provide considerable information about the dynamical structure of the scatterer.

A general theory of neutron scattering by arbitrary systems of atoms has been presented by Van Hove,[4] based on the Fermi pseudo-potential approximation.[5] In this theory, the differential scattering cross section is expressed as a four-dimensional Fourier transform of a space-time correlation function $G(\underline{r},t)$. Such a formulation appears, then, as a natural time dependent generalization of the Zernike-Prins "static approximation,"[6] in which the differential scattering cross section is given in terms of the well-known pair distribution function $g(\underline{r})$. In fact, the latter function is equal to the nondiagonal component of $G(\underline{r},t)$ evaluated at $t = 0$.

Accurate calculations of $G(\underline{r},t)$ are, however, only possible for systems where the many-particle Hamiltonian may be replaced by a sum of many single-particle Hamiltonians. This is the case of dilute gases and crystals, for which the predicted angular and energy distributions of the scattered neutrons are, indeed, in good agreement with experiment.

For dense fluids, the complexity of the atomic dynamics is much greater than in the above mentioned cases, and a calculation of $G(\underline{r},t)$, by reduction of the problem to a soluble one-body problem, necessitates highly simplifying assumptions in the specific dynamical models used.

There is, however, an alternate approach to the analysis of neutron scattering experiments based on the physical interpretation of the space-time correlation function $G(\underline{r},t)$ in the limit $\hbar \to 0$. In this limit, it is the conditional probability density that given an atom at the origin at time $t = 0$ there will be an atom (the same or another) a distance $\underline{r}$ away at time t; i.e., it provides a "moving picture" of the motions of the atoms in the system.

The plausibility of this approach is then subject to the existence of a relationship between this classical $G^c(\underline{r},t)$ and the differential scattering cross section. Various semi-empirical prescriptions have been proposed in an attempt to establish such a relationship. The most intuitive of them all results simply from replacing $G(\underline{r},t)$ in the Van Hove formulism by its classical limit. This, as observed by Vineyard,[7] corresponds to a development in which the neutron is treated quantum mechanically and the scatterer classically. It has the unsatisfactory features that recoil effects are inadequately treated in that the average energy loss is set equal to zero. Also, as observed by Schofield,[8] it violates the constraint of detailed balance. Schofield has suggested a recipe to remedy these defects in which he sets $G^c(\underline{r},t)$ equal to $G(\underline{r},t+\frac{i\beta\hbar}{2})$, where $\beta = 1/k_BT$, instead of $G(\underline{r},t)$ and asserts its validity to first order in $\hbar$.

This assertion is wrong, however, as may be seen from the fact that the prescription fails to yield the correct result for the ideal monatomic gas, for which the cross section is, in terms of the significant variables $\underline{\Delta}p$ and ϵ($\underline{\Delta}p$, ϵ = momentum and energy transfer respectively), actually independent of $\hbar$.

Other existing prescriptions, which are discussed in more detail in Chapter V, are again based on more or less intuitive arguments and leave the problem of establishing an unambiguous connection between $G^c(\underline{r},t)$ and the differential scattering cross section unsolved. It is the purpose of this work to approach the subject in a deductive, rather than inductive fashion with the hope of removing such ambiguities. In particular, and in order to relate the cross section to classical dynamical variables, use is made of a Wigner representation[9,10] for the thermal average occurring in the expression for $G(\underline{r},t)$.

This results in the replacement of the conventional quantum average by a phase-space average, over a Wigner distribution, of the "Weyl equivalent" of the operator present in the thermal average.[11] For the incoherent cross section, this "Weyl equivalent" admits an asymptotic series expansion in powers of $\hbar$ where the first contributing correction to the leading term is shown to be of order $\hbar^4$ for randomly oriented systems.

It is further noted that because of the presence of an essential singularity in $G(\underline{r},t)$ the above indicated procedure may not be applied to the coherent component of the cross section, the exceptions being the cases of harmonic and lower degree potentials. This limitation is not considered too strong, however, because the interference scattering is quite insensitive to target dynamics (see Chapter VII for elucidation of this point).

For ordinary temperatures, the Wigner distribution may also be expanded conveniently in powers of $\hbar^2$.[13] The first term in this expansion, of zeroth order in $\hbar$, is just the classical canonical joint distribution function. Combining this series with the above mentioned asymptotic expansion results in an expression in which the first term, which we have chosen to call the "quasi-classical" approximation,[12] is now the classical thermal average of the leading term in the asymptotic expansion, plus correction terms of order $\hbar^2$ and higher.

Additional rearrangement of the results obtained, preserving their order of validity plus the use of time translational invariance, leads to the desired relation between the cross section and the classical correlation $G^c(\underline{r},t)$. It is found that the first term in this expression is the same as the prescription proposed from empirical considerations by Singwi and Sjölander.[14] The correction terms of order $\hbar^2$ have been obtained explicitly and shown to be small for systems at ordinary temperatures. It is also shown that the results obey the constraint of detailed balance[15] and satisfy the Placzek moments[16] to order $\hbar^2$. The analysis is then used for deriving other existing prescriptions and for examining their implications and range of validity. Numerical computations are presented in which the cross sections for some simple systems, as calculated by the Vineyard prescription, are compared with the results of this work.[17]

As an illustration of the rigorous attack provided by the formulism to harmonic and gas-like Hamiltonians, a crystalline dislocation model of a liquid, originally proposed by Ookawa,[18] is considered. In this model, thermal agitation is represented by a superposition of longitudinal waves plus shear waves that lead to either translational or vibrational modes, depending upon the wavelength. The Hamiltonian is derived in a less intuitive manner than in Ookawa's paper, and the parameters entering this Hamiltonian are obtained from Thermodynamics. On the basis of the model, expressions are obtained for the incoherent cross section.

In Chapter II, the general theory on neutron scattering from macroscopic aggregates is reviewed, and the Van Hove formulism is extended to the case of polyatomic systems; although, for simplicity, only monatomic and monoisotopic systems are considered in the subsequent chapters. In Chapter III, several pertinent properties of the correlation function $G(\underline{r},t)$ are discussed. In particular, its physical meaning for various limiting cases is established, and a fluctuation-dissipation theorem which relates its real and imaginary components is obtained. Some properties of the Abelian type, relating the asymptotic behavior of the intermediate scattering function $\chi(\underline{\Delta p},t)$ (obtained by spatial-Fourier inversion of $G(\underline{r},t)$) to the behavior of its time-Fourier inversion $S(\underline{\Delta p},\epsilon)$ for small energy transfers, are also considered. Finally, it is shown that the cross section obeys the principle of detailed balancing, and the Placzek moments of the scattering function $S(\underline{\Delta}p, \epsilon)$ are introduced. These properties are investigated because they provide useful information on the dynamics of the scatterer as well as for their utility as checks on the approximate descriptions of the scattering cross section. The isomorphism between the Weyl-Wigner quasi-probability distributional formulation and the density matrix formulation of von Neumann[19] is derived in Chapter IV in what is felt to be a somewhat simpler and more self-contained manner. It is then generalized to Heisenberg operators and applied in Chapter V to the scattering problem, thus resulting in an asymptotic expansion for the incoherent cross section in which the leading term contains the classical self space-time correlation $G_s^c(\underline{r},t)$. The analysis is also shown to cast light on existing semi-empirical prescriptions for relating $G_s^c(\underline{r},t)$ to the cross section. In Chapter VI, Ookawa's crystalline model for a monatomic liquid is discussed and formulae for the scattering cross section are obtained. The width of the diagonal part of the intermediate scattering function is computed for the case of lead, and the results are compared with those for a stochastic model proposed by Rahman and Singwi and Sjölander,[20] as well as with Brockhouse and Pope's data obtained from experiments.[21] A summary and concluding remarks are given in Chapter VII, and recommendations are made for further work, both experimental and theoretical.

CHAPTER II

NEUTRON SCATTERING BY NUCLEI IN AN ARBITRARY MACROSCOPIC AGGREGATE

2.1 THE FERMI PSEUDO-POTENTIAL[22]

A direct application of perturbation theory to the problem of slow neutron scattering by nuclei* of chemically bound atoms is inadequate due to the intensity of the nuclear forces involved. These forces, however, have a short range of action compared to the relevant molecular dimensions, and neutron-nuclear collisions may be described to a good approximation by "contact interactions."

Moreover, for slow neutrons (energies $\lesssim$ 1 ev), only S-wave scattering is important and the scattering amplitude for an individual atom is independent of energy.

Thus, the elastic scattering cross section for an isolated atom is isotropic in the center of mass coordinate system and is given by

$$\sigma_{\ell,el} = 4\pi A_\ell^2 \tag{2.1}$$

A_ℓ is the scattering amplitude for the interaction, and though energy independent, it is in general a function of the total spin angular momentum of the neutron and the nucleus.

Equation (2.1) can be formally obtained from the first Born approximation by making use of the Fermi pseudo-potential method,[3,5,23,24]

*We neglect magnetic scattering and neutron-electron interaction.

which essentially consists of replacing a boundary condition on the wave function of the system by the pseudo-potential

$$V(\underline{r}-\underline{R}_j) = \frac{2\pi\hbar^2}{m}\left(\frac{M_j+m}{M_j}\right) A_j\delta(\underline{r}-\underline{R}_j) \tag{2.2}$$

introduced in the wave equation.*

In Eq. (2.2), M_j denotes the mass of the jth nucleus, $\underline{r}_j$ its vector position and m the mass of the neutron. The quantity

$$a_j = \frac{M_j+m}{M_j} A_j \tag{2.3}$$

is usually known as the bound scattering length while A_j is referred to as the free-atom scattering length.

2.2 DIFFERENTIAL CROSS SECTION[22,28-30]

Consider an arbitrary macroscopic aggregate (thin enough, however, so that multiple scattering is negligible) from which a monoenergetic beam of neutrons with momentum $\hbar\underline{k}_0$ and spin** state $|\tau_0\rangle$ is scattered into a group of spatial states with propagation vector in $d\underline{k}$ about $\underline{k}$ and spin state $|\tau\rangle$. Simultaneously the scatterer undergoes a transition from an initial state $|i\rangle$ to a final state $|f\rangle$.*** The transition rate

*Lippmann and Schwinger[25] have derived Fermi's results by means of a variational treatment of neutron scattering. A test on the reliability of the Fermi approximation for the case of neutron scattering from parahydrogen is given by Lippmann.[26] See also Summerfield, et al.[27]

**τ denotes the z-component of the neutron spin.

***The spin states of the scatterer are also included in the kets $|i\rangle$ and $|f\rangle$.

for such a process is given in the context of the first Born approximation by:

$$(\omega_{i\to f})\,\rho(\underline{k})\,d^3k \;=\; \frac{1}{\hbar L^3}\,\frac{m}{(2\pi\hbar)^2}\,k\,d\Omega\,d\epsilon \left|\sum_j \langle f\tau\right| \int e^{i(\underline{k}_o-\underline{k})\cdot\underline{r}} \tag{2.4}$$

$$(x)\;\; V(\underline{r}-\underline{R}_j)\,d^3r\,|\tau_o i\rangle|^2\;\delta(E_f+\epsilon_f-E_i-\epsilon_i)\,.$$

Here E_i and E_f are the initial and final energies of the scatterer and

$$\epsilon_i \;=\; \frac{\hbar^2 k_o{}^2}{2m}\,, \quad \epsilon_f \;=\; \frac{\hbar^2 k^2}{2m}\,, \quad \epsilon \;=\; \epsilon_i - \epsilon_f\,. \tag{2-5}$$

The factor L^{-3} is due to box normalization of the neutron wave function.

Substituting Eq. (2.2) into (2.4) and dividing the result by the total number (N) of scatterers in the sample and the probability current density of the incident beam $I = \hbar k_o/mL^3$ yields

$$\frac{(\omega_{i\to f})\,\rho(\epsilon)\,d\epsilon}{NI\,d\Omega\,d\epsilon} \;=\; \frac{k}{Nk_o}\left|\sum_j \langle f\tau\right|\, a_j\; e^{i\underline{\kappa}\cdot\underline{R}_j}\,|i\tau_o\rangle|^2\;\delta(E_f-E_i-\epsilon) \tag{2.6}$$

where

$$\underline{\kappa} \;=\; \underline{k}_o - \underline{k}\,. \tag{2.7}$$

Note that the expression on the left side of Eq. (2.6) is the definition of the differential scattering cross section per atom, per unit solid angle, and per unit interval of neutron energy transfer for transitions $|i\tau_o\rangle \to |f\tau\rangle$ of the neutron-scatterer system. Hence, in the laboratory system,

$$\frac{\partial^2 \sigma_{if}}{\partial\Omega\partial\epsilon} = \frac{k}{Nk_o} \left| \sum_j < f\tau | a_j \, e^{i\underline{\kappa}\cdot\underline{R}_j} \, | i\tau_o > \right|^2 \delta(E_f - E_i - \epsilon), \tag{2.8}$$

which upon introducing the Fourier representation of the delta function and after some straightforward manipulations becomes

$$\frac{\partial^2 \sigma}{\partial\Omega\partial\epsilon} = \frac{1}{2\pi\hbar} \frac{k}{Nk_o} \int_{-\infty}^{\infty} dt \; e^{-\frac{it\epsilon}{\hbar}} \sum_{j,k} < i\tau_o | a_k^{\dagger} \, e^{-\underline{\kappa}\cdot\underline{R}_k} \, e^{\frac{itH_s}{\hbar}} | \tau f >$$
$$(x) \; < f\tau | a_j \, e^{i\underline{\kappa}\cdot\underline{R}_j} \, e^{-\frac{itH_s}{\hbar}} | i\tau_o > . \tag{2.9}$$

H_s is used in the above expression to denote the molecular Hamiltonian of the scattering system.

Moreover, since the incident beam of neutrons is usually not polarized and the target system is in thermal equilibrium rather than in an initially prepared state, we average (2.9) over all initial states of the neutron + scatterer. Subsequently, we sum over all final states $|f\tau>$ since these are also not observed.

The appropriate expression to which experimental observations are to be compared is then given

$$\frac{\partial^2 \sigma}{\partial\Omega\partial\epsilon} = \sum_{\tau_o = \pm\frac{1}{2}} \frac{1}{2} \sum_i p_i \sum_f \frac{\partial^2 \sigma_{if}}{\partial\Omega\partial\epsilon}$$

$$= \frac{k}{2\pi\hbar Nk_o} \sum_{\tau_o = \pm\frac{1}{2}} \frac{1}{2} \sum_i p_i \int_{-\infty}^{\infty} dt \; e^{-\frac{it\epsilon}{\hbar}} \sum_{\ell,k} < i\tau_o | a_k^{\dagger} a_\ell \, e^{-i\underline{\kappa}\cdot\underline{R}_k}$$
$$(x) \; e^{i\underline{\kappa}\cdot\underline{R}_\ell(t)} \, | i\tau_o > \tag{2.10}$$

where

$$\underline{R}_\ell(t) = e^{\frac{iH_s t}{\hbar}} \underline{R}_\ell \, e^{-\frac{iH_s t}{\hbar}} \tag{2.11}$$

and p_λ is the statistical weight of the initial states $|\lambda>$ of the scatterer.

In deriving (2.10) the states $|\not{f}\tau>$ are assumed to form a complete set, and use is made of the closure property

$$\sum_{\tau, \not{f}} |\not{f}\tau><\not{f}\tau| = 1 . \tag{2.12}$$

It is now convenient to consider the dependence of the scattering length on the total angular momentum* j of the system neutron + scatterer more explicitly. To this end, note that if i_ℓ is the spin of the ℓth nucleus then

$$j_\ell = i_\ell \pm \frac{1}{2} \tag{2.13}$$

where the (+) or (-) signs denote "parallel" or anti-parallel spin states. The scattering lengths corresponding to these two possible values of j_ℓ are $a_\ell^{(+)}$ and $a_\ell^{(-)}$. We thus construct an expression for a_ℓ such that it is equal to $a_\ell^{(+)}$ or $a_\ell^{(-)}$ for $j_\ell = i_\ell \pm \frac{1}{2}$ respectively. This expression is

$$a_\ell = a_\ell^{(+)}\mathcal{P}_\ell^{(+)} + a_\ell^{(-)}\mathcal{P}_\ell^{(-)} \tag{2.14}$$

*In order to distinguish operators from their eigenvalues, we use upper case to denote the former and lower case for the eigenvalues.

where $\mathcal{P}_\ell^{(+)}$ and $\mathcal{P}_\ell^{(-)}$ are projection operators[22,29] defined by

$$\mathcal{P}_\ell^{(\pm)} \, |i \pm \frac{1}{2}> \; = \; |i \pm \frac{1}{2}> \qquad (2.15a)$$

and

$$\mathcal{P}_\ell^{(\pm)} \, |i \mp \frac{1}{2}> \; = \; 0 \qquad (2.15b)$$

It can be readily verified that Eqs. (2.15a) and (2.15b) are satisfied by

$$\mathcal{P}^{(+)} = \frac{J^2 - j^2_{i-\frac{1}{2}}}{j^2_{i+\frac{1}{2}} - j^2_{i-\frac{1}{2}}} = \frac{\underline{I}^2 + 2\underline{I}\cdot\underline{S} + \underline{S}^2 - i^2 + \frac{1}{4}}{2i+1} = \frac{i+1+2\underline{I}\cdot\underline{S}}{2i+1} \qquad (2.16)$$

and

$$\mathcal{P}^{(-)} = \frac{J^2 - j^2_{i+\frac{1}{2}}}{j^2_{i-\frac{1}{2}} - j^2_{i+\frac{1}{2}}} = \frac{i - 2\underline{I}\cdot\underline{S}}{2i+1} \qquad (2.17)$$

where $\underline{S}$ is the neutron spin operator.

Hence,

$$a_\ell = \left[a_\ell^{(+)} \left(\frac{i_\ell+1}{2i_\ell+1}\right) + a_\ell^{(-)} \left(\frac{i_\ell}{2i_\ell+1}\right) \right] + 2 \left\{ \frac{[(i_\ell+1)i_\ell]^{\frac{1}{2}}}{2i_\ell+1} \left(a_\ell^{(+)} - a_\ell^{(-)}\right) \right\}$$

$$(x) \quad \frac{\underline{I}_\ell\cdot\underline{S}}{[(i_\ell+1)i_\ell]^{\frac{1}{2}}} \qquad (2.18)$$

$$= \mathcal{A}_\ell + 2\mathcal{B}_\ell \, \frac{\underline{I}_\ell\cdot\underline{S}}{[i_\ell(i_\ell+1)]^{\frac{1}{2}}}$$

$\mathcal{A}_\ell$ and $\mathcal{B}_\ell$ are the so-called coherent and incoherent scattering amplitudes respectively.

Noting that

$$\sum_{\tau_o=\pm\frac{1}{2}} < \tau_o|\underline{I}_\ell\cdot\underline{S}|\tau_o > = \sum_{\alpha=1}^{3} I_{\ell\alpha}\mathrm{Tr}S_\alpha = 0 \qquad (2.19)$$

and

$$\sum_{\tau_o=\pm\frac{1}{2}} < \tau_o|(\underline{I}_\ell\cdot\underline{S})(\underline{I}_k\cdot\underline{S})|\tau_o> = \sum_{\tau_o=\pm\frac{1}{2}}\left[< \tau_o|\frac{1}{4}\,\underline{I}_\ell\cdot\underline{I}_k + \frac{1}{2}\,\underline{S}\cdot(\underline{I}_\ell x\underline{I}_k)|\tau_o>\right] \qquad (2.20)$$

$$= \frac{1}{2}\,\underline{I}_\ell\cdot\underline{I}_k + \frac{1}{2}\sum_{\alpha=1}^{3}(\underline{I}_\ell x\underline{I}_k)_\alpha\,\mathrm{Tr}S_\alpha = \frac{1}{2}\,\underline{I}_\ell\cdot\underline{I}_k$$

yields, when substituting (2.20) and (2.18) into (2.10),

$$\frac{\partial^2\sigma}{\partial\Omega\partial\epsilon} = \frac{1}{2\pi\hbar}\frac{k}{Nk_o}\int_{-\infty}^{\infty} dt\, e^{-\frac{it\epsilon}{\hbar}}\sum_{\ell,k}\sum_{i} p_i <i|\left\{\mathcal{A}_k\mathcal{A}_\ell\right. \qquad (2.21)$$

$$\left. + \frac{\mathcal{B}_k\mathcal{B}_\ell\underline{I}_\ell\cdot\underline{I}_k}{[i_k i_\ell(i_k+1)(i_\ell+1)]^{\frac{1}{2}}}\right\} e^{-i\underline{\kappa}\cdot\underline{R}_k}\, e^{i\underline{\kappa}\cdot\underline{R}_\ell(t)}\,|i>$$

For a system with spin independent Hamiltonian, the eigenstates $|i>$ may be expressed as a product of spatial and spin eigenstates. Moreover, when exchange interactions are negligible

$$\left(\frac{\hbar^2\beta}{Md^2} \ll 1, \quad d \simeq \text{interatomic distance}\right),$$

there is no correlation between spins and positions of the nuclei, and the average in (2.21) can be split into a product of spatial and spin averages, i.e.,

$$\frac{\partial^2\sigma}{\partial\Omega\partial\epsilon} = \frac{1}{2\pi\hbar}\frac{k}{Nk_o}\int_{-\infty}^{\infty} dt\, e^{-\frac{it\epsilon}{\hbar}} \sum_{\ell,k} < m|\mathcal{A}_k\mathcal{A}_\ell + \frac{\mathcal{B}_k\mathcal{B}_\ell \underline{I}_\ell\cdot\underline{I}_k}{[i_k i_\ell(i_k+1)(i_\ell+1)]^{\frac{1}{2}}} |m>_{avg} \mathrm{Tr}\left\{\rho e^{-i\underline{\kappa}\cdot\underline{R}_k} e^{i\underline{\kappa}\cdot\underline{R}_\ell(t)}\right\} . \tag{2.22}$$

$|m>$ is a projection state of the nuclear spins, and ρ denotes the von Neumann density matrix[19]

$$\rho = \frac{1}{\mathcal{J}}\sum_{\nu=1}^{\mathcal{J}} |\psi^\nu><\psi^\nu| . \tag{2.23}$$

$|\psi^\nu>$ is the state vector of the νth system in the Gibbsian ensemble, and the summation is carried over all systems of the ensemble.

In the absence of exchange interactions, the directions of the spins of the different nuclei are also uncorrelated and

$$< m|\underline{I}_\ell\cdot\underline{I}_k|m>_{avg} = i_\ell(i_\ell+1)\delta_{k\ell} . \tag{2.24}$$

Hence, Eq. (2.22) becomes*

$$\frac{\partial^2\sigma}{\partial\Omega\partial\epsilon} = \frac{1}{2\pi\hbar}\frac{k}{k_o}\int_{-\infty}^{\infty} dt\, e^{-\frac{it\epsilon}{\hbar}} \left\{\sum_{\ell=1}^{N}\mathcal{B}_\ell^2\,\chi_s^\ell(\underline{\kappa},t) + \sum_{\ell,j=1}^{N}\mathcal{A}_\ell\mathcal{A}_j\chi^{\ell,j}(\underline{\kappa},t)\right\} \tag{2.25}$$

where

$$\chi_s^\ell(\underline{\kappa},t) \equiv N^{-1}\mathrm{Tr}\left\{\rho e^{-i\underline{\kappa}\cdot\underline{R}_\ell} e^{i\underline{\kappa}\cdot\underline{R}_\ell(t)}\right\} \tag{2.26}$$

*Equation (2.25) is essentially the same as that obtained by Van Hove[4] and Zemach and Glauber.[29]

and*

$$\chi^{\ell,j}(\underline{\kappa},t) \equiv N^{-1}\mathrm{Tr}\left\{\rho e^{-i\underline{\kappa}\cdot\underline{R}_\ell} e^{i\underline{\kappa}\cdot\underline{R}_j(t)}\right\} . \qquad (2.27)$$

2.3 VAN HOVE FORMULISM[4]

In order to generalize the Zernike-Prins "static approximation" formula[6] to scattering processes where energy tranfers are not negligible in comparison with the energy of the incident particle, Van Hove introduced space-time correlation functions defined by:

$$G^{\ell,j}(\underline{r},t) = \frac{1}{(2\pi)^3}\int d\underline{\kappa}\ \exp(-i\underline{\kappa}\cdot\underline{r})\,\chi^{\ell,j}(\underline{\kappa},t) \qquad (2.28)$$

and

$$G_s^{\ell}(\underline{r},t) = \frac{1}{(2\pi)^3}\int d\underline{\kappa}\ \exp(-i\underline{\kappa}\cdot\underline{r})\,\chi_s^{\ell}(\underline{\kappa},t) \qquad (2.29)$$

The differential cross section of Eq. (2.25) is then given by

$$\frac{\partial^2\sigma}{\partial\Omega\partial\epsilon} = \frac{k}{k_o}\left\{\sum_{\ell=1}^{N} \mathcal{B}_\ell^2 S_s^\ell(\underline{\kappa},\epsilon) + \sum_{\ell,j=1}^{N} \mathcal{A}_\ell \mathcal{A}_j S^{\ell,j}(\underline{\kappa},\epsilon)\right\} \qquad (2.30)$$

where

$$S_s^{\ell}(\underline{\kappa},\epsilon) = \frac{1}{2\pi\hbar}\iint dt\ d\underline{r}\ \exp\left[i(\underline{\kappa}\cdot\underline{r} - \frac{\epsilon t}{\hbar})\right] G_s^{\ell}(\underline{r},t) \qquad (2.31)$$

*Note that $\chi^{\ell,\ell}(\underline{\kappa},t) \equiv \chi_s^{\ell}(\underline{\kappa},t)$.

and

$$S^{\ell,j}(\underline{\kappa},\epsilon) = \frac{1}{2\pi\hbar}\iint dt\, d\underline{r}\, \exp\left[i(\underline{\kappa}\cdot\underline{r} - \frac{\epsilon t}{\hbar})\right] G^{\ell,j}(\underline{r},t) . \quad (2.32)$$

Equation (2.30) may be expressed in terms of the contributions of the different atomic species present in the system.[7] For this purpose, let μ_m denote the number of atoms belonging to the mth species and assume there are ν different species present. Then

$$\begin{aligned}\sum_{\ell=1}^{N} \frac{\mu_m}{N}\frac{N}{\mu_m} \mathcal{B}_\ell^2\, \chi_s^\ell(\underline{\kappa},t) &= \sum_{m=1}^{\nu} \frac{\mu_m}{N} \mathcal{B}_m^2 \left\{\frac{N}{\mu_m}\sum_{\ell=1}^{\mu_m} \chi_s^\ell(\underline{\kappa},t)\right\} \\ &\equiv \sum_{m=1}^{\nu} \frac{\mu_m}{N} \mathcal{B}_m^2\, \chi_s^m(\underline{\kappa},t)\end{aligned} \quad (2.33)$$

and

$$\begin{aligned}\sum_{\ell,j=1}^{N} \frac{\mu_m}{N}\frac{N}{\mu_m} \mathcal{A}_\ell \mathcal{A}_j \chi^{\ell,j}(\underline{\kappa},t) &= \sum_{n,m=1}^{\nu} \frac{\mu_m}{N} \mathcal{A}_m \mathcal{A}_n \sum_{j=1}^{\mu_n}\sum_{\ell=1}^{\mu_m} \frac{N}{\mu_m} \chi^{\ell,j}(\underline{\kappa},t) \\ &\equiv \sum_{n,m=1}^{\nu} \frac{\mu_m}{N} \mathcal{A}_m \mathcal{A}_n\, \chi^{n,m}(\underline{\kappa},t) .\end{aligned} \quad (2.34)$$

Hence,

$$\frac{\partial^2\sigma}{\partial\Omega\partial\epsilon} = \frac{k}{k_o}\left\{\sum_{m=1}^{\nu} \frac{\mu_m}{N} \mathcal{B}_m^2\, S_s^m(\underline{\Delta p},\epsilon) + \sum_{n,m=1}^{\nu} \frac{\mu_m}{N} \mathcal{A}_m \mathcal{A}_n\, S^{n,m}(\underline{\Delta p},\epsilon)\right\} \quad (2.35)$$

where the "scattering functions" $S_s(\underline{\Delta p},\epsilon)$ are defined by

$$S_s^m(\underline{\Delta p},\epsilon) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau\; e^{-i\tau\epsilon}\;\chi_s^m(\underline{\Delta p},\hbar\tau)$$

$$\equiv \frac{1}{2\pi}\iint d\tau\; d\underline{r}\; \exp\left[i\left(\frac{\underline{\Delta p}}{\hbar}\cdot\underline{r}-\epsilon\tau\right)\right] G_s^m(\underline{r},\hbar\tau) \tag{2.36}$$

and

$$S^{n,m}(\underline{\Delta p},\epsilon) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau\; e^{-i\tau\epsilon}\;\chi^{n,m}(\underline{\Delta p},\hbar\tau)$$

$$\equiv \frac{1}{2\pi}\iint d\tau\; d\underline{r}\; \exp\left[i\left(\frac{\underline{\Delta p}}{\hbar}\cdot\underline{r}-\epsilon\tau\right)\right] G^{n,m}(\underline{r},h\tau)\,. \tag{2.37}$$

The new variables

$$\hbar\underline{\kappa} = \underline{\Delta p} \quad \text{and} \quad \hbar\tau = t \tag{2.38}$$

have been introduced for reasons which will become obvious in Chapter V.

For the sake of simplicity in the following chapters we shall consider only monatomic and monoisotopic systems. The reduction of Eqs. (2.35)-(2.37) to such systems is straightforward.

CHAPTER III

SOME RELEVANT PROPERTIES OF THE FUNCTIONS
$G(\underline{r},t)$, $\chi(\underline{\Delta p},t)$, AND $S(\underline{\Delta p},\epsilon)$

3.1 PHYSICAL INTERPRETATION OF $G(\underline{r},t)$ [4]

The space-time correlation function $G(\underline{r},t)$ was introduced in the preceding chapter as a natural time-dependent generalization of the pair distribution function $g(\underline{r})$, familiar in X-ray scattering theory.

In particular, for a monatomic and monoisotopic system, the definition Eqs. (2.27), (2.28), and (2.34) lead to

$$\begin{aligned} G(\underline{r},t) &= \left(\frac{1}{2\pi}\right)^3 \int d\underline{\kappa}\; e^{-i\underline{\kappa}\cdot\underline{r}}\, \chi(\underline{\kappa},t) \\ &= \left(\frac{1}{2\pi}\right)^3 \sum_{j,\ell=1}^{N} N^{-1} \left\langle \int d\underline{\kappa}\; e^{-i\underline{\kappa}\cdot\underline{r}}\, e^{-i\underline{\kappa}\cdot\underline{R}_\ell}\, e^{i\underline{\kappa}\cdot\underline{R}_j(t)} \right\rangle_T \end{aligned} \tag{3.1}$$

where the bracket $\langle\ \rangle_T$, usually known as the "thermal average," stands for

$$\langle \Omega \rangle_T = \mathrm{Tr}(\rho\, \Omega) \; . \tag{3.2}$$

The Fourier transform of the product of (non-commuting) operators in (3.1) may be expressed as a convolution of delta functions by noting that

$$\int d\underline{\kappa}\; e^{-i\underline{\kappa}\cdot\underline{r}}\; e^{-i\underline{\kappa}\cdot\underline{R}_\ell}\; e^{i\underline{\kappa}\cdot\underline{R}_j(t)}$$

$$= \int d\underline{\kappa}\; e^{-i\underline{\kappa}\cdot\underline{r}}\; e^{-i\underline{\kappa}\cdot\underline{R}_\ell} \int d\underline{\kappa}'\; e^{i\underline{\kappa}'\cdot\underline{R}_j(t)}\, \delta(\underline{\kappa}-\underline{\kappa}')$$

$$= \frac{1}{(2\pi)^3} \int d\underline{\kappa}\; e^{-i\underline{\kappa}\cdot\underline{r}}\; e^{-i\underline{\kappa}\cdot\underline{R}_\ell} \int d\underline{\kappa}'\; e^{i\underline{\kappa}'\cdot\underline{R}_j(t)} \int d\underline{r}'\; e^{i\underline{r}'\cdot(\underline{\kappa}-\underline{\kappa}')} \tag{3.3}$$

$$= (2\pi)^3 \int d\underline{r}'\; \delta(\underline{r}+\underline{R}_\ell-\underline{r}')\,\delta(\underline{r}'-\underline{R}_j(t))\,.$$

Thus,

$$G(\underline{r},t) = \sum_{j,\ell=1}^{N} N^{-1} \left< \int d\underline{r}'\; \delta(\underline{r}+\underline{R}_\ell-\underline{r}')\,\delta(\underline{r}'-\underline{R}_j(t)) \right>_T . \tag{3.4}$$

Because of the non-commutativity of the operators $\underline{R}_\ell$ and $\underline{R}_j(t)$, the spatial integration in (3.4) may not be performed. In the "classical" limit $\hbar \to 0$, however, the above mentioned operators may be replaced by their corresponding classical dynamical variables $\underline{q}_\ell$ and $\underline{q}_j(t)$, respectively. These are commuting c-numbers and, hence,

$$\lim_{\hbar\to 0} G(\underline{r},t) = G^c(\underline{r},t) = N^{-1} \sum_{j,\ell=1}^{N} \left< \delta(\underline{r}+\underline{q}_\ell-\underline{q}_j(t)) \right>_{TC} \tag{3.5}$$

where $\langle\;\rangle_{TC}$ denotes now the classical thermal average.

Equation (3.5) has a simple physical interpretation, i.e., it is the conditional probability density that given an atom at the origin at time t = 0 there will be an atom (the same or another) a distance $\underline{r}$ away at time t.

Other instances where a physical meaning may be ascribed to $G(\underline{r},t)$ occur at t = 0 and for $\underline{r} \to \infty$.

In the case t = 0, the operators reduce again to c-numbers and

$$G(\underline{r},0) = \delta(\underline{r}) + N^{-1} \sum_{j\neq\ell=1}^{N} < \delta(\underline{r}+\underline{R}_\ell-\underline{R}_j)>_T \;.$$

Upon noting that the second term on the right of the above equation is the definition of the ordinary pair distribution $g(\underline{r})$, we have

$$G(\underline{r},0) = \delta(\underline{r}) + g(\underline{r}) \;. \tag{3.6}$$

The asymptotic form of $G(\underline{r},t)$ for $\underline{r} \to \infty$ is readily obtained by making the substitution $\underline{R}_\ell \to \underline{r} + \underline{R}_\ell$ in Eq. (3.4) and noting that, for sufficiently large $\underline{r}$, the particle at $\underline{R}_\ell+\underline{r}$ is statistically independent of all other particles in the system. Thus,

$$\begin{aligned}\lim_{\underline{r}\to\infty} G(\underline{r},t) &\simeq \sum_{j,\ell=1}^{N} N^{-1}\int d\underline{r}' \,\frac{1}{\mathcal{S}} \sum_{\nu=1}^{\mathcal{S}} < \psi^\nu(\underline{r}+\underline{R}_\ell)\,|\delta(\underline{r}+\underline{R}_\ell-\underline{r}'+\underline{r})\,|\psi^\nu(\underline{r}+\underline{R}_\ell)> \\ &\quad (x)\; <\psi^\nu(\underline{R}\neq\underline{R}_\ell)\,|\delta(\underline{r}'-\underline{R}_j(t))\,|\psi^\nu(\underline{R}\neq\underline{R}_\ell)> \\ &\simeq N^{-1}\int d\underline{r}'\;\rho(\underline{r}'-\underline{r})\rho(\underline{r}')\end{aligned} \tag{3.7}$$

where $\rho(\underline{r}')$ is the average number density at $\underline{r}'$. For an homogeneous system, ρ is a constant and Eq. (3.7) becomes

$$\lim_{\underline{r}\to\infty} G(\underline{r},t) \simeq \rho = \frac{N}{V} \;. \tag{3.8}$$

3.2 ASYMPTOTIC BEHAVIOR OF $\chi(\underline{\Delta p},\hbar\tau)$[31]

Assume it is possible to expand $\chi(\underline{\Delta p},\hbar\tau)$ in a series in inverse powers of τ:

$$\chi(\underline{\Delta p},\hbar\tau) = \sum_{n=1}^{\infty} \frac{a_n^{(+)}(\underline{\Delta p})}{(-i\tau)^n} \qquad (\epsilon > 0) \tag{3.9a}$$

and

$$\chi(\underline{\Delta p},\hbar\tau) = \sum_{n=1}^{\infty} \frac{a_n^{(-)}(\underline{\Delta p})}{(i\tau)^n} \qquad (\epsilon < 0) . \tag{3.9b}$$

Introducing these expansions into Eq. (2.37) yields

$$\begin{aligned} S(\underline{\Delta p},\pm|\epsilon|) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau\, e^{\mp i|\epsilon|\tau}\, \chi(\underline{\Delta p},\hbar\tau) \\ &= \frac{1}{2\pi}\sum_{n=1}^{\infty} a_n^{(\pm)}(\underline{\Delta p}) \int_{-\infty}^{\infty} \frac{e^{-i|\epsilon|\tau} d\tau}{(-i\tau)^n} . \end{aligned} \tag{3.10}$$

Furthermore, noting that[32]

$$\int_{-\infty}^{\infty} \frac{e^{-i\epsilon'\tau} d\tau}{i\tau} = -\pi\, \mathrm{sgn}(\epsilon') \tag{3.11}$$

and integrating both sides of this expression with respect to ϵ' between the limits of 0 and ϵ, we obtain the general formula:

$$\int_{-\infty}^{\infty} \frac{d\tau\, e^{-i|\epsilon|\tau}}{(-i\tau)^n} = \frac{\pi|\epsilon|^{n-1}}{(n-1)!} . \tag{3.12}$$

Consequently,

$$S(\underline{\Delta p},\epsilon) = \frac{1}{2}\sum_{n=1}^{\infty} a_n^{(+)}(\underline{\Delta p}) \frac{\epsilon^{n-1}}{(n-1)!} \qquad (\epsilon > 0) \tag{3.13}$$

and

$$S(\underline{\Delta p},\epsilon) = \frac{1}{2}\sum_{n=1}^{\infty} a_n^{(-)}(\underline{\Delta p}) \frac{|\epsilon|^{n-1}}{(n-1)!} \qquad (\epsilon < 0) . \tag{3.14}$$

The expansion coefficients $a^{(\pm)}(\underline{\Delta}p)$ follow immediately from (3.13) and (3.14) by successive differentiation, i.e.,

$$a_n^{(\pm)} = 2(\pm 1)^{n-1} \left| \frac{d^{(n-1)}}{d\epsilon^{(n-1)}} \left[S(\underline{\Delta}p,\epsilon) \right] \right|_{\epsilon=0_\pm} \tag{3.15}$$

In particular, for the case

$$\lim_{\tau\to\infty} \chi(\underline{\Delta}p,\hbar\tau) = 0 , \tag{3.16}$$

Equations (3.9) require that the expansion coefficients be bounded and, hence,

$$\lim_{\Delta\epsilon\to 0} \int_{-\Delta\epsilon}^{\Delta\epsilon} S(\underline{\Delta}p,\epsilon)\,d\epsilon = 2\lim_{\Delta\epsilon\to 0} \Delta\epsilon\,[a_1^{(+)}(\underline{\Delta}p) + a_1^{(-)}(\underline{\Delta}p)] = 0 . \tag{3.17}$$

This implies that $S(\underline{\Delta}p,\epsilon)$ is also bounded and differentiable from the left and from the right of $\epsilon = 0$. It precludes then the possibility of $S(\underline{\Delta}p,\epsilon)$ having a $\delta(\epsilon)$ singularity, although a pronounced but finite peak about the incident energy may still exist.

It is also clear from Eq. (3.15) that the intensity and width of this "quasi-elastic" peak depend on the expansion coefficients $a_n^{(\pm)}$. That is to say, they depend on the rapidity with which $\chi(\underline{\Delta}p,\hbar\tau)$ goes to zero as $\tau \to \infty$.

Conversely, the existence of an elastic component in the scattering function, represented by a $\delta(\epsilon)$ singularity, implies that

$$\lim_{\tau\to\infty} \chi(\underline{\Delta}p,\hbar\tau) \neq 0 . \tag{3.18}$$

This case is characteristic of a system where every atom has a well localized neighborhood in which it always moves, i.e., a solid. Thus we see that the Abelian properties discussed above provide useful information on the dynamics of the scattering system.

3.3 HERMITIAN SYMMETRY

Except for the limiting cases discussed previously, the non-Hermitian character of the convolution of delta functions in Eq. (3.4) implies that $G(\underline{r},t)$ is generally complex. In fact, its complex conjugate has the Hermitian symmetry

$$G^*(\underline{r},t) = G(-\underline{r},-t) \tag{3.19}$$

which follows immediately from the reality of $S(\underline{\Delta p},\epsilon)$ and the defining Eq. (2.37).

3.4 THE PRINCIPLE OF DETAILED BALANCING

Consider the function[8,33]

$$S_0^{\ell,j}(\underline{\Delta p},\epsilon) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau\, e^{-i\tau\epsilon}\, \chi^{\ell,j}(\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2}) \tag{3.20}$$

where $\chi^{\ell,j}(\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2})$ is defined, in accordance with Eq. (2.27), by

$$\chi^{\ell,j}(\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2}) = N^{-1}\mathrm{Tr}\left\{\rho \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{R}_\ell\right]\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{R}_j(\hbar\tau + \frac{i\beta\hbar}{2})\right]\right\}. \tag{3.21}$$

By taking the complex conjugate of (3.21) and rearranging the terms inside the trace, it follows readily that

$$\left[\chi^{\ell,j}(\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2})\right]^* = \chi^{\ell,j}(-\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2}) \qquad (3.22)$$

and, hence,

$$S_o^{\ell,j}(\underline{\Delta p},\epsilon) = S_o^{*\ell,j}(-\underline{\Delta p},-\epsilon) \, . \qquad (3.23)$$

Moreover, writing (3.21) as

$$\chi^{\ell,j}(\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2}) = N^{-1}\sum_{i,f} e^{-\frac{\beta}{2}(E_f-E_i)} e^{i\tau(E_f-E_i)}$$
$$(x) \;\; \langle i|\rho \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{R}_\ell\right]|f\rangle \langle f|\exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{R}_j\right]|i\rangle \qquad (3.24)$$

and inserting this expression into (3.20) leads to

$$S_o^{\ell,j}(\underline{\Delta p},\epsilon) = e^{-\frac{\beta\epsilon}{2}} N^{-1}\sum_{i,f} \langle i|\rho \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{R}_\ell\right]|f\rangle$$
$$(x) \;\; \langle f|\exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{R}_j\right]|i\rangle\, \delta(E_f-E_i-\epsilon) \, . \qquad (3.25)$$

In a similar fashion, it can be shown that

$$S^{\ell,j}(\underline{\Delta p},\epsilon) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau \; e^{-i\tau\epsilon} \chi^{\ell,j}(\underline{\Delta p},\hbar\tau)$$

is given by

$$S^{\ell,j}(\underline{\Delta p},\epsilon) = N^{-1}\sum_{i,f}\langle i|\rho \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{R}_\ell\right]|f\rangle$$
$$(x) \;\; \langle f|\exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{R}_j\right]|i\rangle\, \delta(E_f-E_i-\epsilon) \qquad (3.26)$$

and, consequently,

$$S_o^{\ell,j}(\underline{\Delta p},\epsilon) = e^{-\frac{\beta\epsilon}{2}} S^{\ell,j}(\underline{\Delta p},\epsilon). \qquad (3.27)$$

Substituting this result into (3.23), after noting that $S^{\ell,j}(\underline{\Delta p},\epsilon)$ is real, yields

$$S^{\ell,j}(\underline{\Delta p},\epsilon) = e^{\beta\epsilon} S^{\ell,j}(-\underline{\Delta p},-\epsilon). \qquad (3.28)$$

We now use this identity to establish a relation between the neutron scattering cross section given by formula (2.30) and its converse obtained by interchanging the initial and final states of the neutron. To this end, let

$$\frac{\partial^2\sigma}{\partial\Omega_f\partial\epsilon_f} \equiv \sigma(\epsilon_i\to\epsilon_f,\underline{\Omega}_f) = \frac{k}{k_o}\left[\mathcal{B}^2\sum_{\ell=1}^{N} S_s^{\ell}(\underline{\Delta p},\epsilon) + \mathcal{A}^2\sum_{\ell,j=1}^{N} S^{\ell,j}(\underline{\Delta p},\epsilon)\right] \qquad (3.29)$$

and

$$\frac{\partial^2\sigma}{\partial\Omega_i\partial\epsilon_i} = \sigma(\epsilon_f\to\epsilon_i,\underline{\Omega}_i) = \frac{k_o}{k}\left[\mathcal{B}^2\sum_{\ell=1}^{N} S_s^{\ell}(-\underline{\Delta p},-\epsilon) + \mathcal{A}^2\sum_{\ell,j} S^{\ell,j}(-\underline{\Delta p},-\epsilon)\right]. \qquad (3.30)$$

It then follows at once from (3.28) that

$$\sigma(\epsilon_f\to\epsilon_i,\underline{\Omega}_i) = \frac{k_o^2}{k^2} e^{-\beta\epsilon}\sigma(\epsilon_i\to\epsilon_f,\underline{\Omega}_f) \qquad (3.31)$$

or

$$k_o^2 e^{-\beta\epsilon_i}\sigma(\epsilon_i\to\epsilon_f,\underline{\Omega}_f) = k^2 e^{-\beta\epsilon_f}\sigma(\epsilon_f\to\epsilon_i,\underline{\Omega}_i). \qquad (3.32)$$

This last expression is usually referred to as the "principle of detailed balancing" for a system of neutrons in thermal equilibrium with a pure scatterer.

3.5 FLUCTUATION-DISSIPATION THEOREM

As a corollary of Eq. (3.22), it is possible to establish a relationship between the real and imaginary parts of $G(\underline{r},t)$. For this purpose, note that

$$\exp\left[\frac{i\beta}{2}\frac{\partial}{\partial\tau}\right] G(\underline{r},\hbar\tau) = \left(\frac{1}{2\pi}\right)^3 \int d\underline{\kappa}\; e^{-i\underline{\kappa}\cdot\underline{r}}\, \chi(\underline{\kappa},\hbar\tau + \frac{i\beta\hbar}{2}) \,. \tag{3.33}$$

Taking the complex conjugate of this expression and using (3.22) leads to

$$\exp\left[-\frac{i\beta}{2}\frac{\partial}{\partial\tau}\right] G^*(\underline{r},\hbar\tau) = \left(\frac{1}{2\pi}\right)^3 \int d\underline{\kappa}\; e^{-i\underline{\kappa}\cdot\underline{r}}\, \chi(\underline{\kappa},\hbar\tau + \frac{i\beta\hbar}{2}) \tag{3.34}$$

Equating now (3.33) and (3.34) results in

$$\exp\left[\frac{i\beta}{2}\frac{\partial}{\partial\tau}\right] G(\underline{r},\hbar\tau) = \exp\left[-\frac{i\beta}{2}\frac{\partial}{\partial\tau}\right] G^*(\underline{r},\hbar\tau) \tag{3.35}$$

or

$$\begin{aligned}&\left[\cos\left(\frac{\beta}{2}\frac{\partial}{\partial\tau}\right) + i\sin\left(\frac{\beta}{2}\frac{\partial}{\partial\tau}\right)\right]\left[\mathcal{R}G(\underline{r},\hbar\tau) + i\mathcal{I}G(\underline{r},\hbar\tau)\right]\\ &= \left[\cos\left(\frac{\beta}{2}\frac{\partial}{\partial\tau}\right) - i\sin\left(\frac{\beta}{2}\frac{\partial}{\partial\tau}\right)\right]\left[\mathcal{R}G(\underline{r},\hbar\tau) - i\mathcal{I}G(\underline{r},\hbar\tau)\right]\end{aligned} \tag{3.36}$$

i.e.,

$$\mathcal{I}G(r,\hbar\tau) = -\tan\left(\frac{\beta}{2}\frac{\partial}{\partial\tau}\right) \mathcal{R}G(\underline{r},\hbar\tau) \,. \tag{3.37}$$

This result was first derived by Schofield[8] by Fourier inversion of $S(\underline{\Delta p},\epsilon)$ and use of (3.28).* It is felt, however, that the above proof is simpler and more straightforward.

Observing that the delta functions in (3.4) may be interpreted as Heisenberg density operators $\mathcal{I}G(\underline{r},t)$ and $\mathcal{R}G(r,t)$ may be expressed, for homogeneous systems, in terms of the average of the commutator and anti-commutator, respectively, of these operators. By doing so, Van Hove[34] was able to relate the real part of $G(\underline{r},t)$ to the time-correlation function of spontaneous fluctuations in the equilibrium density of the scattering system. He also showed, by means of a perturbation analysis of first order in the interaction potential between neutron and scattering medium, that $\mathcal{I}G(\underline{r},t)$ is connected with the local disturbance produced by the neutron in the density of the medium.

We thus see, in view of the above given physical interpretation of $\mathcal{R}G(\underline{r},t)$ and $\mathcal{I}G(\underline{r},t)$, that Eq. (3.37) has the character of a fluctuation-dissipation theorem.

3.6 THE PLACZEK MOMENTS[16]

Aside from their intrinsic interest, the properties discussed in the preceding sections constitute valuable checks when considering approximate descriptions of the scattering function. Another set of consistency tests is provided by the moments of the scattering function for a fixed momentum transfer, defined by

*See also Nelkin[33] and Singwi and Sjölander[14] for similar proofs.

$$\overline{\epsilon^n} = \int_{-\infty}^{\infty} \epsilon^n S(\underline{\Delta p},\epsilon)\, d\epsilon \quad . \tag{3.38}$$

A more explicit form for these moments can be obtained by expressing $S(\underline{\Delta p},\epsilon)$ in terms of $\chi(\underline{\Delta p},\hbar\tau)$:

$$\overline{\epsilon^n} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau\; \chi(\underline{\Delta p},\hbar\tau) \int_{-\infty}^{\infty} \epsilon^n\, e^{-i\epsilon\tau}\, d\epsilon \tag{3.39}$$

and noting that

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \epsilon^n\, e^{-i\epsilon\tau}\, d\epsilon = i^n \frac{d^n}{d\tau^n}\, \delta(\tau) \quad . \tag{3.40}$$

It then follows at once that

$$\overline{\epsilon^n} = (-i)^n \frac{d^n}{d\tau^n}\, \chi(\underline{\Delta p},\hbar\tau) \Big|_{\tau=0} \tag{3.41}$$

i.e., the moments $\overline{\epsilon^n}$ are just the coefficients $S_n(\underline{\Delta p})$ in the power series expansion

$$\chi(\underline{\Delta p},\hbar\tau) = \sum_{n=0}^{\infty} \frac{1}{n!}\, S_n(\underline{\Delta p})(i\tau)^n \ . \tag{3.42}$$

Furthermore, from

$$\chi(\underline{\Delta p},\hbar\tau) = N^{-1} \sum_{j,\ell} < \exp\left[-\frac{i}{\hbar}\, \underline{\Delta p}\cdot\underline{R}_\ell\right] e^{iH\tau} \exp\left[\frac{i}{\hbar}\, \underline{\Delta p}\cdot\underline{R}_j\right] e^{-iH\tau} >_T$$

we have that

$$(-i)^n \frac{d^n}{d\tau^n}\, \chi(\underline{\Delta p},\hbar\tau) \Big|_{\tau=0} = N^{-1} \sum_{j,\ell} < \exp\left[-\frac{i}{\hbar}\, \underline{\Delta p}\cdot\underline{R}_\ell\right] \left[H, \exp\left(\frac{i}{\hbar}\, \underline{\Delta p}\cdot\underline{R}_j\right)\right]_n >_T \tag{3.43}$$

and (3.41) becomes

$$\overline{\epsilon^n} = N^{-1} \sum_{j,\ell} < \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{R}_\ell\right] \left[H, \exp\left(\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{R}_j\right)\right] n >_T \quad (3.44)$$

This expression was first considered by Placzek (hence the designation of $\overline{\epsilon^n}$ as Placzek moments) in the analysis of the scattering cross section for relatively high energy neutrons and heavy scatterers. For $\ell = j$, Eq. (3.44) is most easily evaluated by making use of the unitary transformation[35]

$$\exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{R}\right] f(\underline{P},\underline{R}) \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{R}\right] = f(\underline{P}+\underline{\Delta p},\underline{R}) \quad (3.45)$$

where $f(\underline{P},\underline{R})$ is an arbitrary function of the momentum and position operators. By doing so, and considering only randomly oriented systems, one obtains for the first five Placczek moments of $S_s(\underline{\Delta p},\epsilon)$ the following expressions:

$$\begin{aligned}
\overline{\epsilon_s^0} &= 1 \\
\overline{\epsilon_s^1} &= \frac{\Delta p^2}{2M} \\
\overline{\epsilon_s^2} &= \frac{2}{3M}\,\Delta p^2 < K > + (\Delta p^2/2M)^2 \\
\overline{\epsilon_s^3} &= 4\left(\frac{\Delta p^2}{2M}\right)^2 < K > + \left(\frac{\Delta p^2}{2M}\right)^3 + \frac{\hbar^2 \Delta p^2}{6M^2} < \nabla^2 V > \\
\overline{\epsilon_s^4} &= \frac{4}{5}\,\frac{\Delta p^4}{M^2} < K^2 > + \frac{\Delta p^6}{M^3} < K > + \left(\frac{\Delta p^2}{2M}\right)^4 \\
&\quad + \frac{\hbar^2 \Delta p^2}{3M^2} < |\nabla V|^2 > + \frac{\hbar^2 \Delta p^4}{3M^3} < \nabla^2 V >
\end{aligned} \quad (3.46)$$

K here denotes the kinetic energy of the scattering atom, and V is the total potential energy of the scattering system.

CHAPTER IV

QUASI-PROBABILITY DISTRIBUTIONAL FORMULATION OF QUANTUM MECHANICS

By introducing a quasi-probability distribution in phase space, which is essentially a Fourier transform of the density matrix of von Neumann, it is possible to obtain a quantum mechanical analog to classical Gibbsian statistical mechanics for the calculation of the expectation value of a function* $\Omega(\underline{P},\underline{R})$.[36,37] Explicitly,

$$\begin{aligned} \langle \Omega(\underline{P},\underline{R})\rangle &= \mathrm{Tr}[\boldsymbol{\rho}\,\Omega(\underline{P},\underline{R})] \\ &= \iint d\underline{p}\,d\underline{q}\,\rho_W(\underline{p},\underline{q},t)\,\Omega_W(\underline{p},\underline{q})\,. \end{aligned} \tag{4.1}$$

Here

$$\rho_W(\underline{p},\underline{q},t) = \left(\frac{1}{2\pi\hbar}\right)^{3N}\int d\underline{z}\,\exp\left[\frac{i}{\hbar}\,\underline{z}\cdot\underline{p}\right]\langle\,\underline{q} - \frac{\underline{z}}{2}\,|\boldsymbol{\rho}|\,\underline{q} + \frac{\underline{z}}{2}\,\rangle \tag{4.2}$$

is the phase-space distribution function initially introduced by Wigner,[9] and $\boldsymbol{\rho}$ is the von Neumann density matrix defined in Chapter II [Eq. (2.23)].

The c-numbers $\underline{p}$ and $\underline{q}$, on which ρ_W and Ω_W depend, will be shown at the end of the chapter to obey the Hamilton classical equations of motion and thus may be interpreted as classical dynamical variables. This is the basic utility of the present approach. Ω_W is related to Ω in a cer-

*$\underline{R}$ and $\underline{P}$ will be consistently used to denote sets of quantum mechanical position and momentum operators and $\underline{q}$ and $\underline{p}$ to denote their corresponding variables in classical mechanics.

tain specific way as we shall see below.

Upon noting that Eq. (4.2) gave the correct "marginal" distributions (see Appendix B), Wigner was able to prove Eq. (4.1) for functions that separate as

$$\Omega(\underline{P},\underline{R}) = \Omega_1(\underline{P}) + \Omega_2(\underline{R}) \qquad (4.3)$$

and for which

$$\Omega_W(\underline{p},\underline{q}) = \Omega_1(\underline{p}) + \Omega_2(\underline{q}) \,. \qquad (4.4)$$

It was also observed by Wigner that (4.2) is not the only bilinear expression in ψ which gives the expectation values correctly for a quantity of type (4.3). In fact, any function

$$f(\underline{p},\underline{q},t) = P(\underline{p},t)\,Q(\underline{q},t) + f_1(\underline{p},\underline{q},t) \qquad (4.5)$$

would be equally valid provided

$$\int f_1(\underline{p},\underline{q},t)\,d\underline{p} = \int f_1(\underline{p},\underline{q},t)\,d\underline{q} = 0 \qquad (4.6)$$

and $P(\underline{p},t)$ and $Q(\underline{q},t)$ are the momentum and configuration-space distribution functions respectively.[38]

Introducing a phase-space distribution function defined as the Fourier inverse of the so-called characteristic function

$$M(\underline{x},\underline{y},t) = \left(\psi,\ e^{i(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})}\psi\right) \qquad (4.7)$$

Moyal[39] showed that (4.2) also gave the correct joint distribution provided that $\Omega_W(\underline{p},\underline{q})$ is obtained from first defining a function by

$$\Omega(\underline{P},\underline{R}) = \iint d\underline{x}d\underline{y}\ \alpha(\underline{x},\underline{y})\ \exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right] \qquad (4.8)$$

and then setting

$$\Omega_W(\underline{p},\underline{q}) = \iint d\underline{x}d\underline{y}\ \alpha(\underline{x},\underline{y})\ \exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right] . \qquad (4.9)$$

Equations (4.8) and (4.9) are known as "Weyl's correspondence" and were first obtained by Weyl from group theoretical considerations.[11] A rederivation of these equations, based only on the orthonormality and completeness of the set of operators

$$\left\{\left(\frac{1}{2\pi\hbar}\right)^{3N/2} \exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]\right\}$$

is given by Groenewold.[40]

Moyal and Groenewold have also shown that the application of "Weyl's correspondence" to the commutator

$$\frac{i}{2}\left[\Omega_1(\underline{P},\underline{R})\,\Omega_2(\underline{P},\underline{R}) - \Omega_2(\underline{P},\underline{R})\,\Omega_1(\underline{P},\underline{R})\right]$$

results in

$$(\Omega_1\ \Omega_2)_W = \Omega_1^W(\underline{p},\underline{q})\sin(\tfrac{\hbar}{2}\Lambda)\,\Omega_2^W(\underline{p},\underline{q}) \qquad (4.10)$$

where Λ is the Poisson bracket operator

$$\Lambda = (\overleftarrow{\nabla}_p\cdot\vec{\nabla}_q-\overleftarrow{\nabla}_q\cdot\vec{\nabla}_p) \qquad (4.11)$$

with the arrows indicating the function which is being differentiated.

Conversely, Irving and Zwanzig[41] proved that in order to obtain the correct averages the use of "Weyl's correspondence" between operators and phase-space functions leads necessarily to ρ_W as given by (4.2).

In the next section this latter approach is extended to the calculation of the average of a product of two operators, leading to a formulation which envelopes the results of Groenewold, Moyal, and Irving and Zwanzig in what is felt to be a somewhat simpler and more self-contained manner.

Moreover, making use of the fact that any known quantum mechanical function of $\underline{P}$ and $\underline{R}$ may be expressed as a series in which each term is given by products of functions of $\underline{R}$ and $\underline{P}$ only, a knowledge of $[\Omega_1(\underline{P},\underline{R})(x)\,\Omega_2(\underline{P}\cdot\underline{R})]_W$ together with $[\Omega(\underline{P})]_W$ and $[\Omega(\underline{R})]_W$ is sufficient for the explicit evaluation of the "Weyl correspondence" of any arbitrary function $\Omega(\underline{P},\underline{R})$.

The properties of the Wigner distribution function ρ_W are discussed in detail in Appendix B, and for a system in thermal equilibrium an expansion, in powers of $\hbar^2$, is obtained of the form

$$\rho_W = f_N^c(1+\hbar^2 A_2+\hbar^4 A_4+\cdots) \tag{4.12}$$

where f_N^c is the classical canonical distribution function.

The coefficients in this expression can be derived, in principle, by substituting (4.12) into the quantum mechanical analog of Liouville's equation [see Eq. (B.16)]. For higher powers than $\hbar^2$, however, their complexity increases greatly and, hence, only A_2 was obtained explicitly in Appendix B.

Furthermore, owing to the positive powers of β which they contain, the A_n's become very large at very low temperatures and Eq. (4.12) will diverge near absolute zero. A different method of approximation applicable to this latter case has been developed by Green.[13]

For certain particularly simple systems, ρ_W can be found explicitly and in closed form. This is illustrated in Appendix C where we evaluate ρ_W for an harmonic oscillator.

4.1 EXPECTATION VALUE FOR SCHRÖDINGER OPERATORS

In order to derive the isomorphism between the Weyl-Wigner quasi-probability distributional formulation and the von Neumann average of a product of Schrödinger operators, we first introduce a coordinate representation for the latter with

$$|\underline{q}\rangle = |\underline{q}_1, \underline{q}_2, \cdots \underline{q}_N\rangle . \tag{4.13}$$

Thus,

$$\begin{aligned} \langle \Omega_1 \, \Omega_2 \rangle &= \int d\underline{q} \, \langle \underline{q} | \boldsymbol{\rho} \, \Omega_1 \, \Omega_2 | \underline{q} \rangle \\ &= \iint d\underline{q} d\underline{q}' \, \langle \underline{q} | \boldsymbol{\rho} | \underline{q}' \rangle \langle \underline{q}' | \Omega_1 \, \Omega_2 | \underline{q} \rangle \end{aligned} \tag{4.14}$$

Moreover, it has been shown in Appendix A that, due to the orthonormality and completeness of the set of operators

$$\left\{\left(\frac{1}{2\pi\hbar}\right)^{3N/2} \exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]\right\},$$

it is possible to expand $\Omega_n(\underline{P},\underline{R},t)$ (n=1,2) in terms of this set as:

$$\Omega_n(\underline{P},\underline{R},t) = \iint d\underline{x}d\underline{y}\ \alpha_n(\underline{x},\underline{y},t)\exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right] \tag{4.15}$$

with

$$\alpha_n(\underline{x},\underline{y},t) = \left(\frac{1}{2\pi\hbar}\right)^{3N} \mathrm{Tr}\left\{\Omega_n(\underline{P},\underline{R},t)\exp\left[-\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]\right\}. \tag{4.16}$$

Substituting Eq. (4.15) into (4.14) and making use of the property (A.11) results in

$$\begin{aligned} <\Omega_1\ \Omega_2> = &\iint d\underline{q}d\underline{q}'\ <\underline{q}|\rho|\underline{q}'>\iiiint d\underline{x}d\underline{y}d\underline{x}'d\underline{y}' \\ &(x)\ \alpha_1(\underline{x},\underline{y},t)\alpha_2(\underline{x}',\underline{y}',t)\exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{y}+\underline{x}'\cdot\underline{y}')\right] \\ &(x)\int d\underline{q}''\ <\underline{q}'|\exp\left[\frac{i}{\hbar}\underline{y}\cdot\underline{R}\right]\exp\left[\frac{i}{\hbar}\underline{x}\cdot\underline{P}\right]|\underline{q}''> \\ &(x)\ <\underline{q}''|\exp\left[\frac{i}{\hbar}\underline{y}'\cdot\underline{R}\right]\exp\left[\frac{i}{\hbar}\underline{x}'\cdot\underline{P}\right]|\underline{q}> \end{aligned} \tag{4.17}$$

or since

$$\begin{aligned} <\underline{q}'|\exp\left[\frac{i}{\hbar}\underline{y}\cdot\underline{R}\right]\exp\left[\frac{i}{\hbar}\underline{x}\cdot\underline{P}\right]|\underline{q}> &= \exp\left[\frac{i}{\hbar}\underline{y}\cdot\underline{q}'\right]<\underline{q}'|\exp\left[\frac{i}{\hbar}\underline{x}\cdot\underline{P}\right]|\underline{q}> \\ &= \exp\left[\frac{i}{\hbar}\underline{y}\cdot\underline{q}'\right]\delta(\underline{q}'-\underline{q}+\underline{x}) \end{aligned} \tag{4.18}$$

it follows, after making the dummy variable substitution $\underline{q} \to \underline{z}$, that

$$< \Omega_1 \, \Omega_2 > \;=\; \int d\underline{z} \iiiint d\underline{x}d\underline{y}d\underline{x}'d\underline{y}' \;\alpha_1(\underline{x},\underline{y},t)\,\alpha_2(\underline{x}',\underline{y}',t)$$

$$(x)\;\exp\left[-\frac{i}{2\hbar}\,(\underline{x}\cdot\underline{y}+\underline{x}'\cdot\underline{y}')\right] < \underline{z}|\rho|\underline{z}-\underline{x}-\underline{x}' > \qquad (4.19)$$

$$(x)\;\exp\left[\frac{i}{\hbar}\,\underline{z}\cdot(\underline{y}+\underline{y}')\right]\exp\left[-\frac{i}{\hbar}\,\underline{y}\cdot\underline{x}'\right].$$

Now defining a new quantity $\Omega_n^W(\underline{p},\underline{q},t)$ by

$$\Omega_n^W(\underline{p},\underline{q},t) \;\equiv\; \iint d\underline{x}d\underline{y}\;\alpha_n(\underline{x},\underline{y},t)\exp\left[\frac{i}{\hbar}\,(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right] \qquad (4.20)$$

or by its Fourier transform

$$\alpha_n(\underline{x},\underline{y},t) \;=\; \left(\frac{1}{2\pi\hbar}\right)^{6N} \iint d\underline{p}d\underline{q}\;\exp\left[-\frac{i}{\hbar}\,(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right]\Omega^W(\underline{p},\underline{q},t) \qquad (4.21)$$

and substituting the latter into (4.20) yields:

$$< \Omega_1 \, \Omega_2 > \;=\; \left(\frac{1}{2\pi\hbar}\right)^{12N} \int d\underline{z} \iiiint d\underline{p}d\underline{q}d\underline{p}'d\underline{q}' \iiiint d\underline{x}d\underline{y}d\underline{x}'d\underline{y}'$$

$$(x) < \underline{z}|\rho|\underline{z}-\underline{x}'-\underline{x} > \exp\left[\frac{i}{\hbar}\,\underline{y}\cdot(-\frac{\underline{x}}{2} - \underline{x}'+\underline{z}-\underline{q})\right]$$

$$(x)\;\exp\left[-\frac{i}{\hbar}\,\underline{x}\cdot\underline{p}\right]\Omega_1{}^W(\underline{p},\underline{q},t)\exp\left[\frac{i}{\hbar}\,\underline{y}'\cdot(-\frac{\underline{x}'}{2} + \underline{z} - \underline{q}')\right] \qquad (4.22)$$

$$(x)\;\exp\left[-\frac{i}{\hbar}\,\underline{x}'\cdot\underline{p}'\right]\Omega_2{}^W(\underline{p}',\underline{q}',t)\;.$$

This result may be simplified further by noting that

$$\left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\underline{y}'\;\exp\left[\frac{i}{\hbar}\,\underline{y}'\cdot(\underline{z}-\underline{q}' - \frac{\underline{x}'}{2})\right] \;=\; (2)^{3N}\;\delta(2\underline{z}-2\underline{q}'-\underline{x}') \qquad (4.23)$$

and

$$\left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\underline{y}\, \exp\left[\frac{i}{\hbar}\, \underline{y}\cdot(\underline{z}-\underline{x}'-\underline{q}-\frac{\underline{x}}{2})\right] = (2)^{3N}\, \delta(2\underline{z}-2\underline{x}'-2\underline{q}-\underline{x}). \tag{4.24}$$

Hence,

$$\begin{aligned} < \Omega_1\, \Omega_2 > \; = \left(\frac{1}{\pi\hbar}\right)^{6N} \int d\underline{z} \iiiint d\underline{p}d\underline{q}d\underline{p}'d\underline{q}' \, < \underline{z}|\rho|\underline{z}+2\underline{q}-2\underline{q}' > \\ (x)\;\; \Omega_1{}^{W}(\underline{p},\underline{q},t)\,\Omega_2{}^{W}(\underline{p}',\underline{q}',t)\exp\left[-\frac{i}{\hbar}\,\underline{p}\cdot(-2\underline{z}+4\underline{q}'-2\underline{q})\right] \\ (x)\;\; \exp\left[-\frac{2i}{\hbar}\,\underline{p}'\cdot(\underline{z}-\underline{q}')\right] . \end{aligned} \tag{4.25}$$

Upon setting

$$\underline{p}' = \underline{p} - \underline{\xi} \quad \text{and} \quad \underline{q}' = \underline{q} - \underline{\eta} \tag{4.26}$$

Equation (4.25) transforms into

$$\begin{aligned} < \Omega_1\, \Omega_2 > \; = \left(\frac{1}{\pi\hbar}\right)^{6N} \int d\underline{z} \iiiint d\underline{p}d\underline{q}d\underline{\xi}d\underline{\eta} \, <\underline{z}|\rho|\underline{z}+2\underline{\eta} > \\ (x)\;\; \Omega_1{}^{W}(\underline{p},\underline{q},t)\left[e^{-\underline{\xi}\cdot\vec{\nabla}_p}\, e^{-\underline{\eta}\cdot\vec{\nabla}_q}\,\Omega_2{}^{W}(\underline{p},\underline{q},t)\right] \\ (x)\;\; \exp\left[\frac{2i}{\hbar}\,\underline{p}\cdot\underline{\eta}\right]\exp\left[\frac{2i}{\hbar}\,\underline{\xi}\cdot(\underline{z}-\underline{q}+\underline{\eta})\right] . \end{aligned} \tag{4.27}$$

or

$$\begin{aligned} < \Omega_1\, \Omega_2 > \; = \left(\frac{1}{\pi\hbar}\right)^{6N} \int d\underline{z} \iiiint d\underline{p}d\underline{q}d\underline{\xi}d\underline{\eta} \, < \underline{z}|\rho|\underline{z}+2\underline{\eta} > \\ (x)\;\; \exp\left[\frac{2i}{\hbar}\,\underline{\xi}\cdot(\underline{z}+\underline{\eta})\right]\; \Omega_1{}^{W}(\underline{p},\underline{q},t)\left\{\exp\left[\frac{2i}{\hbar}\,(\underline{p}\cdot\underline{\eta}-\underline{q}\cdot\underline{\xi})\right]\right. \\ (x)\;\; \left.\exp\left[\frac{\hbar}{2i}\,\overleftarrow{\nabla}_q\cdot\vec{\nabla}_p-\overleftarrow{\nabla}_p\cdot\vec{\nabla}_q\right]\,\Omega_2{}^{W}(\underline{p},\underline{q},t)\right\} . \end{aligned} \tag{4.28}$$

If we now integrate the above equation by parts with respect to $\underline{p}$ and $\underline{q}$ we get

$$< \Omega_1 \Omega_2 > = \left(\frac{1}{\pi\hbar}\right)^{6N} \int d\underline{z} \iiiint d\underline{p}d\underline{q}d\underline{\xi}d\underline{\eta} < \underline{z}|\boldsymbol{\rho}|\underline{z}+2\underline{\eta} >$$

$$(x) \exp\left[\frac{2i}{\hbar} \underline{\xi}\cdot(\underline{z}+\underline{\eta}-\underline{q})\right] \exp\left[\frac{2i}{\hbar} \underline{p}\cdot\underline{\eta}\right] \left[\Omega_1{}^W e^{\frac{\hbar}{2i}\Lambda} \Omega_2{}^W\right]$$

$$= \left(\frac{1}{\pi\hbar}\right)^{3N} \int d\underline{z}' \iint d\underline{p}d\underline{q}' <\underline{z}'|\boldsymbol{\rho}|2\underline{q}'-\underline{z}'> \tag{4.29}$$

$$(x) \exp\left[\frac{2i}{\hbar} \underline{p}\cdot(\underline{q}'-\underline{z}')\right] \left[\Omega_1{}^W e^{\frac{\hbar}{2i}\Lambda} \Omega_2{}^W\right] .$$

Finally, the additional transformation of variables

$$\underline{z}' = \underline{q} - \frac{\underline{z}}{2} \tag{4.30}$$

and

$$2\underline{q}' - \underline{z}' = \underline{q} + \frac{\underline{z}}{2} \tag{4.31}$$

yields

$$< \Omega_1 \Omega_2 > = \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\underline{z} \iint d\underline{p}d\underline{q} <\underline{q} - \frac{\underline{z}}{2} |\boldsymbol{\rho}| \underline{q} + \frac{\underline{z}}{2} >$$

$$(x) \exp\left[\frac{i}{\hbar} \underline{p}\cdot\underline{z}\right] \left[\Omega_1{}^W(\underline{p},\underline{q},t) e^{\frac{\hbar}{2i}\Lambda} \Omega_2{}^W(\underline{p},\underline{q},t)\right] \tag{4.32}$$

or

$$< \Omega_1 \Omega_2 > = \iint d\underline{p}d\underline{q}\ \rho_W(\underline{p},\underline{q},t) \left[\Omega_1{}^W(\underline{p},\underline{q},t) e^{\frac{\hbar}{2i}\Lambda} \Omega_2{}^W(\underline{p},\underline{q},t)\right] . \tag{4.33}$$

Equations (4.2) and (4.33) are thus our basic results. Specifically, we have

$$(\Omega_1 \, \Omega_2)_W = \Omega_{1W} \, e^{\frac{\hbar}{2i} \Lambda} \, \Omega_{2W} \, . \tag{4.34}$$

As indicated previously, the Weyl correspondence for an arbitrary function of $\underline{P}$ and $\underline{R}$ can be derived from (4.34) by making use of the following results:

(1) If $\Omega = C$ where C is any constant, then from Eqs. (4.16) and (A.12)

$$\alpha(\underline{x},\underline{y}) = C\delta(\underline{x})\delta(\underline{y}),$$

so that Eq. (4.20) yields

$$\Omega_W = C \, . \tag{4.35}$$

(2) If $\Omega = \Omega(\underline{R})$, i.e., independent of $\underline{P}$, then from Eqs. (4.16) and (4.20)

$$\begin{aligned} \Omega_W(\underline{q}) &= \left(\frac{1}{2\pi\hbar}\right)^{3N} \iint d\underline{x}d\underline{y} \exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right] \\ &\quad (x) \; \mathrm{Tr}\left\{\Omega(\underline{R}) \exp\left[-\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]\right\} \\ &= \left(\frac{1}{2\pi\hbar}\right)^{3N} \iint d\underline{x}d\underline{y} \exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right] \int d\underline{q}'\Omega(\underline{q}') \\ &\quad (x) \; \langle\underline{q}'|\exp\left[-\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]|\underline{q}'\rangle \, . \end{aligned} \tag{4.36}$$

Furthermore, in view of Eqs. (A.11) and (4.18),

$$\Omega_W(\underline{q}) = \Omega(\underline{q}) \, . \tag{4.37}$$

(3) Finally, if $\Omega = \Omega(\underline{P})$, i.e., independent of $\underline{R}$, then Eqs. (4.16) and (4.20) lead to

$$\Omega_W(\underline{p}) = \left(\frac{1}{2\pi\hbar}\right)^{3N} \iint d\underline{x}d\underline{y} \exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right] \iint d\underline{q}'d\underline{q}''$$

$$(x) < \underline{q}'|\Omega(\underline{P})|\underline{q}''> < \underline{q}''|\exp\left[-\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]|\underline{q}' > . \tag{4.38}$$

Moreover, noting that

$$< \underline{q}'|\Omega(\underline{P})|\underline{q}''> = \int d\underline{q}\, \delta(\underline{q}-\underline{q}')\,\Omega\left(\frac{\hbar}{i}\vec{\nabla}_{\underline{q}}\right)\delta(\underline{q}-\underline{q}'')$$

$$= \left(\frac{1}{2\pi\hbar}\right)^{3N} \iint d\underline{q}d\underline{\sigma}\, \delta(\underline{q}-\underline{q}')\,\Omega\left(\frac{\hbar}{i}\vec{\nabla}_{\underline{q}}\right)\exp\left[\frac{i\underline{\sigma}}{\hbar}\cdot(\underline{q}-\underline{q}'')\right] \tag{4.39}$$

$$= \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\underline{\sigma}\, \Omega(\underline{\sigma})\exp\left[\frac{i\underline{\sigma}}{\hbar}\cdot(\underline{q}'-\underline{q}'')\right],$$

and again making use of (A.11) and (4.18), yields

$$\Omega_W(\underline{p}) = \Omega(\underline{p}) \tag{4.40}$$

after a few straightforward operations. As an example, consider the Hamiltonian for a velocity independent potential:

$$H(\underline{P},\underline{R}) = \frac{P^2}{2M} + V(\underline{R}) .$$

In this case it readily follows from Eqs. (4.37) and (4.40) that

$$H_W(\underline{p},\underline{q}) = H(\underline{p},\underline{q}) = \frac{p^2}{2M} + V(\underline{q}) . \tag{4.41}$$

Equations (4.34), (4.35), (4.37), and (4.40) are very convenient and lead immediately to an expansion of Ω_W in powers of $\hbar$. Hence, a canonical average can be obtained as a power series in $\hbar$. In principle, this can be done to any power, but for most practical purposes the method will be useful only when a small number of terms gives a good description of the system, i.e., for "quasi-classical" systems.

4.2 WEYL'S CORRESPONDENCE FOR HEISENBERG OPERATORS

Consider now the Heisenberg operator

$$\Omega(\underline{P},\underline{R},t) = \exp\left[\frac{iHt}{\hbar}\right] \Omega(\underline{P},\underline{R}) \exp\left[-\frac{iHt}{\hbar}\right] . \qquad (4.42)$$

It is possible to obtain a prescription which relates $\Omega_W(\underline{p},\underline{q},t)$ to $\Omega^W(\underline{p},\underline{q})$ by application of Weyl's correspondence [Eqs. (4.15) and (4.20)]. To this end, note that expressing Eq. (4.16) in a coordinate representation and making use of Eqs. (A.11) and (4.18) results in:

$$\alpha(\underline{x},\underline{y},t) = \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\underline{q}' < \underline{q}' |\Omega(\underline{P},\underline{R},t) |\underline{q}'+\underline{x} > \\ (x) \exp\left[-\frac{i}{2\hbar} \underline{x}\cdot\underline{y}\right] \exp\left[-\frac{i}{\hbar} \underline{y}\cdot\underline{q}'\right] . \qquad (4.43)$$

Moreover, since

$$\frac{\partial\Omega}{\partial t} (\underline{P},\underline{R},t) = \frac{i}{\hbar} [H,\Omega(\underline{P},\underline{R},t)] \qquad (4.44)$$

it readily follows that

$$\frac{\partial\alpha}{\partial t} (\underline{x},\underline{y},t) = \frac{i}{\hbar} \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\underline{q}' < \underline{q}' | [H,\Omega]|\underline{q}'+\underline{x} > \\ (x) \exp\left[-\frac{i}{2\hbar} \underline{x}\cdot\underline{y}\right] \exp\left[-\frac{i}{\hbar} \underline{y}\cdot\underline{q}'\right] \qquad (4.45)$$

or

$$\frac{\partial\alpha}{\partial t} (\underline{x},\underline{y},t) = \frac{i}{\hbar} \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\underline{q} <\underline{q} - \frac{\underline{x}}{2}| [H,\Omega] |\underline{q} + \frac{\underline{x}}{2} > \exp\left[-\frac{i}{\hbar} \underline{y}\cdot\underline{q}\right] \qquad (4.46)$$

where

$$\underline{q} = \underline{q}' + \frac{\underline{x}}{2} .$$

The matrix element in (4.46) can be evaluated in a straightforward manner to give

$$\begin{aligned} < \underline{Q}|[H,\Omega]|\underline{Q}' > &= \frac{\hbar^2}{2M}(\nabla^2_{Q'} - \nabla^2_{Q}) < \underline{Q}|\Omega|\underline{Q}' > \\ &+ < \underline{Q}|\Omega|\underline{Q}'> [V(\underline{Q}) - V(\underline{Q}')] . \end{aligned} \tag{4.47}$$

In the particular case

$$\begin{aligned} Q &= \underline{q} - \frac{\underline{x}}{2} \\ Q' &= \underline{q} + \frac{\underline{x}}{2} , \end{aligned} \tag{4.48}$$

the difference of Laplacian operators simplifies to

$$\nabla^2_{Q'} - \nabla^2_{Q} = 2\nabla_{\underline{q}} \cdot \nabla_{\underline{x}} \tag{4.49}$$

and

$$V(\underline{q} \pm \frac{\underline{x}}{2}) = \exp\left[\pm 2\underline{q}\cdot\vec{\nabla}_{\underline{x}}\right] V(\pm \frac{\underline{x}}{2}) . \tag{4.50}$$

Hence, Eq. (4.46) becomes

$$\begin{aligned} \frac{\partial\alpha}{\partial t}(\underline{x},\underline{y},t) &= \frac{i\hbar}{M}\left(\frac{1}{2\pi\hbar}\right)^{3N}\int d\underline{q}\, \exp\left[-\frac{i}{\hbar}\,\underline{y}\cdot\underline{q}\right]\vec{\nabla}_{\underline{q}}\cdot\vec{\nabla}_{\underline{x}} < \underline{q} - \frac{\underline{x}}{2}|\Omega|\underline{q} + \frac{\underline{x}}{2} > \\ &- \frac{i}{\hbar}\left(\frac{1}{2\pi\hbar}\right)^{3N}\int d\underline{q}\, \exp\left[-\frac{i}{\hbar}\,\underline{y}\cdot\underline{q}\right] < \underline{q} - \frac{\underline{x}}{2}\,|\Omega|\underline{q} + \frac{\underline{x}}{2} > \\ &(x) \left\{\exp\left[2\underline{q}\cdot\vec{\nabla}_{\underline{x}}\right] V(\frac{\underline{x}}{2}) - \exp\left[-2\underline{q}\cdot\vec{\nabla}_{\underline{x}}\right] V(-\frac{\underline{x}}{2})\right\} . \end{aligned} \tag{4.51}$$

Furthermore, since

$$\int d\underline{q}\, \exp\left[-\frac{i}{\hbar}\,\underline{y}\cdot\underline{q}\right] \vec{\nabla}_{\underline{q}}\cdot\vec{\nabla}_{\underline{x}} < \underline{q} - \frac{\underline{x}}{2}\,|\Omega|\underline{q} + \frac{\underline{x}}{2} >$$

$$= \left(\frac{i}{\hbar}\right) \underline{y}\cdot\vec{\nabla}_{\underline{x}} \int d\underline{q}\, \exp\left[-\frac{i}{\hbar}\,\underline{y}\cdot\underline{q}\right] < \underline{q} - \frac{\underline{x}}{2}\,|\Omega|\underline{q} + \frac{\underline{x}}{2} > \qquad (4.52)$$

$$= (2\pi\hbar)^{3N} \left(\frac{i}{\hbar}\right) \underline{y}\cdot\vec{\nabla}_{\underline{x}}\, \alpha(\underline{x},\underline{y},t)$$

and

$$\int d\underline{q}\, \exp\left[-\frac{i}{\hbar}\,\underline{y}\cdot\underline{q}\right] < \underline{q} - \frac{\underline{x}}{2}\,|\Omega|\underline{q} + \frac{\underline{x}}{2} > \exp\left[2\underline{q}\cdot\vec{\nabla}_{\underline{x}}\right] V\left(\frac{\underline{x}}{2}\right)$$

$$= \int d\underline{q}\, \exp\left[-\frac{i}{\hbar}\,\underline{y}\cdot\underline{q}\right] < \underline{q} - \frac{\underline{x}}{2}|\Omega|\underline{q} + \frac{\underline{x}}{2} > \exp\left[-\frac{2\hbar}{i}\,\overleftarrow{\nabla}_{\underline{y}}\cdot\vec{\nabla}_{\underline{x}}\right] V\left(\frac{\underline{x}}{2}\right)$$

$$= (2\pi\hbar)^{3N}\, \alpha(\underline{x},\underline{y},t) \exp\left[-\frac{2\hbar}{i}\,\overleftarrow{\nabla}_{\underline{y}}\cdot\vec{\nabla}_{\underline{x}}\right] V\left(\frac{\underline{x}}{2}\right), \qquad (4.53)$$

it follows that

$$\frac{\partial\alpha}{\partial t} = -\frac{1}{M}\,\underline{y}\cdot\vec{\nabla}_{\underline{x}}\,\alpha - \frac{i}{\hbar}\,\alpha \left\{\exp\left[-\frac{2\hbar}{i}\,\overleftarrow{\nabla}_{\underline{y}}\cdot\vec{\nabla}_{\underline{x}}\right] V\left(\frac{\underline{x}}{2}\right) - \exp\left[\frac{2\hbar}{i}\,\overleftarrow{\nabla}_{\underline{y}}\cdot\vec{\nabla}_{\underline{x}}\right] V\left(-\frac{\underline{x}}{2}\right)\right\}. \qquad (4.54)$$

Double-Fourier transforming the above equation and using (4.20) yields

$$\frac{\partial\Omega^{W}}{\partial t}(\underline{p},\underline{q},t) = \frac{1}{M}\iint d\underline{x}d\underline{y}\; \alpha(\underline{x},\underline{y},t)\,\underline{p}\cdot\vec{\nabla}_{\underline{q}} \exp\left[\frac{i}{\hbar}\,(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right]$$

$$-\frac{i}{\hbar}\iint d\underline{x}d\underline{y}\; \alpha(\underline{x},\underline{y},t) \exp\left[\frac{i}{\hbar}\,(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right] \qquad (4.55)$$

$$(\mathrm{x}) \left[\exp(2\underline{q}\cdot\vec{\nabla}_{\underline{x}})\, V\left(\frac{\underline{x}}{2}\right) - \exp(-2\underline{q}\cdot\vec{\nabla}_{\underline{x}})\, V\left(-\frac{\underline{x}}{2}\right)\right],$$

or

$$\frac{\partial \Omega^W}{\partial t}(\underline{p},\underline{q},t) = \frac{1}{M}\,\underline{p}\cdot\vec{\nabla}_{\underline{q}}\,\Omega^W(\underline{p},\underline{q},t) - \frac{i}{\hbar}\iint d\underline{x}d\underline{y}\;\alpha(\underline{x},\underline{y},t)$$

$$(x)\;\exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right]\left\{\exp\left[\frac{\underline{x}}{2}\cdot\vec{\nabla}_q\right] - \exp\left[-\frac{\underline{x}}{2}\cdot\vec{\nabla}_q\right]\right\}V(\underline{q})$$

$$= \frac{1}{M}\,\underline{p}\cdot\vec{\nabla}_q\Omega^W(\underline{p},\underline{q},t) - \frac{i}{\hbar}\iint d\underline{x}d\underline{y}\;\alpha(\underline{x},\underline{y},t)\exp\left[\frac{i}{h}(\underline{x}\cdot\underline{p}+\underline{y}\cdot\underline{q})\right] \tag{4.56}$$

$$(x)\;\frac{1}{2i}\left\{\exp\left[\frac{i\hbar}{2}\overleftarrow{\nabla}_{\underline{p}}\cdot\vec{\nabla}_{\underline{q}}\right] - \exp\left[-\frac{i\hbar}{2}\overleftarrow{\nabla}_{\underline{p}}\cdot\vec{\nabla}_{\underline{q}}\right]\right\}V(\underline{q})$$

$$= \frac{2}{\hbar}\left\{H_W\,\frac{\hbar}{2}(\overleftarrow{\nabla}_{\underline{p}}\cdot\vec{\nabla}_{\underline{q}}) - H_W\left[\sin(\frac{\hbar}{2}\overleftarrow{\nabla}_{\underline{q}}\cdot\vec{\nabla}_{\underline{p}})\right]\right\}\Omega^W(\underline{p},\underline{q},t)\;.$$

For $n \geq 1$, it can be shown that

$$H_W(\overleftarrow{\nabla}_{\underline{p}}\cdot\vec{\nabla}_{\underline{q}}-\overleftarrow{\nabla}_{\underline{q}}\cdot\vec{\nabla}_{\underline{p}})^{2n+1} = -H_W(\overleftarrow{\nabla}_{\underline{q}}\cdot\vec{\nabla}_{\underline{p}})^{2n+1}\;, \tag{4.57}$$

and

$$H_W\left[\frac{\hbar}{2}(\overleftarrow{\nabla}_{\underline{p}}\cdot\vec{\nabla}_{\underline{q}}) - \sin(\frac{\hbar}{2}\overleftarrow{\nabla}_{\underline{q}}\cdot\vec{\nabla}_{\underline{p}})\right] = H_W\,\frac{\hbar}{2}(\overleftarrow{\nabla}_p\cdot\vec{\nabla}_q-\overleftarrow{\nabla}_q\cdot\vec{\nabla}_p)$$

$$-\sum_{n=1}^{\infty}\frac{(-1)^n}{(2n+1)!}\left(\frac{\hbar}{2}\right)^{2n+1}H_W(\overleftarrow{\nabla}_q\cdot\vec{\nabla}_p)^{2n+1}$$

$$= H_W\sum_{n=0}^{\infty}\left(\frac{\hbar}{2}\right)^{2n+1}\frac{(-1)^n}{(2n+1)!}(\overleftarrow{\nabla}_{\underline{p}}\cdot\vec{\nabla}_{\underline{q}}-\overleftarrow{\nabla}_{\underline{q}}\cdot\vec{\nabla}_{\underline{p}})^{2n+1} \tag{4.58}$$

$$= H_W\sin\left(\frac{\hbar}{2}\Lambda\right)\;.$$

Thus, Eq. (4.56) takes the form

$$\frac{\partial \Omega^W}{\partial t}(\underline{p},\underline{q},t) = \frac{2}{\hbar}\,H_W\sin\left(\frac{\hbar}{2}\Lambda\right)\Omega^W(\underline{p},\underline{q},t) \tag{4.59}$$

which, when solved formally, yields

$$\Omega^W(\underline{p},\underline{q},t) = \exp\left[\frac{2t}{\hbar} H_W \sin\left(\frac{\hbar}{2}\Lambda\right)\right] \Omega^W(\underline{p},\underline{q},0). \qquad (4.60)$$

As a corollary of Eq. (4.60), together with Eqs. (4.37), (4.40), and (4.41), it can be shown at once than when $\Omega^W(\underline{p},\underline{q},0)$ is set equal to $\underline{p}$ and $\underline{q}$ respectively,

$$\dot{\underline{p}} = \dot{\underline{p}}_W(0) = H_W \Lambda \underline{p}_W(0) = -\vec{\nabla}_q H_W \qquad (4.61)$$

and

$$\dot{\underline{q}} = \dot{\underline{q}}_W(0) = H_W \Lambda \underline{q}_W(0) = \vec{\nabla}_p H_W . \qquad (4.62)$$

Thus, as asserted previously, the c-numbers $\underline{q}$ and $\underline{p}$ satisfy Hamilton's equations of motion, and may be interpreted as classical dynamical variables.

CHAPTER V

THE QUASI-CLASSICAL TREATMENT OF NEUTRON SCATTERING

5.1 INTERMEDIATE SCATTERING FUNCTION IN THE WIGNER REPRESENTATION

Because of the appearance of a trace in the intermediate scattering function

$$\chi(\underline{\Delta p},\hbar\tau) = N^{-1}\sum_{i,j=1}^{N} \mathrm{Tr}\left\{\rho \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot R_i\right]\exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot R_j(\hbar\tau)\right]\right\}$$

introduced in Chapter II, the value of the function will be independent of the choice of representation relative to which the matrix elements are defined. Specifically, using the Wigner representation [Eq. (4.33)] discussed in Chapter IV together with Eqs. (4.37) and (4.60) yields*

$$\chi(\underline{\Delta p},\hbar\tau) = N^{-1}\sum_{i,j=1}^{N}\iint d\underline{p}d\underline{q}\ \rho_W(\underline{p},\underline{q})\left\{\exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_i\right]e^{\frac{\hbar}{2i}\Lambda}\Omega_W(\underline{p},\underline{q},\tau)\right\} \tag{5.1}$$

where

$$\Omega_W(\underline{p},\underline{q},\tau) = \exp[2\tau\ H_W\sin(\tfrac{\hbar}{2}\Lambda)]\exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_j\right] . \tag{5.2}$$

Or, since

$$\begin{aligned}\exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_i\right]e^{\frac{\hbar}{2i}\Lambda} &= \sum_n \left(\frac{\hbar}{2i}\right)^n\frac{1}{n!}\exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_i\right](\overleftarrow{\nabla}_p\cdot\overrightarrow{\nabla}_q-\overleftarrow{\nabla}_q\cdot\overrightarrow{\nabla}_p)^n\\ &= \sum_n \frac{1}{n!}\left(\frac{1}{2}\right)^n(\underline{\Delta p}\cdot\overrightarrow{\nabla}_{p_i})^n\exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_i\right]\\ &= \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_i\right]\exp\left[\frac{1}{2}\underline{\Delta p}\cdot\overrightarrow{\nabla}_{p_i}\right]\end{aligned}$$

*Unless the contrary is explicitly indicated, all configuration and momentum coordinates are evaluated at t = 0.

then

$$\chi(\underline{\Delta p},\hbar\tau) = N^{-1} \sum_{i,j=1}^{N} \iint d\underline{p}d\underline{q}\ \rho_W(\underline{p},\underline{q})\ \exp\left[-\frac{i}{\hbar}\ \underline{\Delta p}\cdot\underline{q}_i\right]\exp\left[\frac{1}{2}\ \underline{\Delta p}\cdot\vec{\nabla}_{p_i}\right]$$

$$(x)\ \Omega_W(\underline{p},\underline{q},\hbar\tau)\ . \tag{5.3}$$

It is interesting to note that if V is quadratic or of lower degree in $\underline{q}$ the operator

$$H_W\Lambda^{(2m+1)} = 0 \quad \text{for} \quad m \geq 1\ ,$$

and Eq. (5.3) reduces to

$$\chi(\underline{\Delta p},\hbar\tau) = N^{-1} \sum_{i,j=1}^{N} \iint d\underline{p}d\underline{q}\ \rho_W(\underline{p},\underline{q}) \exp\left[-\frac{i}{\hbar}\ \underline{\Delta p}\cdot\underline{q}_i\right]\exp\left[\frac{1}{2}\ \underline{\Delta p}\cdot\vec{\nabla}_{p_i}\right]$$

$$(x)\ \exp\left[\frac{i}{\hbar}\ \underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] \tag{5.4}$$

where use has been made of the Taylor series expansion property

$$\exp\left[\hbar\tau H_W\Lambda\right]\exp\left[\frac{i}{\hbar}\ \underline{\Delta p}\cdot\underline{q}_j\right] = \exp\left[\frac{i}{\hbar}\ \underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]\ . \tag{5.5}$$

In these cases, the expression for ρ_W may be obtained in closed form (see Appendix C) and the calculation of $\chi(\underline{\Delta p},\hbar\tau)$ is straightforward. This is illustrated in Chapter VI, where Eq. (5.4) has been used to calculate $S(\underline{\Delta p},\epsilon)$ for a monatomic liquid based on a model which, in essence, consists of a combination of harmonic and free gas-type motions.

5.2 ASYMPTOTIC EXPANSION OF $\chi(\underline{\Delta p},\hbar\tau)$

Except for the special cases mentioned previously, an exact solution of Eq. (5.3) is impossible for the following reasons:

(1) The operator $\exp[2\tau H_W \sin(\frac{\hbar}{2}\Lambda)]$ acting on $\exp[\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_j]$ yields an infinite series; and

(2) $\rho_W(\underline{p},\underline{q})$ can not be obtained in closed form, although for a "quasi-classical" system a series expansion in powers of $\hbar^2$ is possible. A similar expansion in powers of $\hbar$ for the rest of the integrand in Eq. (5.3) is not possible, however, because it contains an essential singularity at the point $\hbar = 0$.

All of these considerations lead us to attempt, then, an asymptotic expansion for $\Omega_W(\underline{p},\underline{q},\tau)$. The term $\exp[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_i]$ is retained in toto. To determine the form of this asymptotic expansion, we note that

$$\exp\left[2\tau H_W \sin(\frac{\hbar}{2}\Lambda)\right] = \exp[\tau(\hbar H_W\Lambda + A)] \qquad (5.6a)$$

where

$$A = -2\sum_{n=1}^{\infty}\frac{(-1)^n}{(2n+1)!}\left(\frac{\hbar}{2}\right)^{2n+1}(\nabla_q V\cdot\vec{\nabla}_p)(\overleftarrow{\nabla}_q\cdot\vec{\nabla}_p)^{2n}. \qquad (5.6b)$$

Moreover, making use of the identity (A.1) and Eqs. (A.2) and (A.3) as proven in Appendix A, we get

$$\exp[\tau(\hbar H_W\Lambda + A)] = e^{\hbar\tau H_W\Lambda}\, e^{\tau A}\,\Gamma(\tau) \qquad (5.7)$$

and

$$\frac{\partial\Gamma(\tau)}{\partial\tau} = \Upsilon(\tau)\,\Gamma(\tau), \qquad \Gamma(\tau=0) = 1$$

where

$$\Upsilon(\tau) = e^{-\tau A} \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \tau^n [\hbar H_W \Lambda, A]_n \, e^{\tau A}$$

$$[\hbar H_W \Lambda, A]_n = [\hbar H_W \Lambda, [\hbar H_W \Lambda, A]_{n-1}] \qquad (5.8)$$

and

$$[\hbar H_W \Lambda, A]_0 = A \, .$$

Equation (5.8) may be integrated formally, leading to the integral equation

$$\Gamma(\tau) = 1 + \int_0^{\tau} \Upsilon(\tau') \Gamma(\tau') d\tau'$$

which is readily solved by Picard's process of successive approximations, yielding

$$\Gamma(\tau) = 1 + \sum_{m=1}^{\infty} \int_0^{\tau} \Upsilon(\tau_1) d\tau_1 \int_0^{\tau_1} \Upsilon(\tau_2) d\tau_2 \cdots \int_0^{\tau_{m-1}} \Upsilon(\tau_m) d\tau_m, \; (\tau_0 = \tau). \qquad (5.9)$$

Observing, however, that each term in the sum in Eq. (5.9), when operating on $\exp[\frac{i}{\hbar} \underline{\Delta p} \cdot \underline{q}_j]$, generates an infinite series in powers of $\hbar$, of which the lowest is $\hbar^0$, we can write

$$\Omega_W(\underline{p}, \underline{q}, \tau) = \exp[\tau(\hbar H_W \Lambda + A)] \exp\left[\frac{i}{\hbar} \underline{\Delta p} \cdot \underline{q}_j\right] = f(\tau)\,[1 + \hbar F_1(\tau) + \hbar^2 F_2(\tau) + \cdots] \qquad (5.10)$$

where

$$f(\tau) = \exp[\hbar \tau H_W \Lambda] \exp\left[\frac{i}{\hbar} \underline{\Delta p} \cdot \underline{q}_j\right] \qquad (5.11)$$

and

$$f(0) = \Omega_W(\underline{p},\underline{q},0) = \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]$$

$$F_n(0) = 0\,, \quad \text{for} \quad n > 0\ . \tag{5.12}$$

The terms in the expansion (5.10) may be evaluated by substituting this equation into (4.59), obtaining:

$$f(\tau)\,[\hbar\dot{F}_1(\tau)+\hbar^2\dot{F}_2(\tau)+\ldots] - f(\tau)\hbar H_W\Lambda[1+\hbar F_1(\tau)+\cdots]$$

$$-\sum_{m=1} \frac{(-1)^m(\hbar)^{2m+1}H_W\Lambda^{2m+1}}{4^m(2m+1)!}\left\{f(\tau)\,[1+\hbar F_1(\tau) + \hbar^2F_2(\tau)+\cdots]\right\} = 0 \tag{5.13}$$

where

$$\dot{F}_n = \frac{\partial F_n}{\partial\tau}\ .$$

Grouping terms with equal powers of $\hbar$, by explicitly taking into account that

$$-\hbar^{2m+1}H_W\Lambda^{2m+1}[f(\tau)\,F_n(\tau)]$$

$$= \hbar^{2m+1}(\nabla_q V\cdot\vec{\nabla}_p)(\overleftarrow{\nabla}_q\cdot\vec{\nabla}_p)^{2m}\left\{F_n(\tau)\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j+\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right.\right.$$

$$\left.\left.-\frac{i\hbar\tau^2}{2M}\,\underline{\Delta p}\cdot\nabla_{q_j}V - \frac{i\hbar^2\tau^3}{6M^2}\,(\underline{p}\cdot\vec{\nabla}_q)(\underline{\Delta p}\cdot\nabla_{q_j}V)+\cdots\right]\right\} \tag{5.14}$$

$$= \mathcal{O}(\hbar^{2m+1})$$

yields the following set of differential equations for the first three terms in the expansion (5.10):

$$\dot{F}_1(\tau) - H_W \Lambda F_0(\tau) = 0$$

$$\dot{F}_2(\tau) - H_W \Lambda F_1(\tau) = 0 \qquad (5.15)$$

$$\dot{F}_3(\tau) - H_W \Lambda F_2(\tau) - \frac{1}{24}\left(\frac{i\tau}{M}\right)^3 (\underline{\Delta p}\cdot\vec{\nabla}_{q_j})^2(\underline{\Delta p}\cdot\nabla_{q_j}V) = 0 .$$

The solutions to these equations, with the initial conditions given by Eqs. (5.12), are

$$F_1(\tau) = F_2(\tau) = 0$$

$$F_3 = -\frac{i\tau^4}{96M^3}(\underline{\Delta p}\cdot\vec{\nabla}_{q_j})^2(\underline{\Delta p}\cdot\nabla_{q_j}V) . \qquad (5.16)$$

Hence, Eq. (5.10) may be expressed as

$$\Omega_W(\underline{p},\underline{q},\tau) = \exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]\left[1 - \frac{i\tau^4\hbar^3}{96M^3}(\underline{\Delta p}\cdot\vec{\nabla}_{q_j})^2(\underline{\Delta p}\cdot\nabla_{q_j}V) + \mathcal{O}(\hbar^4)\right], \qquad (5.17)$$

and inserting this result into Eq. (5.3) yields

$$\chi(\underline{\Delta p},\hbar\tau) = N^{-1}\sum_{i,j} < \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_i\right]\exp\left[\frac{1}{2}\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right]\exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]$$

$$(x)\left[1 - \frac{i\hbar^3\tau^4}{96}(\underline{\Delta p}\cdot\vec{\nabla}_{q_j})^2(\underline{\Delta p}\cdot\nabla_{q_j}V) + \mathcal{O}(\hbar^4)\right] >_{TW} \qquad (5.18)$$

where $< >_{TW}$ denotes the phase space average over ρ_W. Equation (5.18) is the desired asymptotic expansion. As shown below, the contribution of $\mathcal{O}(\hbar^0)$ from the term containing $F_3(\tau)$ vanishes for randomly oriented systems. Retaining only the leading term in the asymptotic expansion, which still contains $\hbar$, and using the $\hbar^0$ term of ρ_W gives what we call the "quasi-classical" approximation.[12] The first correction is of $\mathcal{O}(\hbar^2)$ and comes from the $\hbar^2$ term of ρ_W. The next term is of $\mathcal{O}(\hbar^4)$; one contribution comes from the $\hbar^4$ term in ρ_W; another comes from F_3 and F_4. However, we consider only terms as high as $\hbar^2$.

Note that Eq. (5.18) still contains an essential singularity which, for the diagonal component of χ, is only apparent since in this case $(i=j)$; the term $\exp[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j]$ is cancelled out by the first term resulting from a power series expansion of $\underline{q}_j(\hbar\tau)$. It is shown in Appendix E that only in this case is it possible to have a power series expansion for χ. Hence, the following discussion will be restricted to direct scattering. This is not considered a strong limitation, however, since all the information concerning target dynamics is contained in this portion of the scattering function. (See Chapter VII for further discussion of this point.)

5.3 RANDOMLY ORIENTED SYSTEMS

If in the term involving $F_3(\tau)$ of Eq. (5.18) we write

$$\underline{\Delta p}\cdot\nabla_{\underline{q}_j} = \mu\,|\underline{\Delta p}|\,\frac{\partial}{\partial q_j}$$

where

$$\mu \equiv \frac{\underline{\Delta p}\cdot\underline{q}_j}{|\underline{\Delta p}|\,|q_j|}$$

then

$$\begin{aligned} &< \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right]F_3\,\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] >_{TW} \\ &= -\frac{i\tau^4}{96M^3} < \mu^3|\underline{\Delta p}|^3\,\frac{\partial^3 V}{\partial q_j{}^3}\,\exp\left[\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right] >_{TW}\,\exp\left[\frac{i\tau\Delta p^2}{2M}\right] + \mathcal{O}(\hbar)\,. \end{aligned} \tag{5.19}$$

Moreover, for a randomly oriented system, $\chi(\underline{\Delta p},\hbar\tau)$ can depend only on the magnitude of $\underline{\Delta p}$. Consequently,

$$\chi(\underline{\Delta p},\hbar\tau) \;=\; \chi(|\underline{\Delta p}|,\hbar\tau) \;\cong\; \frac{1}{4\pi}\int \chi(|\underline{\Delta p}|,\hbar\tau)\,d\Omega_{\Delta p}\,.$$

It follows readily from this that the first term on the right of (5.19) vanishes, and (5.18) yields

$$\chi_s(\underline{\Delta p},\hbar\tau) \;=\; \left\langle \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\overleftrightarrow{\nabla}_{\underline{p}_j}\right]\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]\right\rangle_{TW} + \mathcal{O}(h^4)\,. \tag{5.20}$$

Introducing now the expansion [Eq. (4.12)] of the Wigner distribution function into Eq. (5.20) results in

$$\begin{aligned}\chi_s(\underline{\Delta p},\hbar\tau) \;=\; &\left\langle \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\overleftrightarrow{\nabla}_{p_j}\right]\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]\right\rangle_{TC}\\ &+ \hbar^2\left\langle \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]A_2\,\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\overrightarrow{\nabla}_{p_j}\right]\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]\right\rangle_{TC}\\ &+ \mathcal{O}(\hbar^4)\,.\end{aligned} \tag{5.21}$$

Here the phase space average is performed with respect to f_N^c and $\exp[\frac{1}{2}\,\underline{\Delta p}\cdot\overrightarrow{\nabla}_{p_j}]\underline{q}_j(t)$ is the vector position of the jth particle at time t, subject to an impulse at t=0 of the force

$$\underline{F}_{imp} \;=\; \frac{\underline{\Delta p}}{2}\,\delta(t)\,.$$

The above result is extremely useful because the corrections of order $\hbar^2$ to the "quasi-classical" limit come only from ρ_W. Note that this derivation is quite self-consistent in that corrections of $\mathcal{O}(\hbar^4)$ and higher could be obtained in principle by straightforward extension of the manipulations carried out so far. The analysis becomes laborious, but at least the procedure is well defined. However, if correction terms of $\mathcal{O}(\hbar^4)$ to our approximation are important (as is the case for near absolute zero systems[13]), this approach is likely to be poor anyway.

5.4 CORRECTIONS OF $\mathcal{O}(\hbar^2)$ TO THE "QUASI-CLASSICAL" APPROXIMATION

As previously observed, the second term in Eq. (5.21) gives quantum mechanical corrections to our "quasi-classical" approximation and contains all powers of $\hbar$, the lowest being of $\mathcal{O}(\hbar^2)$. Note, however, that retaining terms of order higher than $\hbar^3$ is senseless, since these terms were neglected in the expansions of both Ω_W and ρ_W. Thus, expanding $\underline{q}_j(\hbar\tau)$ in Eq. (5.21) in a Maclaurin series and ignoring terms beyond $\mathcal{O}(\hbar)$ yields

$$\hbar^2 < \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right] A_2 \exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right]\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] >_{TC}$$
$$= \exp\left[\frac{i\tau\Delta p^2}{2M}\right] < \hbar^2 A_2 \exp\left[\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right] >_{TC} - \frac{i\hbar^3\tau^2}{2M}\exp\left[\frac{i\tau\Delta p^2}{2M}\right]$$
$$<(\underline{\Delta p}\cdot\nabla_{\underline{q}_j}V)\,A_2 \exp\left[\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right] >_{TC} + \mathcal{O}(\hbar^4)\,.$$

Again, for a randomly oriented system, the term of $\mathcal{O}(\hbar^3)$ vanishes and

$$\hbar^2 < \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right] A_2 \exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{\underline{p}_j}\right] \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] >_{TC}$$

$$= \exp\left[i\tau\,\frac{\underline{\Delta p}^2}{2M}\right] < \hbar^2 A_2 \exp\left[i\tau\,\frac{\underline{\Delta p}}{M}\cdot\underline{p}_j\right] >_{TC} + \mathcal{O}(\hbar^4)$$

$$= \exp\left[i\tau\,\frac{\underline{\Delta p}^2}{2M}\right] <(1+\hbar^2 A_2+\ldots)\exp\left[\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right] >_{TC} \qquad (5.22)$$

$$- \exp\left[i\tau\,\frac{\underline{\Delta p}^2}{2M}\right] < \exp\left[\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right] >_{TC} + \mathcal{O}(\hbar^4)$$

$$= \exp\left[i\tau\,\frac{\underline{\Delta p}^2}{2M}\right] \iint f_1(\underline{p}_j,\underline{q}_j) \exp\left[\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right] d^3p_j d^3q_j$$

$$- \exp\left[i\tau\,\frac{\underline{\Delta p}^2}{2M}\right] < \exp\left[\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right] >_{TC} + \mathcal{O}(\hbar^4)$$

where

$$f_1(\underline{p}_j,\underline{q}_j) = \left(\frac{\beta}{2\pi M}\right)^{\frac{3}{2}} \exp\left[-\frac{\beta \underline{p}_j^2}{2M}\right]\left[n_1(\underline{q}_j) + \frac{\hbar^2\beta^2}{24M}\left(\frac{\beta}{3}\,\frac{\underline{p}_j^2}{M} - 1\right)(N-1)\right.$$

$$\left.(x) \int n_2^c(\underline{q}_j,\underline{r}+\underline{q}_j)\nabla_{\underline{r}}^2\, \phi(\underline{r})\, d^3r + \cdots\right]$$

is the singlet specific distribution function evaluated in Appendix B [Eq. (B.42)].

Substituting this formula into (5.22) and performing the indicated operations yields

$$\hbar^2 < \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right] A_2 \exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right] \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] >_{TC}$$

$$= -\frac{\beta}{2}(N-1)\left(\frac{\hbar\tau\Delta p}{6M}\right)^2 \exp\left[\frac{i\tau\Delta p^2}{2M}\right] \exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right] \qquad (5.23)$$

$$(x) \iint n_2(\underline{q}_j,\underline{r}+\underline{q}_j)\nabla_{\underline{r}}^2\, \phi(\underline{r})\, d^3r\, d^3q_j + \mathcal{O}(\hbar^4)$$

where the classical specific doublet density distribution function n_2^c has been replaced to first approximation by the actual doublet density distribution function n_2 after noting that [see Appendix B, Eq. (B.26)]

$$n_2 = n_2^c + \mathcal{O}(\hbar^2) .$$

It is conventional to rewrite this quantity according to[42]

$$(N-1)\, n_2(\underline{q}_j, \underline{r}+\underline{q}_j)\, d^3r\; d^3q_j = (N-1)\, n(\underline{q}_j)\, n_2(\underline{q}_j | \underline{r}+\underline{q}_j)\, d^3r\; d^3q_j \tag{5.24}$$

where

$$(N-1)\, n_2(\underline{q}_j | \underline{r}+\underline{q}_j)\, d^3r$$

is the probability of finding a second unspecified particle in d^3r about $\underline{r}$ given that the jth particle is in $\underline{q}_j$ and $n(\underline{q}_j)\, d^3q_j$ is the probability of finding the jth particle in d^3q_j about $\underline{q}_j$. In a fluid, n_2 can depend only on $|\underline{r}+\underline{q}_j-\underline{q}_j| = r$ and Eq. (5.24) simplifies to

$$(N-1)\, n_2(r)\, d^3r\; d^3q_j = n(\underline{q}_j)\; g(r)\, d^3r\; d^3q_j \tag{5.25}$$

where $g(r)$ is just the familiar radial distribution function obtained experimentally from X-ray scattering. Substituting this expression into (5.23) and integrating over $\underline{q}_j$ results in

$$\hbar^2 < \exp\left[-\frac{i}{\hbar}\, \underline{\Delta p}\cdot\underline{q}_j\right] A_2 \exp\left[\frac{1}{2}\, \underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right] \exp\left[\frac{i}{\hbar}\, \underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] >_{TC} \tag{5.26}$$
$$= -\frac{\beta}{2}\left(\frac{\hbar\tau\Delta p}{6M}\right)^2 \exp\left[\frac{i\tau\Delta p^2}{2M}\right] \exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right] \int g(r)\, \nabla_{\underline{r}}^2\, \phi(\underline{r})\, d^3r + \mathcal{O}(\hbar^4) .$$

Thus, the intermediate scattering function is given as

$$\chi_s(\underline{\Delta p},\hbar\tau) = \left< \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right]\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\,(\hbar\tau)\right]\right>_{TC}$$
$$- \frac{\beta}{2}\left(\frac{\hbar\tau\Delta p}{6M}\right)^2 \exp\left[\frac{i\tau\Delta p^2}{2M}\right]\exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right]\int g(r)\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r + \mathcal{O}(\hbar^4)\,. \tag{5.27}$$

Since quantum mechanical corrections to certain thermodynamical quantities contain the factor

$$\int g(r)\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r$$

it is possible to obtain an expression for (5.27) in terms of the deviations of these quantities from classical behavior. In particular, the observation that[13]

$$F = F_c + \frac{h^2\beta}{24M}\int g(r)\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r + \mathcal{O}(\hbar^4) \tag{5.28}$$

where F is the Helmholtz free energy, leads to the following alternate formula:

$$\chi_s(\underline{\Delta p},\hbar\tau) = \left< \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{\underline{p}_j}\right]\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]\right>_{TC}$$
$$- \frac{\tau^2\Delta p^2}{3M}\,(F-F_c)\exp\left[\frac{i\tau\Delta p^2}{2M}\right]\exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right] + \mathcal{O}(\hbar^4)\,. \tag{5.27a}$$

5.5 PLACZEK MOMENTS

A consistency check on the above results is provided by the moments introduced in Chapter III [Eqs. (3.41)]:

$$\overline{\epsilon_s^n} = (-i)^n \frac{d^n}{d\tau^n}\,\chi_s(\underline{\Delta p},\hbar\tau)\,\Big|_{\tau=0}\,.$$

Substitution of Eq. (5.27) into this expression yields

$$\overline{\epsilon_s^0} = \chi_s(\underline{\Delta p},0)$$

and

$$\overline{\epsilon_s{}^n} = -(-i)^{n+1}\hbar^{n-1} \exp\left[-\frac{\beta\Delta p^2}{8M}\right] < \exp\left[\frac{\beta\underline{\Delta p}\cdot\underline{p}_j}{2M}\right] \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]$$

$$(x) \left[\frac{\underline{p}_j}{M}\cdot\vec{\nabla}_{q_j} - \nabla V\cdot\vec{\nabla}_p\right]^{n-1}\left[\frac{1}{M}\,\underline{p}_j\cdot\underline{\Delta p}\right] \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right] >_{TC} \qquad (5.29)$$

$$-\frac{\beta}{2}(-i)^n\left(\frac{\hbar\Delta p}{6M}\right)^2\int g(r)\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r\ (x)\ \exp\left[-\frac{\beta\Delta p^2}{8M}\right]$$

$$(x)\ \frac{d^n}{d\tau^n}\left\{\tau^2\exp\left[-\left(\tau-\frac{i\beta}{2}\right)^2\frac{\Delta p^2}{2M\beta}\right]\right\}\Big|_{\tau=0} + \mathcal{O}(\hbar^3), \quad \text{for } n \geq 1.$$

The first few moments may be evaluated by tedious but straightforward application of these equations, and are given by:

$$\overline{\epsilon_s^0} = 1$$

$$\overline{\epsilon_s^1} = \frac{\Delta p^2}{2M}$$

$$\overline{\epsilon_s^2} = \left\{\frac{2}{3M}\Delta p^2\left[\frac{3}{2\beta} + \frac{\hbar^2\beta}{24M} < \nabla_{q_j}^2 V >_{TC} + \mathcal{O}(\hbar^4)\right] + \frac{\Delta p^4}{4M^2}\right\}$$

$$= \left\{\frac{2}{3M}\Delta p^2 < K > + \frac{\Delta p^4}{4M^2}\right\} + \mathcal{O}(\hbar^4) \qquad (5.30)$$

$$\overline{\epsilon_s^3} = \left\{\frac{\Delta p^4}{M^2} < K > + \frac{\Delta p^6}{8M^3} + \frac{\hbar^2\Delta p^2}{6M^2} < \nabla^2 V >\right\} + \mathcal{O}(\hbar^4)$$

$$\overline{\epsilon_s^4} = \left\{\frac{4\Delta p^4}{5M^2} < K^2 > + \frac{\Delta p^6}{M^3} < K > + \frac{\Delta p^8}{16M^4} + \frac{\hbar^2}{3}\frac{\Delta p^2}{M^2} < |\nabla V|^2 >\right.$$

$$\left. + \frac{\hbar^2}{3}\frac{\Delta p^4}{M^3} < \nabla^2 V >\right\} + \mathcal{O}(\hbar^4).$$

Equations (5.30) are indeed correct to $\mathcal{O}(\hbar^2)$, as may be seen by comparison with Eqs. (3.46) of Chapter III.

5.6 TIME-DISPLACED PAIR DISTRIBUTION FORMULISM

In order to obtain further information from Eqs. (5.27) on the atomic motions of the scattering system, one may resort to specific dynamical models leading to a soluble Hamiltonian. From these models, values for the angular and energy distribution of the scattered neutrons can be predicted, and these predictions are then subjected to experimental test.[43,44]

There is, however, an alternate approach which does not require any assumptions at this point on the dynamics of the scattering system and is based on the physical interpretation of the function $G_s^c(\underline{r},t)$ obtained from Van Hove's $G_s(\underline{r},t)$ according to Eq. (3.5). The plausibility of this approach resides, then, in the possibility of establishing a relationship, if only approximate, between the direct scattering cross section and this "classical" $G_s^c(\underline{r},t)$.

One such relationship was suggested by Vineyard,[7] who proposed that the classical limit of the direct scattering differential cross section could be obtained by substituting $G_s^c(\underline{r},t)$ for $G_s(\underline{r},t)$ in Eq. (2.36). Thus, for a monatomic and monoisotopic system,

$$\begin{aligned} S_{sV}(\underline{\Delta p},\epsilon) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} \cdot d\tau\, e^{-i\epsilon\tau}\chi_s^c(\underline{\Delta p},\hbar\tau) \\ &= \cdot\frac{1}{2\pi}\int d\underline{r}\, \exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{r}\right]\int_{-\infty}^{\infty} d\tau\, e^{-i\epsilon\tau} G_s^c(\underline{r},\hbar\tau) \,. \end{aligned} \tag{5.31}$$

That this approximation is unsatisfactory may be seen from the results of Appendix D, where it is shown [Eq. (D.12)] that in obtaining $G_s^c(\underline{r},t)$ by setting $\hbar = 0$ in $G_s(\underline{r},t)$ zero momentum transfer is implied (since $\underline{\kappa} \equiv \underline{\Delta}p/\hbar$ and $\underline{\kappa}$ was kept finite). This is further illustrated, also in Appendix D, by considering in particular the case of the ideal gas for which it is shown that although the cross section is entirely classical (in terms of the significant variables $\underline{\Delta}p$ and ϵ), Eq. (5.31) yields the incorrect result.

Equation (5.31) was physically interpreted by Vineyard as corresponding to a development where the neutron is treated quantum mechanically and the scatterer classically. The frequency of the wavelets contributed by each atom of the scatterer at each instant of past time is given by the frequency of the incident wave modified by a Doppler shift, which is occasioned by the velocity of the scatterer at that instant without allowing any reaction of the neutron on the scattering system.

Additional evidence of the inacceptability of (5.31) is provided by observing that the symmetry condition

$$G_s^c(\underline{r},t) = G_s^c(-\underline{r},-t) \tag{5.32}$$

implies that the scattering function calculated from $G_s^c(\underline{r},t)$ will obey the relation

$$S_s^c(\underline{\Delta}p,\epsilon) = S_s^c(-\underline{\Delta}p,-\epsilon) \tag{5.33}$$

thus violating (as shown by Schofield) the constraint of detail balance and the Placzek moments. Nonetheless, an improved prescription which relates the cross section to $G_s^c(\underline{r},t)$ and does not suffer from the above mentioned difficulties may be obtained. To this end, we integrate (5.27) by parts to get

$$\chi_s(\underline{\Delta p},\hbar\tau) = \exp\left[-\frac{\beta\Delta p^2}{8M}\right] < \exp\left\{\frac{i}{\hbar}\underline{\Delta p}\cdot\left[\underline{q}_j(\hbar\tau)-\underline{q}_j-\frac{i\beta\hbar}{2M}\underline{p}_j\right]\right\}>_{TC} \tag{5.34}$$
$$-\frac{\beta}{2}\left(\frac{\hbar\tau\Delta p}{6M}\right)^2 \exp\left[\frac{i\tau\Delta p^2}{2M}\right]\exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right]\int g(r)\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r+\mathcal{O}(\hbar^4)\,.$$

Furthermore,

$$\exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_j\left(\frac{i\beta\hbar}{2}\right)\right] = \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\sum_{n=0}^{\infty}\left(\frac{i\beta\hbar}{2}\right)^n\frac{1}{n!}D^n\underline{q}_j\right] \tag{5.35}$$

where

$$D^n\underline{q}_j = \frac{d^n}{dt^n}\underline{q}_j(t)\Big|_{t=0}\,.$$

Therefore

$$\exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot(\underline{q}_j+\frac{i\beta\hbar}{2M}\underline{p}_j)\right] = \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{q}_j\left(\frac{i\beta\hbar}{2}\right)\right]\Big[1+\frac{i\beta^2\hbar}{8M}\underline{\Delta p}\cdot\nabla_{q_j}V$$
$$-\frac{\beta^4\hbar^2}{128M^2}(\underline{\Delta p}\cdot\nabla_{q_j}V)^2-\frac{\beta^3\hbar^2}{48M^2}(\underline{p}\cdot\vec{\nabla}_q)(\underline{\Delta p}\cdot\nabla_{q_j}V) \tag{5.36}$$
$$+\mathcal{O}(\hbar^3)\Big]\,.$$

Substituting this expression into (5.34) results in

$$\chi_s(\underline{\Delta p},h\tau) = \exp\left[-\frac{\beta\Delta p^2}{8M}\right] < \exp\left\{\frac{i}{h}\underline{\Delta p}\cdot\left[\underline{q}_j(h\tau)-\underline{q}_j(\frac{i\beta h}{2})\right]\right\}\left[1+\frac{i\beta^2 h}{8M}\underline{\Delta p}\cdot\nabla_{q_j}V\right.$$

$$\left.-\frac{\beta^4\hbar^2}{128M^2}(\underline{\Delta p}\cdot\nabla_{q_j}V)^2-\frac{\beta^3 h^2}{48M^2}(p\cdot\vec{\nabla}_q)(\underline{\Delta p}\cdot\nabla_{q_j}V)\right]>_{TC} \qquad (5.37)$$

$$-\frac{\beta}{2}\left(\frac{h\tau\Delta p}{6M}\right)^2\exp\left[\frac{i\tau\Delta p^2}{2M}\right]\exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right]\int g(r)\nabla^2_{\underline{r}}\phi(\underline{r})\,d^3r+\mathcal{O}(h^3)$$

or

$$\chi_s(\underline{\Delta p},\hbar\tau) = \exp\left[-\frac{\beta\Delta p^2}{8M}\right] < \exp\left\{\frac{i}{\hbar}\underline{\Delta p}\cdot\left[\underline{q}_j(\hbar\tau)-\underline{q}_j(\frac{i\beta\hbar}{2})\right]\right\}>_{TC}$$

$$+\exp\left[-\frac{\beta\Delta p^2}{8M}\right]\frac{i\beta^2\hbar}{8M} < \underline{\Delta p}\cdot\nabla_{q_j}V\exp\left[\frac{i}{M}(\tau-\frac{i\beta}{2})\underline{\Delta p}\cdot\underline{p}_j\right]>_{TC}$$

$$+\exp\left[-\frac{\beta\Delta p^2}{8M}\right](\tau^2+\frac{\beta^2}{8})\frac{\beta^2\hbar^2}{16M^2} < (\underline{\Delta p}\cdot\nabla_{\underline{q}_j}V)^2\exp\left[\frac{i}{M}(\tau-\frac{i\beta}{2})\underline{\Delta p}\cdot\underline{p}_j\right]>_{TC}$$

$$-\exp\left[-\frac{\beta\Delta p^2}{8M}\right]\frac{\beta^3\hbar^2}{48M^2} <(\underline{p}\cdot\vec{\nabla}_q)(\underline{\Delta p}\cdot\nabla_{q_j}V)\exp\left[\frac{i}{M}(\tau-\frac{i\beta}{2})\underline{\Delta p}\cdot\underline{p}_j\right]>_{TC} \qquad (5.38)$$

$$-\frac{\beta}{2}\left(\frac{h\tau\Delta p}{6M}\right)^2\exp\left[\frac{i\tau\Delta p^2}{2M}\right]\exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right]\int g(r)\nabla^2_{\underline{r}}\phi(\underline{r})\,d^3r+\mathcal{O}(\hbar^3)$$

By the same argument used to justify Eq. (5.20), it can be shown that for a randomly oriented system the second term on the right of (5.38) and terms of $\mathcal{O}(h^3)$ will vanish. The third, fourth, and fifth terms can be combined into one since the mean values involved are connected by the relation

$$<|\nabla_{q_j}V|^2>_{TC} = \frac{1}{\beta} < \nabla^2_{q_j}V>_{TC} \qquad (5.39)$$

which readily follows from applying Green's theorem to the identity

$$\frac{1}{Z}\iint d\underline{q}d\underline{p}\,\vec{\nabla}_{q_j}\cdot(\nabla_{q_j}V\,e^{-\beta H}) = \frac{1}{Z}\iint d\underline{p}d\underline{q}\,(\nabla_{q_j}V\cdot\nabla_{q_j}\,e^{-\beta H})$$

$$+\frac{1}{Z}\iint d\underline{p}d\underline{q}\,(e^{-\beta H}\,\nabla^2_{q_j}V)\,. \qquad (5.40)$$

Thus,

$$\chi_s(\underline{\Delta p},\hbar\tau) = \exp\left[-\frac{\beta\Delta p^2}{8M}\right]\left[< \exp\left\{\frac{i}{\hbar}\,\underline{\Delta p}\cdot\left[\underline{q}_j(\hbar\tau)-\underline{q}_j\left(\frac{i\beta\hbar}{2}\right)\right]\right\}>_{TC}\right.$$
$$+\left(\frac{\tau^2}{\beta} - i\tau - \frac{\beta}{8}\right)\left(\frac{\hbar\beta\Delta p}{12M}\right)^2 \cdot\exp\left[-\left(\tau - \frac{i\beta}{2}\right)^2\frac{\Delta p^2}{2M\beta}\right] \qquad (5.41)$$
$$\left.(x)\int g(r)\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r \;+\; \mathcal{O}(\hbar^4)\right] .$$

Moreover, due to time translational invariance

$$< \exp\left\{\frac{i}{\hbar}\,\underline{\Delta p}\cdot\left[\underline{q}_j(\hbar\tau)-\underline{q}_j\left(\frac{i\beta\hbar}{2}\right)\right]\right\}>_{TC} = < \exp\left\{\frac{i}{\hbar}\,\underline{\Delta p}\cdot\left[\underline{q}_j\left(\hbar\tau-\frac{i\beta\hbar}{2}\right) - \underline{q}_j\right]\right\}>_{TC}$$
$$(5.42)$$

and after a simple transformation of variables, Eq. (5.41) becomes

$$\chi_s\left(\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2}\right) = \exp\left[-\frac{\beta\Delta p^2}{8M}\right]\left\{\chi_s^c(\underline{\Delta p},\hbar\tau) + \left(\frac{\tau^2}{\beta}+\frac{\beta}{8}\right)\left(\frac{\hbar\beta\Delta p}{12M}\right)^2\right. \qquad (5.43)$$
$$\left.(x)\;\exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right]\int g(r)\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r\right\} + \mathcal{O}(\hbar^4)$$

where

$$\chi_s^c(\underline{\Delta p},\hbar\tau) = < \exp\left\{\frac{i}{\hbar}\,\underline{\Delta p}\cdot\left[\underline{q}_j(\hbar\tau)-\underline{q}_j\right]\right\}>_{TC} . \qquad (5.44)$$

It is interesting to note at this point that the function $\chi_s(\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2})$ satisfies the required condition

$$\chi_s\left(\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2}\right) = \chi^*\left(-\underline{\Delta p},\hbar\tau + \frac{i\beta\hbar}{2}\right)$$

[see Eq. (3.22)], and that the essential singularity in (5.44) is only apparent and disappears, as indicated previously, when expanding $\underline{q}_j(\hbar\tau)$ in a Maclaurin series. Furthermore, multiplying both sides of (5.43) by $\frac{1}{2\pi}\exp(-i\epsilon\tau)\,d\tau$, integrating over all values of τ, and making use of Eqs.

(3.20), (3.27), and (5.31) yields

$$S_s(\underline{\Delta p},\epsilon) = \exp\left[\frac{\beta\epsilon}{2}\right]\exp\left[-\frac{\beta\Delta p^2}{8M}\right]\frac{1}{2\pi}\int d\underline{r}\,\exp\left[\frac{i}{\hbar}\,\Delta p\cdot\underline{r}\right]\int_{-\infty}^{\infty}d\tau\; e^{-i\epsilon\tau}G_s^c(\underline{r},\hbar\tau)$$

$$+\exp\left[\frac{\beta\epsilon}{2}\right]\exp\left[-\frac{\beta\Delta p^2}{8M}\right]\left(\frac{\hbar\beta}{12}\right)^2\left(\frac{\beta}{2\pi M\Delta p^2}\right)^{\frac{1}{2}}\left(1-\frac{\epsilon^2 M\beta}{\Delta p^2}+\frac{\Delta p^2\beta}{8M}\right)$$

$$(x)\;\exp\left[-\frac{M\beta\epsilon^2}{2\Delta p^2}\right]\int g(r)\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r + \Theta(\hbar^4)\;. \qquad (5.45)$$

We thus obtain explicitly the factor exp $\left(\frac{\beta\epsilon}{2}\right)$ essential to satisfy the condition of detailed balance. Equation (5.45) is our sought for connection between $S_s(\underline{\Delta p},\epsilon)$ and $G_s^c(\underline{r},t)$. The first term in this expression is the form suggested by Singwi and Sjölander,[14] who speculated that it might be correct because it works exactly for the ideal gas. It differs from the Vineyard prescription [Eq. (5.31)] by the factor

$$\exp\left[\frac{\beta\epsilon}{2}\right]\exp\left[-\frac{\beta\Delta p^2}{8M}\right].$$

The order of magnitude of this correction is illustrated in Figs. 1-4, where a comparison is made between the direct differential scattering cross section for some simple systems, as calculated by the Vineyard prescription, and the cross section obtained from the first term in (5.45).[17] The differences are seen to be significant, particularly at high incident energy.

For sufficiently high temperatures the second term in (5.45) is negligible and, in analogy with Eq. (5.27a), may be expressed in terms of the deviation of the free energy from its classical value. Accordingly, we get the following alternate result:

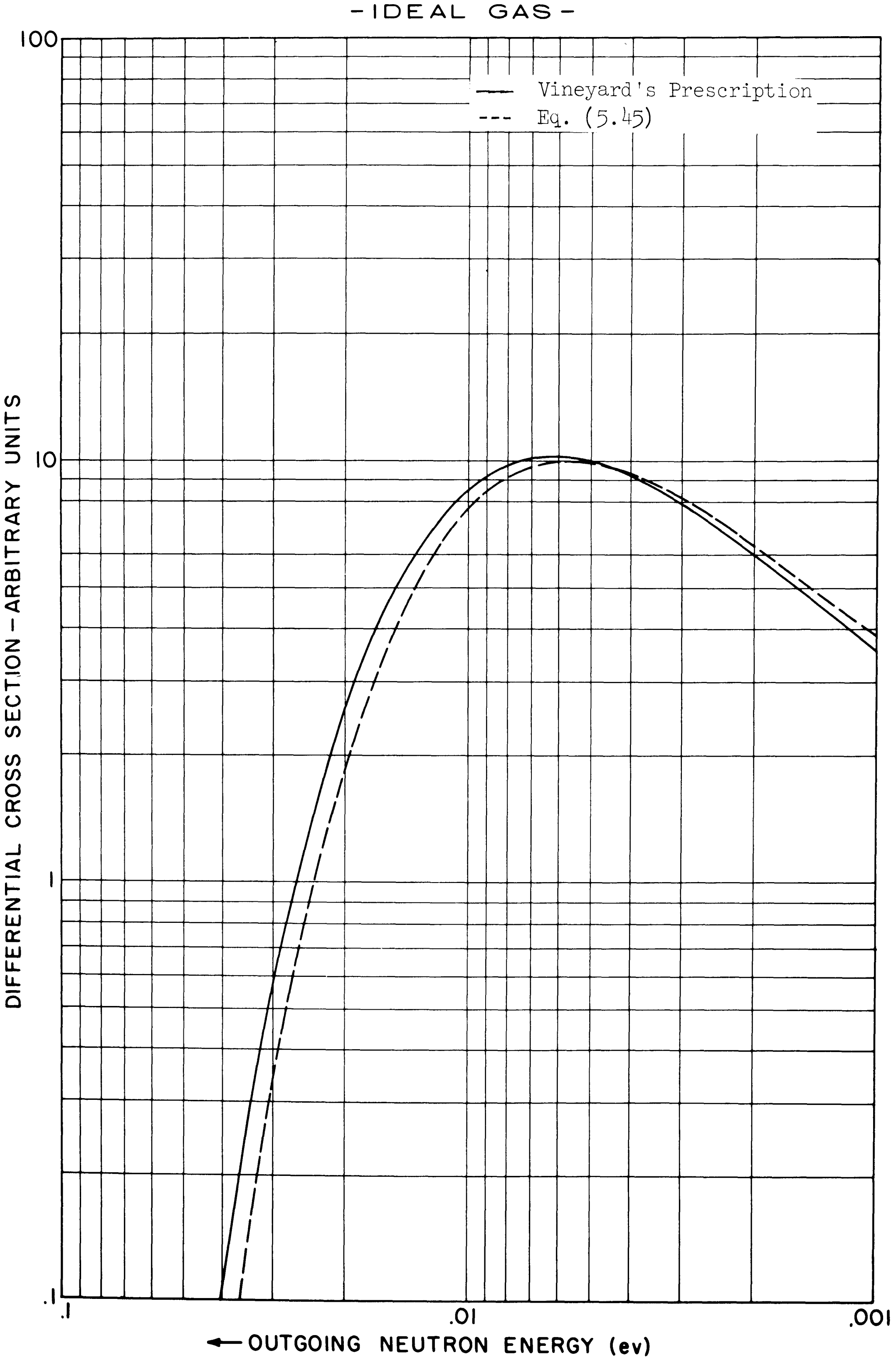

Fig. 1. Differential scattering cross section versus outgoing neutron energy for neutrons of incident energy 5×10^{-3} ev scattered at 90° by an ideal gas of mass 18 at 295°K.

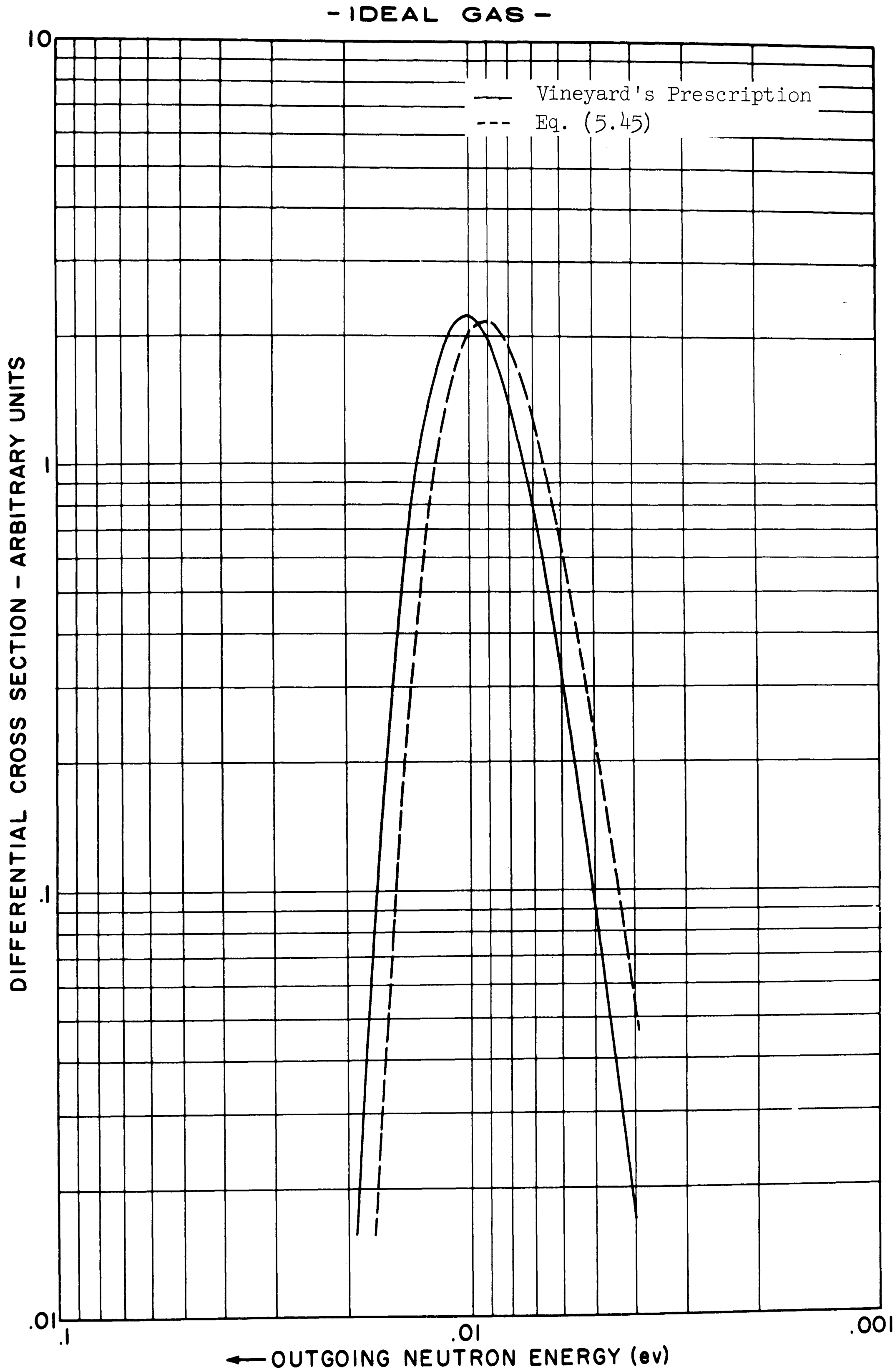

Fig. 2. Differential scattering cross section versus outgoing neutron energy for neutrons of incident energy 0.1 ev scattered at 90° by an ideal gas of mass 18 at 295°K.

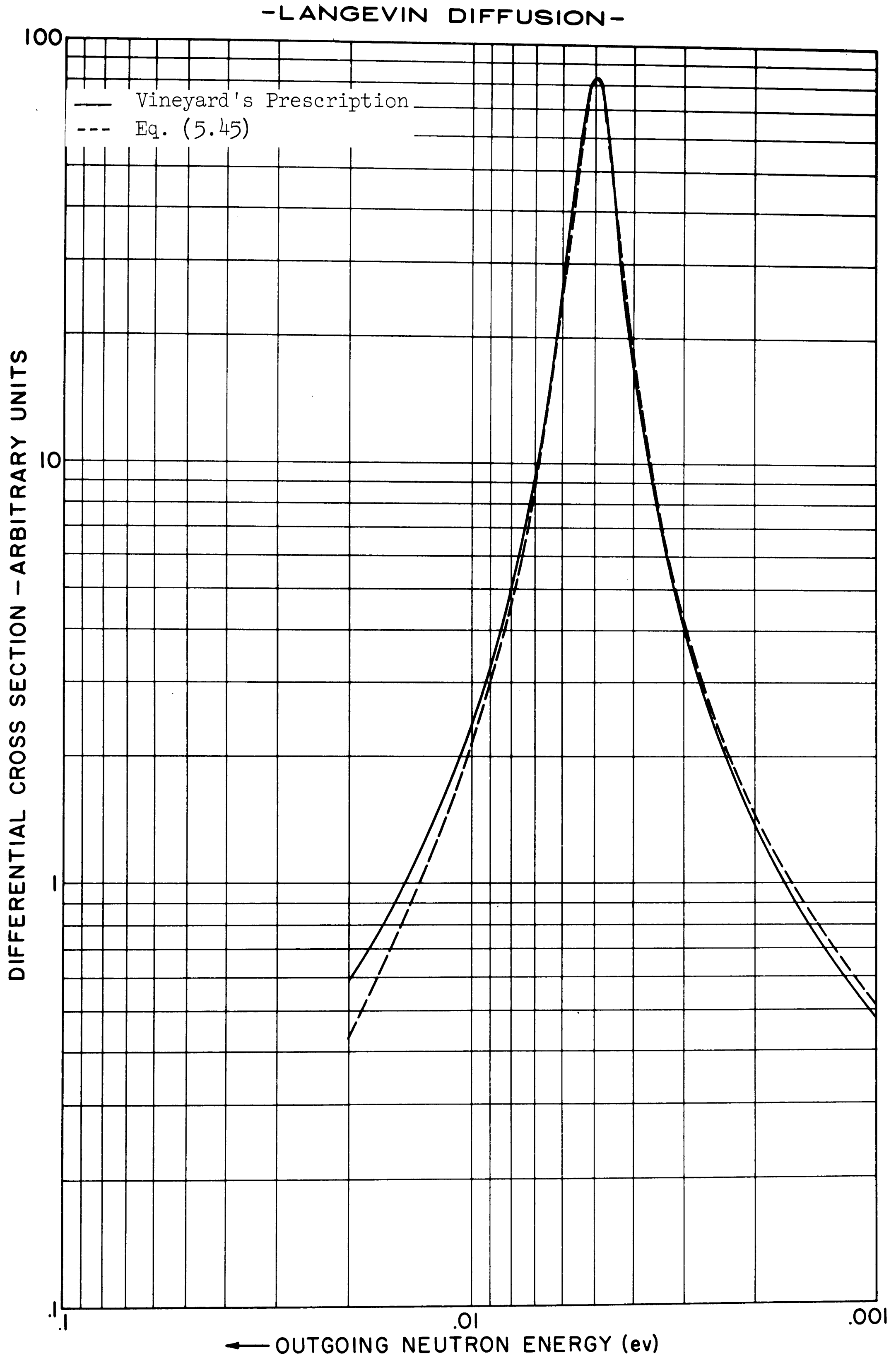

Fig. 3. Differential scattering cross section versus outgoing neutron energy for neutrons of incident energy 5×10^{-3} ev scattered at 90° by a system of particles of mass 18 diffusing according to the Langevin model at 295°K.

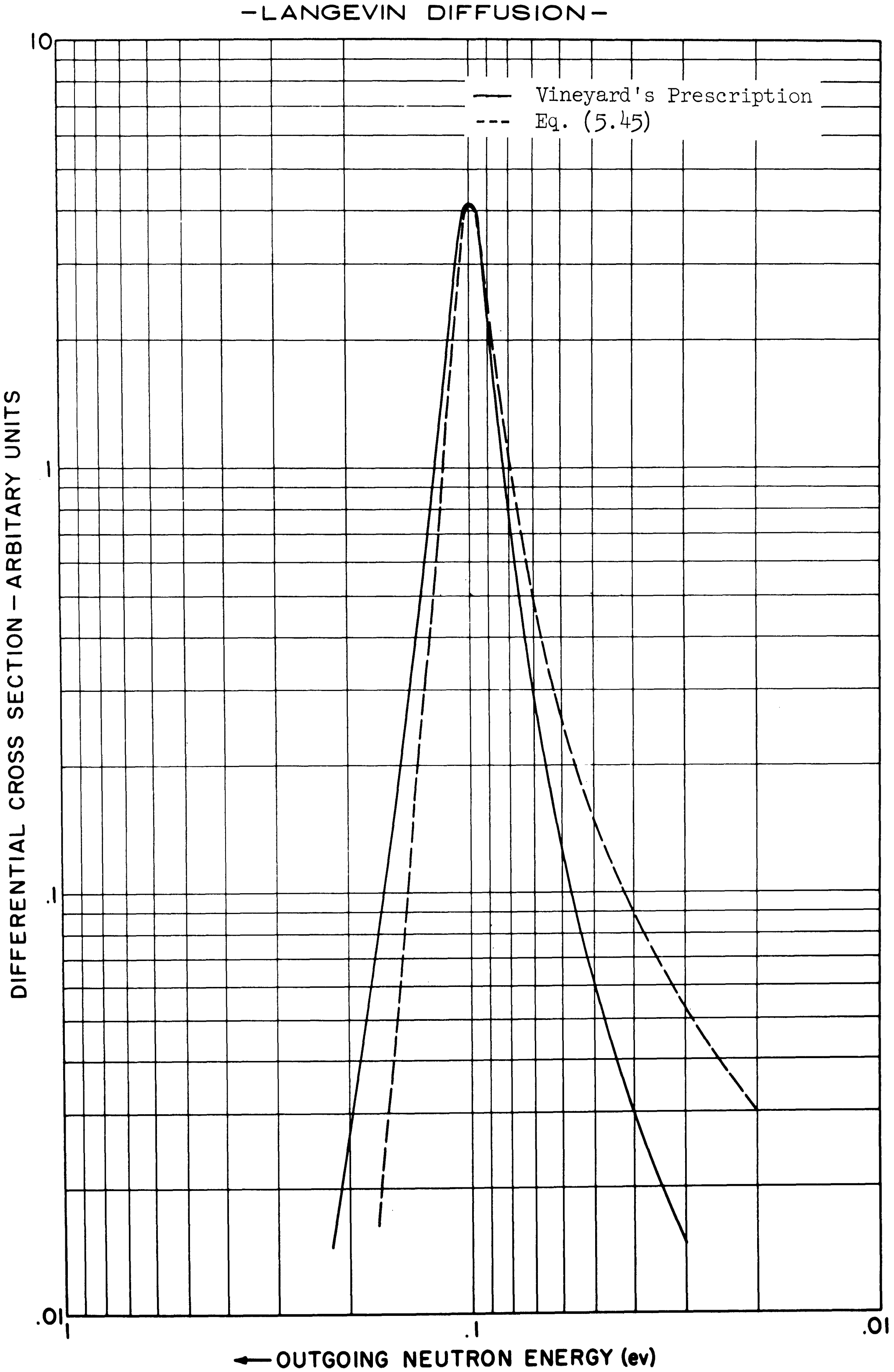

Fig. 4. Differential scattering cross section versus outgoing neutron energy for neutrons of incident energy 0.1 ev scattered at 90° by a system of particles of mass 18 diffusing according to the Langevin model at 295°K.

$$S_s(\underline{\Delta p},\epsilon) = \exp\left[\frac{\beta\epsilon}{2}\right]\exp\left[-\frac{\beta\Delta p^2}{8M}\right]\left\{\frac{1}{2\pi}\int d^3r\int d\tau\ \exp\left[\frac{i}{\hbar}(\underline{\Delta p}\cdot\underline{r}-\epsilon\hbar\tau)\right]G_s^c(\underline{r},\hbar\tau)\right.$$

$$\left. + \frac{\beta}{6}\left(\frac{\beta M}{2\pi\Delta p^2}\right)^{\frac{1}{2}}(F-F_c)\left(1-\frac{\epsilon^2 M\beta}{\Delta p^2}+\frac{\Delta p^2\beta}{8M}\right)\exp\left[-\frac{M\beta\epsilon^2}{2\Delta p^2}\right]\right\} + \mathcal{O}(\hbar^4). \tag{5.46}$$

Detailed Balance and Placzek Moments.—Because of the symmetry condition [Eq. (5.32)] on $G_s^c(\underline{r},t)$, $\exp\left[-\frac{\beta\epsilon}{2}\right]$ $S_s(\underline{\Delta p},\epsilon)$ in (5.45) is invariant [at least to $\mathcal{O}(\hbar^2)$] when interchanging the initial and final states of the neutron, i.e.,

$$\exp\left[-\frac{\beta\epsilon}{2}\right]S_s(\underline{\Delta p},\epsilon) = \exp\left[\frac{\beta\epsilon}{2}\right]S_s(-\underline{\Delta p},-\epsilon). \tag{5.47}$$

Consequently, the condition (3.28) and its corollary, the principle of detailed balancing, are satisfied. Furthermore, as previously indicated, Eq. (5.45) was derived essentially by adding a given quantity to the first term in (5.27) and substracting the same quantity from the second term. Therefore, Eqs. (5.45) and (5.46) will also satisfy the Placzek moments [Eqs. (5.30)] to $\mathcal{O}(\hbar^2)$.

5.7 OTHER PRESCRIPTIONS

In the light of the above analysis, it is possible to critically examine various other "prescriptions."

(a) Schofield's Prescription.—From the observation that the time correlation function $F(\underline{r},t)$, defined by

$$F(\underline{r},t) = \left(\frac{1}{2\pi\hbar}\right)^3\int d^3\Delta p\ \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{r}\right]\chi_s(\underline{\Delta p},\hbar\tau+\frac{i\beta\hbar}{2}) \tag{5.48}$$

is real and that its double Fourier transform satisfies the condition (3.28), Schofield[8] suggested that this function be made equal to $G_s^c(\underline{r},t)$. This leads to an expression for $S_s(\underline{\Delta p},\epsilon)$ which, with the exception of the factor $\exp\left[-\frac{\beta \Delta p^2}{8M}\right]$, is equal to the first term in (5.45). Therefore this approximation will be valid only for small momentum transfers and heavy scatterers. Turner[45] has attempted to justify Schofield's recipe by making use of an argument which is wrong for the following reasons:

(1) It incorrectly uses "Weyl's rule" for Heisenberg operators. This results in an expression that can be obtained from (5.27) by expanding the operator $\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right]$ in a formal power series and retaining only the first two terms in the expansion.

(2) It attempts to expand a function in powers of $\hbar$ about an essential singularity.

(b) Letting $S_s(\Delta p,\epsilon) \approx S_s^c[\Delta p,\epsilon-(\Delta p^2/2M)]$.[33]—Since (5.45) is an asymptotic expansion, clearly it will not be unique. In fact, if instead of integrating

$$< \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right] \exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right] \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] >_{TC} \qquad (5.48)$$

by parts in (5.27), $\underline{q}_j(\hbar\tau)$ is formally expanded in a Taylor series and is operated on by $\exp\left[\frac{1}{2}\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right]$, it can be shown that

$$\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right] \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] = \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] \exp\left[\frac{i\Delta p^2\tau}{2M}\right]$$

$$(x)\ \exp\left[-\frac{ih^2\tau^3}{12M^2}\,(\underline{\Delta p}\cdot\vec{\nabla}_q)(\underline{\Delta p}\cdot\nabla_{q_j}V)\right]\left[1 + J(\tau,\underline{q},\underline{\Delta p})\right] \qquad (5.50)$$

where $J(\tau,\underline{q},\underline{\Delta p})$ is of $\mathcal{O}(\hbar^4)$. In this case, the thermal average (5.49) becomes

$$< \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_j}\right]\;\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]\;>_{TC}$$

$$= \exp\left[\frac{i\Delta p^2\tau}{2M}\right]< \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]\;\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]>_{TC}$$

$$- \frac{i\hbar^2\tau^3}{12M^2}\exp\left[\frac{i\Delta p^2\tau}{2M}\right] < \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot q_j\right]\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right] \qquad (5.51)$$

$$(x)\;\;(\underline{\Delta p}\cdot\vec{\nabla}_q)(\underline{\Delta p}\cdot\nabla_{\underline{q}_j}V)\;>_{TC} + \mathcal{O}(\hbar^4)$$

$$= \exp\left[\frac{i\Delta p^2\tau}{2M}\right]< \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j\right]\;\exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_j(\hbar\tau)\right]>_{TC}$$

$$- \frac{i\hbar^2\tau^3\Delta p^2}{36M^2}\exp\left[\frac{i\Delta p^2\tau}{2M}\right]\exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right]\int g(r)\,\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r + \mathcal{O}(\hbar^4)$$

and

$$S_s(\underline{\Delta p},\epsilon) = S_s^c(\underline{\Delta p},\epsilon - \frac{\Delta p^2}{2M}) - 4\left(\frac{\hbar\beta}{12}\right)^2\left(\frac{\beta}{2\pi M\Delta p^2}\right)^{\frac{1}{2}}\left\{\frac{\epsilon M}{\Delta p^2}\left[3 - \frac{M\beta}{\Delta p^2}\,(\epsilon - \frac{\Delta p^2}{2M})^2\right] - 1\right\} \qquad (5.52)$$

$$(x)\;\exp\left[-\frac{\beta\Delta p^2}{8M}\right]\;\exp\left[\frac{\beta\epsilon}{2}\right]\exp\left[-\frac{\epsilon^2 M\beta}{2\Delta p^2}\right]\int g(r)\,\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r + \mathcal{O}(\hbar^4)\,.$$

Although Eq. (5.52) is also correct to $\mathcal{O}(\hbar^2)$ and satisfies the Placzek moments to this order, it differs from Eq. (5.45) in that, due to the way the terms are grouped, it does not satisfy the condition (3.28). This makes (5.45) preferable.

(c) $\underline{y^2}$ Time Approximation.—Based on the fact that Schofield's prescription does not satisfy the zeroth Placzek moment, it was suggested by Egelstaff[46] and Schofield[47] that, for an isotropic system, $\chi_s(\underline{\Delta p},t)$ may be obtained from $\chi_s^c(\underline{\Delta p},t)$ by replacing t^2 by $y^2 = t^2 - i\hbar t\beta$. In order to establish connection between this recipe and the quasi-classical approximation, note that for a randomly oriented system $\chi_s^c(\underline{\Delta p},t)$ is real and is given by

$$\chi_s^c(\underline{\Delta p},t) = \chi_s^c(|\underline{\Delta p}|,t) = \left< \exp\left[\frac{i\Delta p}{\hbar}(z_j(t)-z_j)\right] \right>_{TC}$$
$$= \left< \cos\left[\frac{\Delta p}{\hbar}(z_j(t)-z_j)\right] \right>_{TC} = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!}\left(\frac{\Delta p}{\hbar}\right)^{2n} \left<[z_j(t)-z_j]^{2n}\right>_{TC} \tag{5.53}$$

where z_j is the component of $\underline{q}_j$ along the direction of $\underline{\Delta p}$ and $\underline{\Delta p}$ is chosen along the z-axis. Hence, the formal expansion in powers of $\underline{\Delta p}^2$

$$\ln\left\{\chi_s^c(\underline{\Delta p},t) + \left(\frac{\tau^2}{\beta}+\frac{\beta}{8}\right)\left(\frac{\hbar\beta\Delta p}{12M}\right)^2 \exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right] \left<\nabla_j^2 V\right>\right\} = \sum_{n=0}^{\infty}\left(\frac{\Delta p^2}{\hbar^2}\right)^n \frac{C_n(t)}{n!} \tag{5.54}$$

is justified. The coefficients $C_n(t)$ may be evaluated from (5.53) by noting that

$$C_n(t) = \hbar^{2n}\frac{d^n}{d(\Delta p^2)^n}\ln\left\{\chi_s^c(\underline{\Delta p},t)+\left(\frac{\tau^2}{\beta}+\frac{\beta}{8}\right)\left(\frac{\hbar\beta\Delta p}{12M}\right)^2\exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right]\left<\nabla_j^2 V\right>\right\}\Bigg|_{\Delta p^2=0} \tag{5.55}$$

yielding

$$C_0(t) = 0$$

and

$$C_1(t) = -\frac{1}{2}\left[\frac{t^2}{M\beta} - \frac{1}{36\beta M^2}\left(t^2+\frac{\hbar^2\beta^2}{4}\right)^2\left<\nabla_j^2 V\right>_{TC} + \frac{1}{360}\frac{t^6}{\beta M^3}\left<\left(\frac{\partial^2 V}{\partial z\partial z_j}\right)^2\right>_{TC} + \mathcal{O}(t^8)\right] \tag{5.56}$$

for the first two terms. Consequently, Eq. (5.43) becomes

$$\ell n\ \chi_s(\underline{\Delta p},\hbar\tau+\frac{i\beta\hbar}{2}) = -\frac{\Delta p^2}{2\hbar^2\beta M}\left[\hbar^2(\tau^2+\frac{\beta^2}{4}) - \frac{h^4(\tau^2+\frac{\beta^2}{4})^2}{36M} <\nabla_j^2 V>_{TC} + \frac{\hbar^6}{360M^2}(\tau^2+\frac{\beta^2}{4})^3 <\left(\frac{\partial^2 V}{\partial z\partial z_j}\right)^2>_{TC} + \mathcal{O}(\tau^2\hbar^6)\right] + \mathcal{O}(\Delta p^4) \tag{5.57}$$

or

$$\ell n\ \chi_s(\underline{\Delta p},\hbar\tau) = -\frac{\Delta p^2}{2\hbar^2\beta M}\left[y^2 - \frac{1}{36M}y^4 <\nabla_j^2 V>_{TC} + \frac{y^6}{360M^2} <\left(\frac{\partial^2 V}{\partial z\partial z_j}\right)^2>_{TC} + \mathcal{O}(\tau^2\hbar^6)\right] + \mathcal{O}(\Delta p^4)\,. \tag{5.58}$$

That is,

$$\ell n\ \chi_s(|\underline{\Delta p}|,t) = \ell n\ \chi_s^c[|\underline{\Delta p}|,(t^2-i\hbar t\beta)^{\frac{1}{2}}] + \text{correction terms of } \mathcal{O}(\hbar^2 t^2). \tag{5.59}$$

The first term on the right of the above equation is indeed the y^2 time approximation of Egelstaff and Schofield. Note, however, that because of the nature of the correction terms, this approximation is valid only for small values of t. The need for the small time constraint can be easily verified by applying the recipe to the case of an isotropic harmonic oscillator for which one obtains

$$\ell n\ \chi_s^c[|\underline{\Delta p}|,(t^2-i\beta\hbar t)^{\frac{1}{2}}] = -\frac{\Delta p^2}{M\beta(\hbar\omega)^2}[(1-\cos\omega t) - \frac{i\beta\hbar\omega}{2}\sin\omega t] + \frac{\Delta p^2\beta}{4M\omega^2}\left[\frac{\omega\sin\omega t}{t} - \omega^2\cos\omega t\right] + \cdots \tag{5.60}$$

Here we see that the first term on the right is in fact the high temperature limit of $\ell n\ \chi_s(|\underline{\Delta p}|,t)$. The additional terms, however, become negligible only for small values of t.

(d) The Rigorous Classical Limit.—In order to investigate the limiting behavior of $S_s(\underline{\Delta p},\epsilon)$ as $\hbar \to 0$, it is convenient to expand $\chi_s^c(\underline{\Delta p},\hbar\tau)$ in Eq. (5.44) in a power series in $\hbar\tau$. Thus,

$$\chi_s^c(\underline{\Delta p},\hbar\tau) = \left\langle \exp\left[\frac{i\tau}{M}\underline{\Delta p}\cdot\underline{p}_j\right]\right\rangle_{TC} - \frac{i\hbar\tau^2}{2M}\left\langle \underline{\Delta p}\cdot\nabla_{q_j} V \exp\left[\frac{i\tau}{M}\underline{\Delta p}\cdot\underline{p}_j\right]\right\rangle_{TC}$$
$$- \frac{i\hbar^2\tau^3}{6M^2}\left\langle (\underline{p}\cdot\vec{\nabla}_q)(\underline{\Delta p}\cdot\nabla_{q_j} V)\exp\left[\frac{i\tau}{M}\underline{\Delta p}\cdot\underline{p}_j\right]\right\rangle_{TC} \tag{5.61}$$
$$- \frac{\hbar^2\tau^4}{8M^2}\left\langle (\underline{\Delta p}\cdot\nabla_{q_j} V)^2 \exp\left[\frac{i\tau}{M}\underline{\Delta p}\cdot\underline{p}_j\right]\right\rangle_{TC} + \mathcal{O}(\hbar^3) .$$

Performing the indicated thermal averages gives

$$\chi_s^c(\underline{\Delta p},\hbar\tau) = \exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right] + \frac{\hbar^2\tau^4\Delta p^2}{72\beta M^2}\exp\left[-\frac{\tau^2\Delta p^2}{2M\beta}\right]\int g(r)\,\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r + \mathcal{O}(\hbar^4). \tag{5.62}$$

Substituting this result into Eq. (5.45) yields

$$S_s(\underline{\Delta p},\epsilon) = \left(\frac{M\beta}{2\pi\Delta p^2}\right)^{\frac{1}{2}} \exp\left[\frac{\beta\epsilon}{2}\right]\exp\left[-\frac{\beta\Delta p^2}{8M}\right]\exp\left[-\frac{\beta M\epsilon^2}{2\Delta p^2}\right]\left\{1 + \left[\frac{M}{2\beta\Delta p^2}H_4(E)\right.\right. \tag{5.63}$$
$$\left.\left. - \frac{1}{4}\left(H_2(E) - \frac{\Delta p^2\beta}{8M}\right)\right]\frac{\hbar^2\beta^2}{36M}\int g(r)\nabla_{\underline{r}}^2\,\phi(\underline{r})\,d^3r\right\} + \mathcal{O}(\hbar^4)$$

where

$$E = (\epsilon^2 M\beta/\Delta p^2)^{\frac{1}{2}}$$
$$H_2(E) = E^2 - 1 \tag{5.64}$$
$$H_4(E) = E^4 - 6E^2 + 3 .$$

From Eq. (5.63) it immediately follows that

$$\lim_{\hbar\to 0} S_s(\underline{\Delta p},\epsilon) = \left(\frac{M\beta}{2\pi\Delta p^2}\right)^{\frac{1}{2}}\exp\left[\frac{\beta\epsilon}{2}\right]\exp\left[-\frac{\beta\Delta p^2}{8M}\right]\exp\left[-\frac{\beta M\epsilon^2}{2\Delta p^2}\right] . \tag{5.65}$$

That is, the exact classical limit of any system, defined in this way, is the ideal-gas result. This is physically understandable since classically the neutron-nuclear collision is instantaneous; thus the neutron never samples the potential which binds the scattering system (since the Fermi pseudo-potential is a contact potential). In fact, since the quantum mechanical corrections in (5.63) contain the factor β, the idealization to a monatomic gas is not far from reality at sufficiently high temperatures. The rapidity of convergence to this asymptotic behavior is determined by the factor $(M/\beta\Delta p^2)\ H_4(E)$, and therefore increases with increasing momentum transfers.

CHAPTER VI

A CRYSTALLINE DISLOCATION MODEL FOR A MONATOMIC LIQUID

The complexity of atomic dynamics in liquids has been pointed out in the preceding chapter. In fact, for dilute gases the movement of a molecule may be considered independent of the movement of the other molecules. Conversely, for monatomic crystals atomic motions can be resolved into independent modes of vibrations. For monatomic liquids, however, both intermolecular interactions and spatial transitions of the atoms must be considered. The neglect of either one of these factors results in simplified models which describe correctly only a limited group of properties of the liquid state.

It is presently accepted,[48] however, that at least in the neighborhood of the crystallization point, the thermal motion of the molecules in a liquid resembles that of a crystal more closely than that of a gas. This is substantiated by the following experimental facts.

(a) In melting a crystal, the increase in volume is relatively small as a rule. Also, the latent heat of fusion is much smaller than the latent heat of vaporization. These facts indicate only a small decrease in the cohesive forces between molecules in the process of fusion and, consequently, a similarity between inter-molecular relationships in the liquid and solid states.

(b) A similarity between specific heats of solids and liquids near the crystallization point further indicates that a liquid, particularly with regard to molecular motions and inter-molecular forces, resembles a polycrystalline solid.

(c) The existence of a certain degree of local order in the relative distribution and orientation of the molecules in a liquid, as disclosed by X-ray and neutron spectroscopy,[1] again suggests that the character of the thermal motion of the molecules in a liquid remains fundamentally the same as in solids.

Conclusion (c) appears to lead to a contradiction. For crystals, the conception that the thermal motion of the atoms reduces to slight oscillations about fixed equilibrium positions is in full agreement with their rigidity. For liquids, on the contrary, this conception seems to be in disaccord with their characteristic fluidity. Such an opposition between the solid and liquid states is, however, of a quantitative rather than qualitative nature, since liquids are known to display elements of rigidity and order whereas elements of fluidity and disorder exist in solids. In fact, various "quasi-crystalline" models for liquids may be proposed which still account for their characteristic fluidity. Thus, Frenkel[49] has suggested that the equilibrium positions of the atoms in a liquid have a temporary character, each atom vibrating about its equilibrium position for a certain time after which it would jump to a new equilibrium position. If the time during which an atom performs an oscillatory motion is large compared with its period of vibration, then this jump diffusion cannot affect the magnitude of the specific heat of the liquid, which remains, in this respect, solid-like.

On the other hand, if this time is small compared with the time during which the liquid is subject to a force of constant magnitude and direction, it will yield to this force in the sense described by the ordinary process of liquid flow. Conversely, when the time of oscillation is large compared with the time during which the force is acting, the liquid will only suffer an elastic deformation, just as in an ordinary solid.

In other proposed modifications of Frenkel's model, the jump diffusion of the atoms from one equilibrium position to another is replaced by continuous diffusion (simple or of the Langevin type).[50] The statistical character of these models leads naturally to a description of the atomic motions in terms of the classical space-time correlation functions introduced in preceding chapters;* the formulism of Chapter V for relating these functions to the differential neutron scattering cross section is most adequate. In this chapter, however, we illustrate a different approach for the description of neutron scattering from liquids. This approach is based again on a "quasi-crystalline" model for a monatomic liquid, although in this case a soluble time-independent Hamiltonian is obtained which does not necessitate the introduction of the classical space-time correlation functions for analyzing the scattering data. The use of the rigorous expression for the cross section developed in Chapter V for quadratic and lower-degree potentials is ex-

*A self space-time correlation function for a combined vibration plus continuous diffusion-type motion has been constructed by Singwi and Sjölander.[51]

tremely convenient here.

6.1 MODEL PROPOSED

It is known that a liquid can propagate sound waves with very little attenuation or dispersion, but that it cannot support low frequency transverse elastic waves. This suggests representation of the thermal agitation of a liquid by superimposing longitudinal (compression) waves treated as in a solid and transverse shear waves, so that those with wavelength above a certain critical value degenerate into translational modes while those with wavelength below the critical value survive as vibrational modes.

These features have been incorporated in a model proposed by Ookawa[18] which essentially assumes that the liquid consists of an aggregate of crystallites, each behaving as a kinetic unit which is in a state of self strain and is stabilized thermodynamically.

The outstanding characteristics of the model are:

(a) The "crystal" is threaded by a fine network of dislocations in which the dislocation segments are expected to be neighboring at a distance of the order of several atom spacings and the interaction between the constituent imperfections is expected to be very strong, to an order seldom experienced in the field of crystalline solids. This leads to a distortion in bulk of the lattice material rather than to a localized distortion at the core of the dislocations.

(b) The elastic shear strain energy associated with the thermal shear waves is dissipated by forcing the dislocation segments to move, thereby resulting in a kind of plastic flow of the material.

For the sake of simplicity, it is assumed that transversal shear waves with wavelength longer than the average spacing $2\,\alpha\,a$ (a being the atomic spacing) between the like dislocation segments degenerate into translational modes, while thermal shear waves with wavelength smaller than $2\,\alpha\,a$ survive as vibrational modes.

(c) The anharmonic modulation of eigenfrequencies of the transversal waves, due mainly to the shear strain of the material, is tentatively assumed, on the basis of symmetry considerations, to be given by the functional relation

$$\omega'_{2ki}(x) = \omega_{2ki} \exp[-\frac{1}{2}\gamma x^2] \qquad (6.1)$$

where $x = a/\alpha a$ is the shear strain, γ is a constant coefficient, $i = 1,2$ specifies the polarization of the wave, and ω_{2ki} is the natural eigenfrequency for unstrained crystal corresponding to a wave number k. This expression may be disputable because it neglects different modulation for waves with different wave vector, dependence of γ on the strain, and its *a posteriori* variation with temperature. Therefore, it is possible to estimate only the probable value of γ from experimental data.

6.2 MODEL HAMILTONIAN

The Hamiltonian for the model system may be obtained from that for an imperfect crystal. The latter, in the context of the Born-Oppenheimer approximation,[51] is given by

$$H = \sum_{j=1}^{3N} \frac{p_j^2}{2M} + V(\underline{q}_1, \underline{q}_2, \cdots \underline{q}_n) \qquad (6.2)$$

where $\underline{q}$ and $\underline{p}$ denote nuclear coordinates and momenta respectively.

Following the standard treatment of developing the potential energy in (6.2) as a Taylor series in powers of the displacements $u_j(j=1,2,\ldots 3N)$ of the nuclei from their equilibrium positions yields

$$V = V_0 + U_0 + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial q_i}\right)_0 u_i + \frac{1}{2} \sum_{i,\ell=1}^{3N} \epsilon_{i\ell} u_i u_\ell + \cdots, \qquad (6.3)$$

in which $\epsilon_{i\ell} = (\partial^2 V/\partial q_i \partial q_\ell)_0$ and U_0 is the configurational excess energy. The constant V_0 can be set equal to zero if the energy is measured from the minimum of the potential function for a perfect crystal. The terms linear in u_i must also vanish since $(\partial V/\partial q_i)_0 = 0$ is the condition for equilibrium. Finally, neglecting terms cubic in u_i as well as higher order terms results in

$$V = U_0 + \frac{1}{2} \sum_{i,\ell} \epsilon_{i\ell} u_i u_\ell \; . \qquad (6.4)$$

Within this approximation, it is possible to resolve (6.2) into normal modes. Explicitly, applying the orthogonal transformation*

$$\mathbf{u} = \mathbf{X}\mathbf{Q} \qquad (6.5)$$

to the quadratic form

$$\epsilon(\mathbf{u}, \mathbf{u}) = \sum_{i,\ell} \epsilon_{i\ell} u_i u_\ell = \tilde{\mathbf{u}} \boldsymbol{\epsilon} \mathbf{u} \qquad (6.6)$$

*Bold letters will be used to denote matrices.

($\tilde{\mathcal{U}}$ is the transposed matrix to $\mathcal{U}$) yields

$$\epsilon(\mathcal{U},\mathcal{U}) = \tilde{Q}\tilde{X}\epsilon X Q = \tilde{Q}X^{-1}\epsilon X Q \ . \qquad (6.7)$$

Furthermore, if X is chosen so that

$$X^{-1}\epsilon X = (\lambda_i \delta_{ij}) \qquad (6.8)$$

(which is always possible because ϵ is symmetric[52]), then

$$\epsilon(\mathcal{U},\mathcal{U}) = \sum_{\ell} \lambda_{\ell} Q_{\ell}^{2} \qquad (6.9)$$

where λ_ℓ are the eigenvalues of ϵ.

In a similar fashion,

$$\sum_j \frac{p_j^{2}}{2M} = \frac{M}{2}\sum_j \dot{u}_j^{2} = \frac{M}{2}\dot{\tilde{\mathcal{U}}}\dot{\mathcal{U}} = \frac{M}{2}\dot{\tilde{Q}}\dot{Q} = \frac{M}{2}\sum_{\ell}\dot{Q}_{\ell}^{2} \ . \qquad (6.10)$$

Consequently, (6.2) becomes

$$H = U_0 + \sum_{\ell=1}^{3N} \left(\frac{M}{2}\dot{Q}_{\ell}^{2} + \frac{1}{2}\omega_{\ell}^{2}Q_{\ell}^{2}\right) \qquad (6.11)$$

after making use of Eqs. (6.9) and (6.10) and setting $\omega_\ell^2 \equiv \lambda_\ell$.

Resolving the above equation into longitudinal and transversal modes yields

$$H = U_0 + \sum_{k=1}^{N} \frac{1}{2M}\left(C_k^{2} + M\omega_{1k}^{2}A_k^{2}\right) + \sum_{k=1}^{N}\sum_{i=1}^{2}\frac{1}{2M}\left(D_{ki}^{2} + M\omega_{2ki}'^{2}B_{ki}^{2}\right) \qquad (6.12)$$

where C_k and D_{ki} are the longitudinal and transversal normal momenta respectively and A_k and B_{ki} their corresponding normal coordinates. Now, allowing the transversal modes with $k \le k_c$ to degenerate into translations of the N/α^3 crystallites results in

$$H = U_0 + \sum_{k \leq k_c} \sum_{i=1}^{2} \frac{M\dot{B}_{ki}^2}{2} + \sum_{k=1}^{N} \frac{1}{2M} (C_k^2 + M\omega_{1k}^2 A_k^2) + \sum_{k > k_c} \sum_{i=1}^{2} \frac{1}{2M} (D_{ki}^2 + M\omega_{2ki}^{\prime 2} B_{ki}^2) \quad . \tag{6.13}$$

Moreover, since each crystallite behaves as a kinetic unit,

$$\sum_{k \leq k_c} \frac{M\dot{B}_{ki}^2}{2} = \sum_{\nu=1}^{N/\alpha^3} \frac{P_{\nu i}^2}{2M\alpha^3} \tag{6.14}$$

where $P_{\nu i}$ is the component of the momentum of the center of mass of the νth crystallite along one of the polarizations of the transversal waves, and $M\alpha^3$ is the mass of each crystallite.

Hence

$$H = U_0 + \sum_{\nu=1}^{N/\alpha^3} \sum_{i=1}^{2} \frac{P_{\nu i}^2}{2M\alpha^3} + \sum_{k=1}^{N} \frac{1}{2M} (C_k^2 + M\omega_{1k}^2 A_k^2) + \sum_{k > k_c} \sum_{i=1}^{2} \frac{1}{2M} (D_{ki}^2 + M\omega_{2ki}^{\prime 2} B_{ki}^2) \quad . \tag{6.15}$$

Equation (6.5) may also be expressed in terms of longitudinal and transversal modes. Thus,

$$\underline{u}_j(t) = \sum_{k=1}^{3N} \underline{X}_{jk} Q_k(t) = \sum_{k=1}^{N} \underline{a}_j^k A_k(t) + \sum_{k > k_c} \sum_{i=1}^{2} \underline{b}_{ji}^k B_{ki}(t) + \sum_{k \leq k_c} \sum_{i=1}^{2} \underline{b}_{ji}^k B_{ki}(t) \tag{6.16}$$

where

$$\underline{X}_{jk} = \begin{cases} \underline{a}_j^k & \text{for longitudinal modes} \\ \underline{b}_{ji}^k & \text{for transversal modes.} \end{cases} \tag{6.17}$$

The first two terms on the right of (6.16) represent the instantaneous vibrational displacement of the jth nucleus from its equilibrium position. The third term represents the contribution, due to translation, to the nucleus position at time t and is equal to the displacement of the center of mass of the crystallite to which the nucleus belongs.

The position of the jth nucleus at time t (see Fig. 5) may now be expressed as

$$\underline{q}_j(t) = \underline{R}_\nu(t) + \underline{b}_j + \underline{u}_j'(t) \tag{6.18}$$

where

$$\underline{u}_j'(t) = \sum_{k=1}^{N} \underline{a}_j^k A_k(t) + \sum_{k>k_c} \sum_{i=1}^{2} \underline{b}_{ji}^k B_{ki}(t) \ , \tag{6.19}$$

$\underline{R}_\nu(t)$ is the position vector of the center of mass of the νth crystallite at time t, and $\underline{b}_j$ is the displacement of the equilibrium position of the jth nucleus from the crystallite's center of mass.

6.3 THE INTERMEDIATE SCATTERING FUNCTION

We now use the above results to evaluated the intermediate scattering function $\chi(\underline{\Delta}p,t)$ in terms of which neutron scattering experiments may be analyzed. For this purpose, note that Eq. (6.15) satisfies the condition

$$H\Lambda^{(2m+1)} = 0 \quad \text{for} \quad m \geq 1 \ ;$$

therefore $\chi(\underline{\Delta}p,t)$ may be obtained conveniently from Eq. (5.4) of Chapter V. Thus, after resorting to the canonical invariance of the Poisson

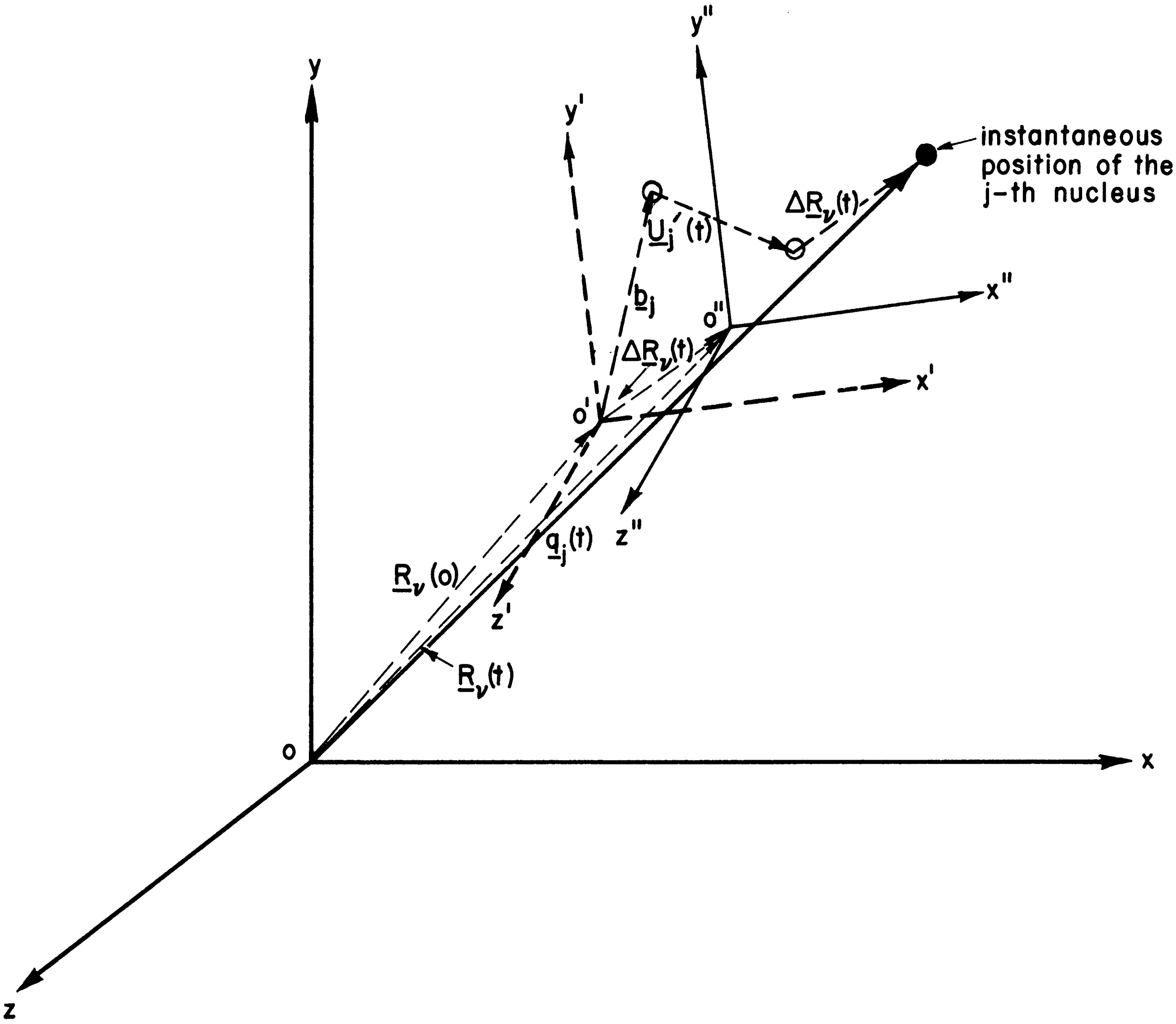

Fig. 5. Nuclear coordinates for a crystalline dislocation model of a monatomic liquid.

bracket, we get

$$\chi(\underline{\Delta p},t) = N^{-1} \sum_{i,j=1}^{N} < \exp\left[-\frac{i}{\hbar} \Delta\underline{p}\cdot(\underline{R}_{\mu}(0)+\underline{b}_i+\underline{u}_i'(0))\right] e^{\frac{\hbar}{2i}\Lambda}$$

$$\exp\left[\frac{i}{\hbar} \underline{\Delta p}\cdot(\underline{R}_{\nu}(t)+\underline{b}_j+\underline{u}_j'(t))\right] >_{TW} \tag{6.20}$$

or

$$\chi(\underline{\Delta p},t) = N^{-1} \sum_{i,j} \exp\left[\frac{i}{\hbar} \underline{\Delta p}\cdot(\underline{b}_j-\underline{b}_i)\right] < \exp\left[-\frac{i}{\hbar} \underline{\Delta p}\cdot\underline{R}_{\mu}(0)\right] e^{\frac{\hbar}{2i}\Lambda}$$

$$(x)\ \exp\left[\frac{i}{\hbar} \underline{\Delta p}\cdot\underline{R}_{\nu}(t)\right] >_{TW} < \exp\left[-\frac{i}{\hbar} \underline{\Delta p}\cdot\underline{u}_i'(0)\right] e^{\frac{\hbar}{2i}\Lambda} \tag{6.21}$$

$$(x)\ \exp\left[\frac{i}{\hbar} \underline{\Delta p}\cdot u_j'(t)\right] >_{TW} .$$

Direct Scattering.—In the case i=j, Eq. (6.21) yields

$$\chi_s(\underline{\Delta p},t) = \left< \exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot(\underline{P}_\nu + \frac{\underline{\Delta p}}{2})\frac{t}{M\alpha^3}\right]\right>_{TW} \left< \exp\left[-\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{u}_j'(0)\right] e^{\frac{\hbar}{2i}\Lambda} \exp\left[\frac{i}{\hbar}\underline{\Delta p}\cdot\underline{u}_j'(t)\right]\right>_{TW}$$

$$= \exp\left[-\frac{\Delta p^2}{2M\alpha^3\hbar^2\beta}(t^2 - i\hbar\beta t)\right] \left< \exp\left[\frac{\underline{\Delta p}}{2}\cdot\left(\sum_k \underline{a}_j^k \frac{\partial}{\partial C_k} + \sum_{k>k_c}\sum_i \underline{b}_{ji}^k \frac{\partial}{\partial D_{ki}}\right)\right]\right.$$

$$\left.(x)\ \exp\left\{\frac{i\underline{\Delta p}}{\hbar}\cdot\left[\sum_k \underline{a}_j^k (A_k(t) - A_k(0)) + \sum_{k>k_c}\sum_i \underline{b}_{ji}^k (B_{ki}(t) - B_{ki}(0))\right]\right\}\right>_{TW}$$

$$= \exp\left[-\frac{\Delta p^2}{2M\alpha^3\hbar^2\beta}(t^2 - i\beta\hbar t)\right] \left< \exp\left\{\sum_k \frac{i\underline{\Delta p}}{\hbar}\cdot\underline{a}_j^k\left[A_k(\cos\omega_{1k}t - 1) + (C_k + \frac{\underline{\Delta p}}{2}\cdot\underline{a}_j^k)\frac{\sin\omega_{1k}t}{M\omega_{1k}}\right]\right\}\right. \tag{6.22}$$

$$\left.(x)\ \exp\left\{\sum_{k>k_c}\sum_i \frac{i\underline{\Delta p}}{\hbar}\cdot\underline{b}_{ji}^k\left[B_{ki}(\cos\omega_{2ki}'t - 1) + (D_{ki} + \frac{\underline{\Delta p}}{2}\cdot\underline{b}_{ji}^k)\frac{\sin\omega_{2ki}'t}{M\omega_{2ki}'}\right]\right\}\right>_{TW}$$

$$= \exp\left[-\frac{\Delta p^2}{2M\alpha^3\beta\hbar^2}(t^2 - i\beta\hbar t)\right] \exp\left\{-\frac{1}{2M\hbar}\sum_k(\underline{\Delta p}\cdot\underline{a}_j^k)^2\frac{1}{\omega_{1k}}\left[(1-\cos\omega_{1k}t)\coth\left(\frac{\beta\hbar\omega_{1k}}{2}\right)\right.\right.$$

$$\left.\left. - i\sin\omega_{1k}t\right]\right\}(x)\ \exp\left\{-\frac{1}{2M\hbar}\sum_{k>k_c}\sum_i(\underline{\Delta p}\cdot\underline{b}_{ji}^k)^2\frac{1}{\omega_{2ki}'}\left[(1-\cos\omega_{2ki}'t)\coth\left(\frac{\beta\hbar\omega_{2ki}'}{2}\right) - i\sin\omega_{2ki}'t\right]\right\}.$$

Now, making the transformation $t \to t + \frac{i\beta\hbar}{2}$ gives

$$\chi_s(\underline{\Delta p}, t + \frac{i\beta\hbar}{2}) = \exp\left[-\frac{\beta\Delta p^2}{8M\alpha^3}\right] \exp\left[-\frac{\Delta p^2 t^2}{2M\alpha^3\beta\hbar^2}\right](x)\ \exp\left\{-\frac{1}{2M\hbar}\sum_k(\underline{\Delta p}\cdot\underline{a}_j^k)^2\frac{1}{\omega_{1k}}\left[\coth\left(\frac{\beta\hbar\omega_{1k}}{2}\right)\right.\right.$$

$$\left.\left. - \operatorname{csch}\left(\frac{\beta\hbar\omega_{1k}}{2}\right)\cos\omega_{1k}t\right]\right\}(x)\ \exp\left\{-\frac{1}{2M\hbar}\sum_{k>k_c}\sum_i(\underline{\Delta p}\cdot\underline{b}_{ji}^k)^2\frac{1}{\omega_{2ki}'}\left[\coth\left(\frac{\beta\hbar\omega_{2ki}'}{2}\right)\right.\right. \tag{6.23}$$

$$\left.\left. - \operatorname{csch}\left(\frac{\beta\hbar\omega_{2ki}'}{2}\right)\cos\omega_{2ki}'t\right]\right\}$$

or

$$\chi_s(\underline{\Delta p}, t + \frac{i\beta\hbar}{2}) = \exp\left[-\frac{\beta\Delta p^2}{8M\alpha^3}\right] \exp\left[-2W'\right] \exp\left[-\frac{\Delta p^2 t^2}{2M\alpha^3\beta\hbar^2}\right]$$

$$(x) \exp\left\{\frac{1}{2M\hbar}\left[\sum_k (\underline{\Delta p}\cdot\underline{a}_j^k)^2 \frac{1}{\omega_{1k}} \operatorname{csch}\left(\frac{\beta\hbar\omega_{1k}}{2}\right) \cos\omega_{1k}t \right.\right. \tag{6.24}$$

$$\left.\left. + \sum_{k>k_c}\sum_i (\underline{\Delta p}\cdot\underline{b}_{ji}^k)^2 \frac{1}{\omega'_{2ki}} \operatorname{csch}\left(\frac{\beta\hbar\omega'_{2ki}}{2}\right) \cos\omega'_{2ki}t\right]\right\}$$

where

$$\exp\left[-2W'\right] = \exp\left\{-\frac{1}{2M\hbar}\left[\sum_k (\underline{\Delta p}\cdot\underline{a}_j^k)^2 \frac{\coth}{\omega_{1k}}\left(\frac{\beta\hbar\omega_{1k}}{2}\right)\right.\right. \tag{6.25}$$

$$\left.\left. + \sum_{k>k_c}\sum_i (\underline{\Delta p}\cdot\underline{b}_{ji}^k)^2 \frac{\coth}{\omega'_{2ki}}\left(\frac{\beta\hbar\omega'_{2ki}}{2}\right)\right]\right\}$$

is the well-known Debye-Waller factor.

In order to obtain a normalization condition for the amplitude vectors, use is made of the Placzek moments introduced in Chapter III; these may be expressed in terms of $\chi_s(\underline{\Delta p}, \hbar\tau + \frac{i\beta\hbar}{2})$ by writing Eq. (3.41) as

$$\overline{\epsilon_s^n} = (-i)^n \frac{d^n}{d\tau^n} \chi_s(\underline{\Delta p}, \hbar\tau + \frac{i\beta\hbar}{2}\Big|_{\tau=-\frac{i\beta}{2}} . \tag{6.26}$$

Thus, Eqs. (6.24) and (6.26), yield

$$\overline{\epsilon_s^1} = \frac{\Delta p^2}{2M} = \left\{\frac{\Delta p^2}{2M\alpha^3} + \frac{1}{2M}\left[\sum_k (\underline{\Delta p}\cdot\underline{a}_j^k)^2 + \sum_{k>k_c}\sum_i (\underline{\Delta p}\cdot\underline{b}_{ji}^k)^2\right]\right\}$$

or

$$\Delta p^2 \xi = \sum_k (\underline{\Delta p}\cdot\underline{a}_j^k)^2 + \sum_{k>k_c}\sum_i (\underline{\Delta p}\cdot\underline{b}_{ji}^k)^2 \tag{6.27}$$

where

$$\xi = (1 - \frac{1}{\alpha^3}) . \tag{6.28}$$

For an isotropic medium the direction of $\underline{\Delta p}$ may be fixed arbitrarily, in which case

$$\xi = \frac{1}{3}\left[\sum_{k} (\underline{a}_j^k)^2 + \sum_{k>k_c} \sum_{i} (\underline{b}_{ji}^k)^2\right]. \qquad (6.29)$$

Also, explicit use of isotropy in Eq. (6.24) yields

$$\ell n\, \chi_s(\underline{\Delta p}, t + \frac{i\beta\hbar}{2}) = -2W'_\sigma - \frac{\beta\Delta p^2}{8M\alpha^3} - \frac{\Delta p^2 t^2}{2M\alpha^3\beta\hbar^2} + \frac{\Delta p^2}{2M\hbar}\left[\sum_{k} (\underline{a}_{j\sigma}^k)^2 f_1(\omega_{1k}, T, t) + \sum_{k>k_c} \sum_{i} (\underline{b}_{ji\sigma}^k)^2 f_2(\omega'_{2ki}, T, t)\right] \qquad (6.30)$$

where W'_σ is the Debye-Waller factor for $\underline{\Delta p}$ chosen along the x, y, or z-axis ($\sigma = 1,2,3$), and $f_1(\omega_{1k},T,t)$ and $f_2(\omega'_{2ki},T,t)$ are self-defined by comparison with Eq. (6.24).

Hence,

$$3\ell n\, \chi_s(\underline{\Delta p}, t + \frac{i\beta\hbar}{2}) = -2\sum_{\sigma} W'_\sigma - 3\underline{\Delta p}^2\left(\frac{\beta}{8M\alpha^3} + \frac{t^2}{2M\alpha^3\beta\hbar^2}\right) + \frac{\Delta p^2}{2M\hbar}\sum_{\sigma} (x) \left[\sum_{k} (\underline{a}_{j\sigma}^k)^2 f_1 + \sum_{k>k_c} \sum_{i} (\underline{b}_{ji\sigma}^k)^2 f_2\right]$$

or

$$\chi_s(\underline{\Delta p}, t + \frac{i\beta\hbar}{2}) = \exp\left[-\frac{2}{3}\sum_{\sigma} W'_\sigma\right] \exp\left[-\frac{\beta\Delta p^2}{8M\alpha^3}\right] \exp\left[-\frac{\Delta p^2 t^2}{2M\alpha^3\beta\hbar^2}\right] (x) \exp\left\{\frac{\Delta p^2}{6M\hbar}\left[\sum_{k} (\underline{a}_j^k)^2 f_1 + \sum_{k>k_c} \sum_{i} (\underline{b}_{ji}^k)^2 f_2\right]\right\}. \qquad (6.31)$$

In accordance with Eq. (6.29), the quantities $\frac{1}{3\xi}(\underline{a}_j^k)^2$ and $\frac{1}{3\xi}(\underline{b}_{ji}^k)^2$ can be interpreted as the probabilities associated with eigenfrequencies ω_{1k} and ω_{2ki} respectively, so that

$$\sum_{k} \frac{(a_j^k)^2}{3\xi} f_1(\omega_{1k},T,t) + \sum_{k>k_c} \sum_{i} \frac{(b_{ji}^k)^2}{3\xi} f_2(\omega'_{2ki},T,t) \tag{6.32}$$

represents an average over a discrete spectrum of frequencies.

If, for the sake of simplicity, the frequency spectrum is approximated by a continuous one of the Debye type, Eq. (6.32) can be replaced by

$$\int_0^{\omega_D} \phi_L(\omega_{1k}) f_1(\omega_{1k},T,t)\, d\omega_{1k} + \sum_i \int_{\omega_C}^{\omega_D} \phi_T(\omega_{2ki}) f_2(\omega'_{2ki},T,t)\, d\omega_{2ki} \tag{6.33}$$

where ω_D = the Debye cutoff frequency

$$\phi_L(\omega_{1k}) = \frac{\omega_{1k}^2}{\omega_D^3} , \tag{6.34}$$

and

$$\phi_T(\omega_{2ki}) = [1 - (\omega_C/\omega_D)^2]^{-1} \frac{\omega_{2ki}^2}{\omega_D^3} = \xi^{-1} \frac{\omega_{2ki}^2}{\omega_D^3} . \tag{6.35}$$

Thus Eq. (6.31) becomes

$$\chi_s(\underline{\Delta}p, \hbar\tau + \frac{i\beta\hbar}{2}) = \exp[-2W] \exp\left[-\frac{\beta\Delta p^2}{8M\alpha^3}\right] \exp[-\Delta p^2 \mathcal{W}(\tau)] \tag{6.36}$$

where

$$2W = \frac{\xi\Delta p^2}{2M\hbar\omega_D}\left[\frac{1}{\omega_D^2}\int_0^{\omega_D} \omega \coth\left(\frac{\beta\hbar\omega}{2}\right) d\omega + \frac{2\xi^{-1}e^{\gamma x^2/2}}{\omega_D^2}\int_{\omega_C}^{\omega_D} \omega \coth\left(\frac{\beta\hbar\omega}{2} e^{-\frac{\gamma x^2}{2}}\right) d\omega\right] \tag{6.37}$$

and

$$\mathcal{W}(\tau) = \frac{\tau^2}{2M\alpha^3\beta} - \frac{\xi}{2M\hbar}\left[\frac{1}{\omega_D^3}\int_0^{\omega_D} \omega \operatorname{csch}\left(\frac{\beta\hbar\omega}{2}\right) \cos(\omega\hbar\tau)\, d\omega + \frac{2\xi^{-1}e^{\gamma x^2/2}}{\omega_D^3}\int_{\omega_C}^{\omega_D} \omega \operatorname{csch}\left(\frac{\beta\hbar\omega}{2} e^{-\frac{\gamma x^2}{2}}\right) \cos(\omega e^{-\frac{\gamma x^2}{2}} \hbar\tau)\, d\omega\right] . \tag{6.38}$$

Observe that for an ideally perfect crystal $\alpha \to \infty$ and

$$\lim_{\alpha\to\infty} w(\tau) = -\frac{3}{2M\hbar\omega_D^3}\int_0^{\omega_D} \omega \operatorname{csch}\left(\frac{\beta\hbar\omega}{2}\right)\cos(\omega\hbar\tau)\,d\omega \tag{6.39}$$

6.4 THE DIRECT SCATTERING FUNCTION

Making use of Eq. (6.36), together with Eqs. (3.20) and (3.27), yields

$$S_s(\underline{\Delta}p,\epsilon) = \frac{1}{2\pi} e^{\beta\epsilon/2} e^{-2W} \exp\left[-\frac{\beta\Delta p^2}{8M\alpha^3}\right]\int_{-\infty}^{\infty} e^{-i\epsilon\tau} e^{-\Delta p^2 w(\tau)}\,d\tau. \tag{6.40}$$

In order to perform the Fourier transformation in Eq. (6.40) we introduce the following expansion:[53]

$$\int_{-\infty}^{\infty} e^{-i\epsilon\tau}\, e^{-\Delta p^2 w(\tau)}\,d\tau = \int_{-\infty}^{\infty} e^{-i\epsilon\tau} \exp\left[-\frac{\Delta p^2\tau^2}{2M\alpha^3\beta}\right]\left[1+\Delta p^2\eta(\tau)+\frac{\Delta p^4}{2}\eta^2(\tau)+\ldots\right]d\tau \tag{6.41}$$

in which

$$\eta(\tau) = \frac{\tau^2}{2M\alpha^3\beta} - w(\tau) . \tag{6.42}$$

Defining a new quantity,

$$\mu_n(\epsilon) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\epsilon\tau} e^{-Q\tau^2}\left[\frac{\eta(\tau)}{\eta(0)}\right]^n d\tau \tag{6.43}$$

where

$$Q \equiv \frac{\Delta p^2}{2M\alpha^3\beta} \tag{6.44}$$

and expanding $\eta(\tau)/\eta(0)$ in a power series in τ whose convergence is guaranteed by the conditions

$$|\eta(\tau)| \leq |\eta(0)| \tag{6.45}$$

and

$$\lim_{\tau\to\infty} \eta(\tau) = \lim_{\tau\to\infty} \frac{\xi}{2M\hbar\omega_D}\left[\frac{1}{\omega_D^2}\int_0^{\omega_D} \omega\left(\frac{2}{\beta\hbar\omega} - \frac{\beta\hbar\omega}{12} + \cdots\right)\cos(\omega\hbar\tau)\,d\omega \right.$$
$$\left. + \frac{2\xi^{-1}e^{\gamma x^2/2}}{\omega_D^2}\int_{\omega_C}^{\omega_D} \omega\left(\frac{2e^{\gamma x^2/2}}{\beta\hbar\omega} - \frac{\beta\hbar\omega}{12}e^{-\frac{\gamma x^2}{2}} + \cdots\right)\cos\left(\hbar\omega e^{-\frac{\gamma x^2}{2}}\tau\right)d\omega\right]$$

i.e.,

$$\lim_{\tau\to\infty} \eta(\tau) = \mathcal{O}(\tau^{-1}) \tag{6.46}$$

we get

$$\mu_n(\epsilon) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\epsilon\tau}\, e^{-Q\tau^2} \exp\left[n\,\ell n\left(\frac{\eta(\tau)}{\eta(0)}\right)\right]d\tau$$
$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\epsilon\tau}\, e^{-Q\tau^2} \exp\left[n\sum_{j=0}^{\infty}\frac{\lambda_j}{j!}(i\tau)^j\right]d\tau \quad . \tag{6.47}$$

The expansion coefficients λ_j may be determined from

$$\lambda_j = (-i)^j \frac{d^j}{d\tau^j}\,\ell n\left[\frac{\eta(\tau)}{\eta(0)}\right]\Bigg|_{\tau=0} \tag{6.48}$$

in particular

$$\lambda_0 = 0 \quad \text{and } \lambda_{2j+1} = 0 \quad \text{for} \quad j = 0,1,2,\ldots.$$

Modifying (6.47) to read

$$\mu_n(\epsilon) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp\left[-i\epsilon\tau' - n(\lambda_2 + \frac{2Q}{n})\frac{\tau'^2}{2}\right] \exp\left[n\sum_{j=3}^{\infty}\frac{\lambda_j}{j!}(i\tau')^j\right]d\tau' \tag{6.49}$$

and making the transformation

$$\tau'\sqrt{\eta(\lambda_2 + \frac{2Q}{n})} = -\tau$$

results in

$$\mu_n(\epsilon) = \frac{1}{2\pi\sqrt{n(\lambda_2 + \frac{2Q}{n})}} \int_{-\infty}^{\infty} \exp\left[-\frac{\tau^2}{2} + \frac{i\epsilon\tau}{\sqrt{n(\lambda_2 + \frac{2Q}{n})}}\right] \exp\left[n \sum_{j=3}^{\infty} \frac{\lambda_j}{j!}\right.$$

$$\left.(x)\left(-\frac{i\tau}{\sqrt{n(\lambda_2 + \frac{2Q}{n})}}\right)^j\right] d\tau \ . \qquad (6.50)$$

Now expanding the second exponential in (6.50) in powers of $i\tau$ leads to

$$\mu_n(\epsilon) = \frac{1}{2\pi\sqrt{n(\lambda_2 + \frac{2Q}{n})}} \sum_{j=0}^{\infty} C_j^{(n)} \int_{-\infty}^{\infty} (i\tau)^j \exp\left[-\frac{\tau^2}{2} + \frac{i\epsilon\tau}{\sqrt{n(\lambda_2 + \frac{2Q}{n})}}\right] d\tau \qquad (6.51)$$

where the coefficients $C_j^{(n)}$ are given by

$$C_j^{(n)} = (-i)^j \frac{1}{j!} \frac{d^j}{d\tau^j} \left\{\exp\left[n \sum_{\ell=3}^{\infty} \frac{\lambda_\ell}{\ell!} \left(-\frac{i\tau}{\sqrt{n(\lambda_2 + \frac{2Q}{n})}}\right)^\ell\right]\right\}\Bigg|_{\tau=0} \qquad (6.52$$

and are nonvanishing only for even values of j. Moreover, noting that

$$\int_{-\infty}^{\infty} (i\tau)^j \exp\left[-\frac{\tau^2}{2} + \frac{i\epsilon\tau}{\sqrt{n(\lambda_2 + \frac{2Q}{n})}}\right] d\tau = \frac{d^j}{dy^j} \int_{-\infty}^{\infty} \exp\left[-\frac{\tau^2}{2} + iy\tau\right] d\tau$$

$$= \sqrt{2}\, \frac{d^j}{dy^j} \left[e^{-\frac{y^2}{2}} \int_{-\infty-(iy/\sqrt{2})}^{\infty-(iy/\sqrt{2})} e^{-\tau^2} d\tau\right] \qquad (6.53)$$

$$= \sqrt{2\pi}\, \frac{d^j}{dy^j}\, e^{-y^2/2}$$

where

$$y = \frac{\epsilon}{\sqrt{n(\lambda_2 + \frac{2Q}{n})}} \ ,$$

substituting into (6.51), and using the definition equation for the Hermite polynomials

$$H_j(y) = (-1)^j e^{y^2} \frac{d^j}{dy^j} e^{-y^2} \tag{6.54}$$

gives

$$\mu_n(\epsilon) = \frac{1}{\sqrt{2\pi n(\lambda_2 + \frac{2Q}{n})}} \exp\left[-\frac{\epsilon^2}{(n\lambda_2+2Q)}\right] \sum_{j=0}^{\infty} C_j^{(n)} (-1)^j H_j\left(\frac{\epsilon}{\sqrt{n(\lambda_2 + \frac{2Q}{n})}}\right). \tag{6.55}$$

Finally, inserting this expression into Eqs. (6.40) and (6.41) results in

$$S_s(\underline{\Delta}p,\epsilon) = e^{\beta\epsilon/2} e^{-2W} \exp\left[-\frac{\beta\Delta p^2}{8M\alpha^3}\right] \sum_{n=0}^{\infty} \left[\frac{\eta(0)}{\mathcal{E}_w}\right]^n \frac{(2W)^n}{n!} \mu_n(\epsilon) \tag{6.56}$$

where

$$\mathcal{E}_w = \frac{2W}{\Delta p^2} .$$

6.5 THE WIDTH OF INTERMEDIATE SCATTERING FUNCTION

As may be seen from Eq. (6.36), all the essential features of the model under consideration are contained in the width function

$$\Omega(\tau) = \frac{2W}{\Delta p^2} + \frac{\beta}{8M\alpha^3} + \mathcal{W}(\tau) , \tag{6.57}$$

therefore it is of interest to calculate this quantity. For this purpose, making use of the fact that for ordinary temperatures

$$\beta^2\hbar^2\omega^2 \leq \beta^2\hbar^2\omega_D{}^2 \ll 1 ,$$

and making use of the expansion

$$\coth\left(\frac{\beta\hbar\omega}{2}\right) = \frac{2}{\beta\hbar\omega} + \frac{\beta\hbar\omega}{6} - \frac{(\beta\hbar\omega)^3}{360} + \ldots. \tag{6.58}$$

the integrals in (6.37) and (6.38) may be approximated by

$$\frac{1}{\omega_D^2}\int_0^{\omega_D} \omega \coth\left(\frac{\beta\hbar\omega}{2}\right) d\omega \simeq \frac{2}{\beta\hbar\omega_D} = \frac{2T}{\theta_D}, \tag{6.59}$$

$$\frac{1}{\omega_D^2}\int_{\omega_C}^{\omega_D} \omega \coth\left(\frac{\beta\hbar\omega}{2} e^{-(\gamma x^2/2)}\right) d\omega \simeq 2\left(\frac{T}{\omega_D}\right)\left(1 - \frac{\omega_C}{\omega_D}\right)e^{\gamma x^2/2} \tag{6.60}$$

$$\int_0^{\omega_D} \omega \operatorname{csch}\left(\frac{\beta\hbar\omega}{2}\right) \cos(\omega\hbar\tau)\, d\omega \simeq \frac{2}{\beta\hbar^2\tau} \sin(\omega_D\hbar\tau), \tag{6.61}$$

and

$$\int_{\omega_C}^{\omega_D} \omega \operatorname{csch}\left(\frac{\beta\hbar\omega}{2} e^{-(\gamma x^2/2)}\right) \cos\left(\hbar\omega\tau\, e^{-(\gamma x^2/2)}\right) d\omega$$
$$\simeq \frac{2e^{\gamma x^2}}{\beta\hbar^2\tau}\left[\sin\left(\hbar\omega_D\tau e^{-(\gamma x^2/2)}\right) - \sin\left(\hbar\omega_C\tau e^{-(\gamma x^2/2)}\right)\right]. \tag{6.62}$$

Hence,

$$\Omega(\tau) \simeq \frac{1}{2M\alpha^3}\left(\frac{\beta}{4} + \frac{\tau^2}{\beta}\right) + \frac{\xi}{M\hbar\omega_D}\left(\frac{T}{\theta_D}\right)\left[1 + 2\xi^{-1}e^{\gamma x^2}\left(1 - \frac{\omega_C}{\omega_D}\right)\right]$$
$$- \frac{\xi \sin(\hbar\omega_D\tau)}{M\hbar^3\omega_D^3\beta\tau} - \frac{2e^{\frac{3}{2}\gamma x^2}}{\beta M\hbar^3\omega_D^3\tau}\left[\sin\left(\hbar\omega_D\tau e^{-(\gamma x^2/2)}\right) - \sin\left(h\omega_C\tau e^{-(\gamma x^2/2)}\right)\right] \tag{6.63}$$

Further progress in the evaluation of $\Omega(\tau)$ requires, however, the knowledge of the quantities α and γ. These may be obtained from the ratio of the specific partition function Z_α, corresponding to a configuration group with average mesh size αa, to the partition function Z_0 for a perfect crystal ($\alpha \to \infty$). According to Ookawa this is given by

$$\frac{1}{N}\ln\left(\frac{Z_\alpha}{Z_0}\right) = \left(\gamma - \frac{\Theta}{T}\right)\alpha^{-2} + \ln\left(\frac{\pi}{3}\frac{\Theta}{T}\alpha\right)\alpha^{-3} - \gamma\alpha^{-5} \tag{6.64}$$

where the temperature Θ is defined by

$$k_B\Theta = \frac{3}{2}\mu v_o = \frac{3}{2} M v_t^2 \qquad (6.65)$$

and μ_1, v_o, and v_t are the rigidity, the atomic volume, and the propagation velocity of transversal waves respectively.

The most probable value of α for a given temperature is determined by

$$\ell n \frac{\pi}{3} - \frac{1}{3} + \ell n\, \alpha_P - \frac{5}{3}\gamma\alpha_P^{-2} = -\ell n \frac{\Theta}{T} + \frac{2}{3}\left(\frac{\Theta}{T} - \gamma\right)\alpha_P \qquad (6.66)$$

which follows immediately from maximizing (6.64). Moreover, assuming that the solid can be represented by the limiting case of infinite mesh size, we have that $Z_\alpha = Z_o$ at the temperature of melting. In this case, Eqs. (6.64) and (6.66) may be solved simultaneously for α_P and γ.

Critical Frequency.--This may be obtained, in terms of α and the Debye frequency, from the condition that the number of degenerated translational modes must be equal to twice the number of crystallites, i.e.,

$$6N \int_0^{\omega_C} \frac{\omega^2}{\omega_D^3}\, d\omega = \frac{2N}{\alpha^3},$$

or

$$\omega_C = \frac{\omega_D}{\alpha}. \qquad (6.67)$$

6.6 CALCULATIONS FOR LIQUID LEAD

The preceding formulae have been applied to the evaluation of the width function $\Omega(\tau)$ for liquid lead at T = 620°K. The parameters used in this calculation are given in Table I, and the results obtained are shown in Fig. 6 together with the widths for a Debye lattice; the Rahman, Singwi and Sjölander model;[20] and the width derived from the experimental

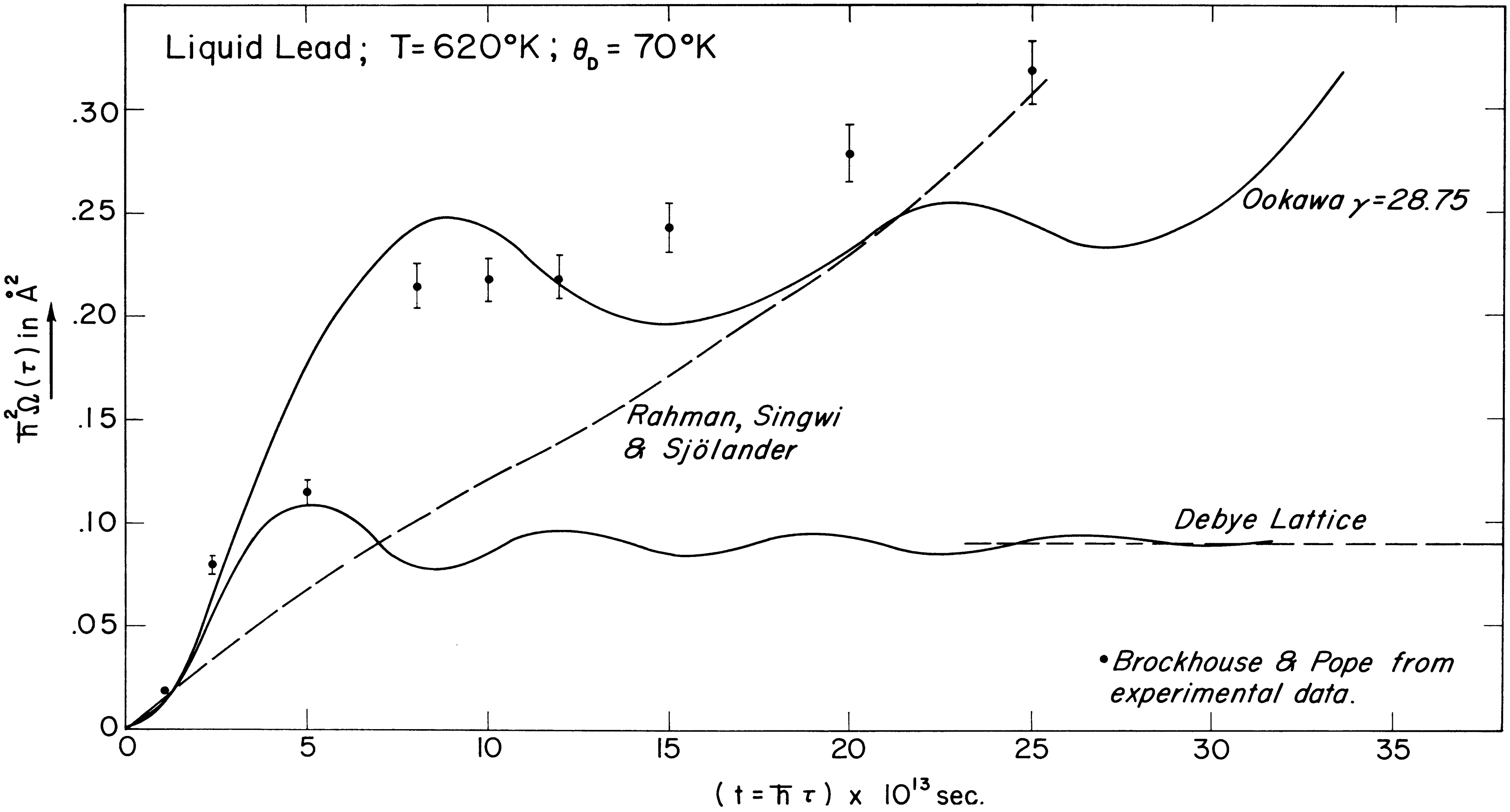

Fig. 6. Comparison of the width function $\Omega(\tau)$ of the direct intermediate scattering function for liquid lead obtained according to Ookawa's model; the Rahman, Singwi and Sjölander's stochastic model; and that obtained by Brockhouse and Pope from their experimental data.

data of Brockhouse and Pope.[21]

TABLE I

CALCULATION PARAMETERS FOR LIQUID LEAD

T	620°K
v_t (Ref. 54)	7 x 10^4 cm/sec
Θ°K	1.831 x 10^4
γ calc.	29.78
γ to fit data	28.75
$\hbar\omega_D$ (Ref. 55)	9.65 x 10^{-15} erg
α	5.1
$\hbar\omega_C$	1.89 x 10^{-15} erg

It is interesting to note the following:

1. The values for γ required to obtain agreement with the Brockhouse and Pope points are close (~3.5%) to the value predicted by the theory.

2. In contrast to the model postulated by Rahman, Singwi and Sjölander, that postulated by Ookawa contains only one adjustable parameter; however, the approximate value of this parameter is fixed by the theory. Thus, a comparison with experimentation constitutes a true test of the model. Since Ookawa's model postulates a Hamiltonian rather than an expression for the velocity correlation, the contribution of interference scattering to the cross section can be calculated for it, whereas it cannot be calculated for the model of Rahman, et al.

3. The increase in the width function $\hbar^2\Omega(\tau)$ without limit as time increases is in sharp contrast to the width for a Debye lattice, which becomes asymptotic to the Debye-Waller factor; this indicates that the atomic motion is not always confined to a well localized vicinity (see Section 3.2 of Chapter III).

4. The asymptotic behavior of the width is essentially different from that corresponding to a diffusive-type motion. In the latter case the asymptotic rise of $\Omega(\tau)$ would be linear in time, while according to the present model it grows parabolically.

5. Since in the presently available experimental data for lead the interaction times are of the order of 10^{-13} seconds whereas the interaction times required for observing the full effect of the above mentioned asymptotic behavior are of the order of 10^{-12} seconds, experiments with colder neutrons (~8Å) are desirable. In particular, it seems plausible that the translational type of motion described by Ookawa's model may be predominant at temperatures just above melting, while the diffusion of individual atoms would become more important with increase of temperature. Evidence in this direction could be obtained by performing the above suggested experiments at various temperatures of the scatterer.

6. It should be observed at this point that due to the uncertainty in the errors introduced by a Fourier analysis of the experimental data, as well as errors that may result from the use of the Gaussian approximation, the agreement between the theory and the Brockhouse and Pope

points should be corroborated by a sounder approach consisting of a direct comparison of the theoretical and experimental cross sections.

6.7 THERMODYNAMICAL FUNCTIONS

An additional check on the model proposed is provided by a comparison of the experimental and calculated values for the entropy of melting. To this end, note that the excess free energy per atom in the liquid state relative to that in the solid state is given by

$$\Delta f = -\frac{k_B T}{N} \ln \frac{Z_\alpha}{Z_0} , \tag{6.68}$$

and that substitution of Eq. (6.64) into this expression results in

$$\Delta f = -k_B T \left[\left(\gamma - \frac{\Theta}{T}\right)\alpha^{-2} + \ln\left(\frac{\pi}{3}\frac{\Theta}{T}\alpha\right)\alpha^{-3} - \gamma\alpha^{-5} \right] . \tag{6.69}$$

Furthermore, for an isobaric process, the thermodynamic identity[52]

$$dh = Tds + vdp \tag{6.70}$$

yields

$$\Delta s(T_m) = \frac{\Delta h(T_m)}{T_m} \tag{6.71}$$

where $\Delta h(T_m)$ is the enthalpy of melting. In terms of the excess free energy, the latter is given by

$$\Delta h = \left[\frac{\partial(\Delta f/T)}{\partial(1/T)}\right]_p = -T^2 \left[\frac{\partial}{\partial T}(\Delta f/T)\right]_p$$
$$= k_B T\left(\alpha^{-2}\frac{\Theta}{T} - \alpha^{-3}\right) = \frac{3}{2}\mu v_0 \alpha^{-2} - k_B T \alpha^{-3} \quad . \tag{6.72}$$

The first term in the right side of the above equation can be identified with the configurational excess energy U_0, while the second term represents the energy deficit due to degeneration into translation of $2N/\alpha^3$ vibrational degrees of freedom.

From Eqs. (6.71) and (6.72) it follows that

$$\Delta s(T_m) = k_B\left(\alpha_m^{-2}\frac{\Theta}{T_m} - \alpha_m^{-3}\right) \quad . \tag{6.73}$$

Inserting the experimental value for the entropy of melting[56] [$\Delta s(T_m)/k_B = 0.95$] into Eq. (6.73) yields a value for $\alpha_m = 5.65$. Substituting this value in Eq. (6.64) and noting that for $T = T_m$

$$(Z_\alpha/Z_0)_{T_m} = 1$$

results in $\gamma = 29.8$ as compared with the value 29.78 predicted by the theory.

As a final illustration of some of the features of the model, the relative thermodynamic probabilities [Eq. (6.64)] for liquid lead have been plotted versus α for $\gamma = 29.78$ and several temperatures (see Fig. 7). It is interesting to note that for $T > T_m$, the curves go through a maximum corresponding to a value Z_α greater than Z_0, thus stabilizing the imperfect crystal as representative of the liquid phase. For $T=T_m$, the maximum occurs when $Z_\alpha = Z_0$; i.e., the imperfect crystal with most probable mesh size α_m is in equilibrium with the perfect crystal of infinite mesh size and is separated from it by an intervening minimum of

Z_α, thereby representing a first-order-type transition (see inset in Fig. 7).

For $T < T_m$, Z_α converges monotonically to Z_o, stabilizing the perfect crystal as representative of the solid phase.

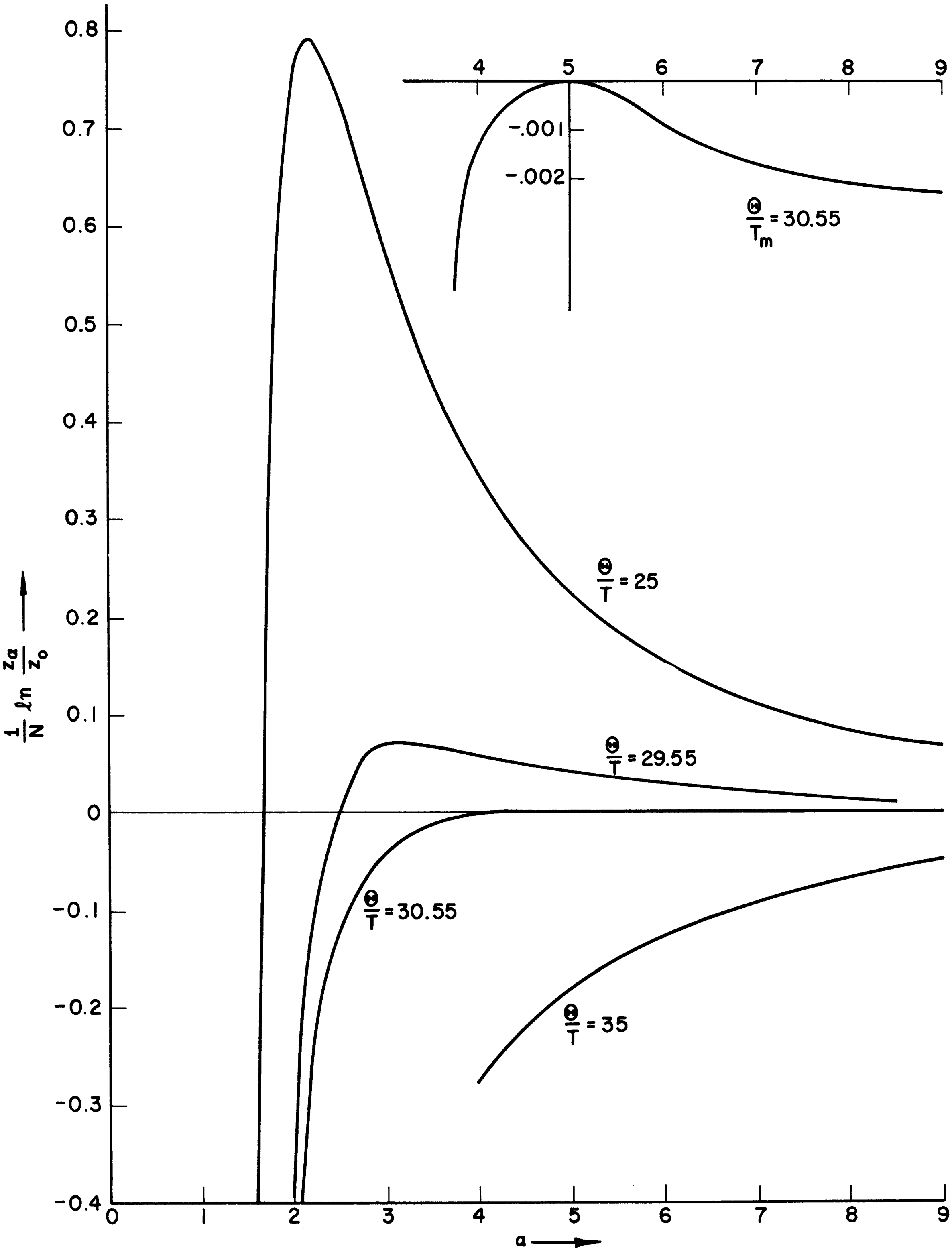

Fig. 7. Relative specific partition function versus mesh size α, for lead at temperatures below, at, and above melting point and γ = 29.78.

CHAPTER VII

SUMMARY AND CONCLUDING REMARKS

The isomorphism between the Weyl-Wigner quasi-probability distributional formulation and the von Neumann density matrix formulation of quantum mechanics has been derived solely on the basis of an extension of the Fourier integral theorem to quantum mechanical functions of the position and momentum operators. The derivation, which encompasses the results of various authors, is felt to be somewhat simpler and more self contained. A generalization to Heisenberg operators is also presented.

The utility of this particular formulation in the discussion of a variety of problems in equilibrium and non-equilibrium statistical mechanics has been established by various authors.[10] In the present work, it has been applied to the Van Hove formulism of neutron scattering, leading to extremely interesting results. For quasi-classical systems it has been found that, to first order in $\hbar$, the incoherent component of the differential scattering cross section may be given, essentially, as a four dimensional Fourier transform of the classical time displaced self-correlation function $G_s^c(\underline{r},t)$. The correction terms of $\mathcal{O}(\hbar^2)$ have been obtained explicitly and are seen to be small for systems at ordinary temperatures.

In addition, this analysis was found convenient for deriving and investigating the implications of other existing semi-empirical prescriptions which attempt to relate the cross section to $G_s^c(\underline{r},t)$. In particular, it was shown that the Egelstaff-Schofield y^2 approximation is valid only for small times. Also, a numerical comparison for some simple systems, between the results obtained here and the so-called Vineyard approximation, indicated significant differences. These differences were found to increase with increasing energy of the incident neutrons. A similar relation between the coherent cross section and the distinct classical time displaced correlation $G_d^c(\underline{r},t)$ does not appear to exist. The reason is that the essential singularity occurring in the expression for χ_S is only apparent; thus, an asymptotic expansion in powers of $\hbar$ is possible. For χ_D, however, the essential singularity may not be removed, preventing a similar asymptotic expansion in this case. It is felt that this limitation is not too strong; it may be possible for some systems to separate the coherent from the incoherent cross section by means of either isotopic substitution which alters the relative amounts of these components, or by making use of a law of corresponding states as suggested by Vineyard.[63,64] Further investigation along these lines undoubtedly deserves special attention.

A separation of the incoherent part from the total cross section, together with a Fourier inversion of the experimental data for liquids, would yield $G_s^c(\underline{r},t)$ and, in Brockhouse's words, "a moving picture of the motions of the atoms in the system."

The controversial accuracy of the inversion procedure suggests another approach based on the probabilistic interpretation of $G_s^c(\underline{r},t)$. The connection of the latter with the incoherent part of the cross section may be used for comparing calculations based on specific dynamical models of the liquid state with scattering data. In fact, for certain statistical models (such as Frenkel's) the only possibility for comparison with experimental scattering data is through the use of the quasi-classical formulism here presented.

Other approaches, consisting of the reduction of the physical many-body Hamiltonian to a sum of single-body Hamiltonians, do not require the introduction of correlation functions. For some of these models, in which combinations of harmonic and free-gas type motions appear, the use of a Wigner representation is particularly convenient and leads to closed expressions for the cross section.

As an illustration, the method has been applied to a crystalline dislocation model for a monatomic liquid. In this model, originally proposed by Ookawa, the thermal agitation of the molecules is represented as a superposition of longitudinal waves plus shear waves that lead to either translational or vibrational modes, depending upon the wavelength. The Hamiltonian was derived in a less intuitive manner than Ookawa's and was found to reduce to a combination of ideal gas and harmonic oscillator Hamiltonians. The parameters entering the Hamiltonian were determined from thermodynamical considerations and the incoherent components of the intermediate and scattering functions were calculated. A comparison was made of the width of $\chi_s(\underline{\Delta}p,t)$ obtained according to this model with both Brockhouse's results for lead and with the width evaluated from Rahman, Singwi and Sjölander's stochastic model. For small times, the agreement of Ookawa's model with Brockhouse's results was found to be better than that predicted by the Rahman, et al., model. In fact, the Ookawa model gave reasonably good agreement over the entire experimental range. The predicted long time behavior was parabolic, differing, thus, from that for a Lagevin-type diffusion model. As suggested in Chapter VI, it seems plausible that the type of translational degree of freedom introduced in Ookawa's model would predominate in liquids just above the melting point and that a diffusive-type motion would become increasingly important with the increase of temperature above fusion. It was suggested that further experiments with colder neutrons (∼8Å) at various scatterer temperatures would be desirable in order to investigate whether this is true.

The possibility of relating the cross section, through $G_s^c(\underline{r},t)$, to other transport properties appears suggestive and of considerable interest for further work. Finally, the establishment of the relationship between the cross section and $G_s^c(\underline{r},t)$ may make possible an additional experimental investigation of the validity of certain calculations of classical non-equilibrium statistical mechanics.

APPENDIX A

ORTHONORMALITY OF THE SET OF OPERATORS[40] $\left\{(1/2\pi\hbar)^{3/2} \exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]\right\}$ AND GENERALIZATION OF THE FOURIER INTEGRAL TO FUNCTIONS OF OPERATORS

ORTHONORMALITY

We prove first the following identity[57]

$$e^{\alpha(A+B)} = e^{\alpha B} e^{\alpha A} \Gamma(\alpha) \tag{A.1}$$

where $\Gamma(\alpha)$ is defined by the differential equation

$$\frac{\partial\Gamma(\alpha)}{\partial\alpha} = e^{-\alpha A} \sum_{n=1}^{\infty} \frac{(-1)^n \alpha^n}{n!} [B,A]_n \, e^{\alpha A} \Gamma(\alpha) \tag{A.2}$$

and the initial condition

$$\Gamma(\alpha=0) = 1 \,. \tag{A.3}$$

To this end, consider the function

$$\psi = e^{\alpha(A+B)} \psi_o \tag{A.4}$$

where $\psi_o = \psi(\alpha=0)$ and the operators A,B are independent of α. Setting

$$\psi = e^{\alpha B} \phi \,, \tag{A.5}$$

and differentiating (A.4) and (A.5) with respect to α gives

$$\frac{\partial\psi}{\partial\alpha} = (A+B)\psi = B\psi + e^{\alpha B} \frac{\partial\phi}{\partial\alpha} \,,$$

or

$$\frac{\partial\phi}{\partial\alpha} = e^{-\alpha B}Ae^{\alpha B}\phi = A\phi + \sum_{n=1} \frac{(-1)^n\alpha^n}{n!} [B,A]_n\phi \ . \qquad (A.6)$$

Letting

$$\phi = e^{\alpha A}\,\Gamma(\alpha)\psi_o \qquad (A.7)$$

and combining (A.4), (A.5), and (A.7) yields Eq. (A.1). Equations (A.2) and (A.3) follow readily from substituting (A.7) into (A.6) and from setting α=0 in (A.7) and (A.5), respectively. Q.E.D.

For the case that A and B each commute with the commutator [A,B], Eq. (A.2) simplifies to

$$\frac{\partial\Gamma}{\partial\alpha} = -\alpha\,[B,A]\Gamma$$

or

$$\Gamma = \exp\left\{-\frac{\alpha^2}{2}[B,A]\right\}\Gamma(\alpha{=}0) = \exp\left\{-\frac{\alpha^2}{2}[B,A]\right\},$$

i.e.,

$$e^{(A+B)} = e^Be^A\exp\left\{\frac{1}{2}[A,B]\right\} \ . \qquad (A.8)$$

In particular, when

$$A = \frac{i}{\hbar}[\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R}]$$

and

$$B = \frac{i}{\hbar}[\underline{x}'\cdot\underline{P}+\underline{y}'\cdot\underline{R}]$$

where $\underline{x}$ and $\underline{y}$ are c-numbers Eq. (A.8) gives

$$\exp\left\{\frac{i}{\hbar}\left[(\underline{x}+\underline{x}')\cdot\underline{P}+(\underline{y}+\underline{y}')\cdot\underline{R}\right]\right\} = \exp\left[\frac{i}{\hbar}(\underline{x}'\cdot\underline{P}+\underline{y}'\cdot\underline{R})\right]\exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right] \times \exp\left[\frac{i}{2\hbar}(\underline{x}\cdot\underline{y}'-\underline{x}'\cdot\underline{y})\right] , \qquad (A.9)$$

after noting that

$$[(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R}),(\underline{x}'\cdot\underline{P}+\underline{y}'\cdot\underline{R})] = -i\hbar[\underline{x}\cdot\underline{y}'-\underline{x}'\cdot\underline{y}] . \qquad (A.10)$$

Moreover, when x' = y = 0, the above result reduces to

$$\exp\left\{\frac{i}{\hbar}[\underline{x}\cdot\underline{P}+\underline{y}'\cdot\underline{R}]\right\} = \exp\left[\frac{i}{2\hbar}\underline{x}\cdot\underline{y}'\right]\exp\left[\frac{i}{\hbar}\underline{y}'\cdot\underline{R}\right]\exp\left[\frac{i}{\hbar}\underline{x}\cdot\underline{P}\right], \qquad (A.11)$$

and

$$\begin{aligned}\mathrm{Tr}\left\{\exp\left[\frac{i}{\hbar}(\underline{x}'\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]\right\} &= \exp\left[\frac{i\underline{x}'\cdot\underline{y}}{2\hbar}\right]\int d\underline{q} < \underline{q}|e^{\frac{i}{\hbar}\underline{y}\cdot\underline{R}}\, e^{\underline{x}'\cdot\nabla_{\underline{R}}}|\underline{q} > \\ &= \exp\left[\frac{i}{2\hbar}\underline{x}'\cdot\underline{y}\right]\int d\underline{q}\, e^{\frac{i}{\hbar}\underline{y}\cdot\underline{q}} < \underline{q}|e^{\underline{x}'\cdot\nabla_{\underline{q}}}|\underline{q} > \qquad (A.12)\\ &= \exp\left[\frac{i\underline{x}'\cdot\underline{y}}{2\hbar}\right]\iint d\underline{q}d\underline{q}'\delta(\underline{q}-\underline{q}')\, e^{\frac{i}{\hbar}\underline{y}\cdot\underline{q}}\delta(\underline{q}+\underline{x}'-\underline{q}') \\ &= (2\pi\hbar)^3\delta(\underline{x}')\delta(\underline{y}) ,\end{aligned}$$

i.e.,

$$\left(\frac{1}{2\pi\hbar}\right)^3\mathrm{Tr}\left\{\exp\left[\frac{i}{\hbar}(\underline{x}-\underline{x}')\cdot\underline{P}+\frac{i}{\hbar}(\underline{y}-\underline{y}')\cdot\underline{R}\right]\right\} = \delta(\underline{x}-\underline{x}')\delta(\underline{y}-\underline{y}') . \qquad (A.13)$$

Inserting now Eq. (A.9) into (A.13) yields the orthonormality condition

$$\left(\frac{1}{2\pi\hbar}\right)^3\mathrm{Tr}\left\{\exp\left[\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]\exp\left[-\frac{i}{\hbar}(\underline{x}'\cdot\underline{P}+\underline{y}'\cdot\underline{R})\right]\right\} = \delta(\underline{x}-\underline{x}')\delta(\underline{y}-\underline{y}') \qquad (A.14)$$

for the set of operators

$$\left\{\left(\frac{1}{2\pi\hbar}\right)^{\frac{3}{2}} \exp\left[\frac{i}{\hbar}\left(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R}\right)\right]\right\} .$$

GENERALIZATION OF THE FOURIER INTEGRAL TO FUNCTIONS OF OPERATORS

We define the inverse Fourier transform of the operator $A(\underline{P},\underline{R},t)$ by

$$A(\underline{P},\underline{R},t) = \iint d\underline{x}'d\underline{y}'\alpha(\underline{x}',\underline{y}',t)\exp\left[\frac{i}{\hbar}\left(\underline{x}'\cdot\underline{P}+\underline{y}'\cdot\underline{R}\right)\right] . \qquad (A.15)$$

This may be considered as an integral equation for the coefficient α. In order to obtain α explicitly from Eq. (A.15), use is made of the orthonormality relation derived in the previous section.

Thus, multiplying Eq. (A.15) from the right by

$$\exp\left[-\frac{i}{\hbar}\left(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R}\right)\right]$$

and making use of (A.9) gives

$$A(\underline{P},\underline{R},t)\exp\left[-\frac{i}{\hbar}\left(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R}\right)\right]$$

$$= \iint d\underline{x}'d\underline{y}'\alpha(\underline{x}',\underline{y}',t)\exp\left[\frac{i}{\hbar}\left(\underline{x}'-\underline{x}\right)\cdot\underline{P} + \frac{i}{\hbar}\left(\underline{y}'-\underline{y}\right)\cdot\underline{R}\right] \qquad (A.16)$$

$$(x) \ \exp\left[\frac{i}{2\hbar}\left(\underline{y}'\cdot\underline{x}-\underline{x}'\cdot\underline{y}\right)\right] .$$

Now taking the trace of this expression and utilizing (A.13) results in

$$\left(\frac{1}{2\pi\hbar}\right)^{3}\mathrm{Tr}\left\{A(\underline{P},\underline{R},t)\exp\left[-\frac{i}{\hbar}\left(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R}\right)\right]\right\}$$

$$= \iint d\underline{x}'d\underline{y}'\alpha(\underline{x}',\underline{y}',t)\,e^{\frac{i}{2\hbar}\left(\underline{y}'\cdot\underline{x}-\underline{x}'\cdot\underline{y}\right)}\,\delta(\underline{x}'-\underline{x})\,\delta(\underline{y}'-\underline{y}) \ ,$$

i.e.,

$$\alpha(\underline{x},\underline{y},t) = \left(\frac{1}{2\pi\hbar}\right)^3 \mathrm{Tr}\left\{A(\underline{P},\underline{R},t)\exp\left[-\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]\right\} . \quad (A.17)$$

Hence,

$$A(\underline{P},\underline{R},t) = \left(\frac{1}{2\pi\hbar}\right)^3 \iint d\underline{x}'d\underline{y}'\mathrm{Tr}\left\{A(\underline{P},\underline{R},t)\exp\left[-\frac{i}{\hbar}(\underline{x}'\cdot\underline{P}+\underline{y}'\cdot\underline{R})\right]\right\} \quad (A.18)$$
$$(x)\ \exp\left[\frac{i}{\hbar}(\underline{x}'\cdot\underline{P}+\underline{y}'\cdot\underline{R})\right] .$$

That (A.18) is a formal identity follows readily from multiplying both sides by $\exp\left[-\frac{i}{\hbar}(\underline{x}\cdot\underline{P}+\underline{y}\cdot\underline{R})\right]$, taking the trace, and resorting to Eq. (A.13).

Equation (A.18) is the generalization of the usual Fourier integral to functions of operators.

APPENDIX B

THE WIGNER DISTRIBUTION

It was shown in Chapter IV that, upon introducing a Wigner representation, it is possible to associate a quasi-probability distribution function on classical phase space to each quantum mechanical state of a physical system.

Expectation values are then taken according to*

$$< \Omega(\underline{P},\underline{R}) >_T = \iint d\underline{p}d\underline{q}\ \rho_W(\underline{p},\underline{q},t)\,\Omega^W(\underline{p},\underline{q}) \ , \tag{B.1}$$

where ρ_W is the so-called Wigner distribution function defined by

$$\rho_W(\underline{p},\underline{q},t) = \left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\underline{z}\ \exp\left[\frac{i}{\hbar}\ \underline{z}\cdot\underline{p}\right] < \underline{q} - \frac{\underline{z}}{2} | \rho | \underline{q} + \frac{\underline{z}}{2} >$$

$$= \frac{1}{\mathcal{S}}\left(\frac{1}{2\pi\hbar}\right)^{3N} \sum_{\nu=1}^{\mathcal{S}} \int d\underline{z}\ \exp\left[\frac{i}{\hbar}\ \underline{z}\cdot\underline{p}\right] \psi^{\nu *}(\underline{q} + \frac{\underline{z}}{2},t)\,\psi^{\nu}(\underline{q} - \frac{\underline{z}}{2},t) \tag{B.2}$$

and $\Omega^W(\underline{p},\underline{q})$ is obtained from the "Weyl correspondence" between operators and phase-space functions.

PROPERTIES[9,41]

Some of the more important properties of the Wigner distribution are as follows:

*Recall that $\underline{q}$ and $\underline{p}$ are used to denote the set of position and momentum vectors of the N particles in the system, while the same variables subindexed refer specifically to the particle denoted by the index.

1. ρ_W is everywhere real. This can be readily seen by taking the complex conjugate of (B.2) and changing the dummy variable $\underline{z}$ to $-\underline{z}$.

2. The projection of ρ_W on coordinate space,

$$n_N \equiv \int \rho_W(\underline{p},\underline{q},t)\,d\underline{p} = \frac{1}{\mathcal{S}} \sum_{\nu=1}^{\mathcal{S}} \psi^{\nu *}(\underline{q},t)\psi^{\nu}(\underline{q},t) \quad , \tag{B.3}$$

gives the correct quantum mechanical probability density in configuration space.

3. The projection of ρ_W on momentum space,

$$\begin{aligned} \int \rho_W(\underline{p},\underline{q},t)\,d\underline{q} &= \left(\frac{1}{2\pi\hbar}\right)^{3N} \frac{1}{\mathcal{S}} \sum_{\nu} \left| \int d\underline{u}\, \exp\left[-\frac{i}{\hbar}\,\underline{u}\cdot\underline{p}\right] \psi^{\nu}(\underline{u},t) \right|^2 \\ &= \frac{1}{\mathcal{S}} \sum_{\nu=1}^{\mathcal{S}} \phi^{\nu}(\underline{p},t)\phi^{\nu *}(\underline{p},t) \quad , \end{aligned} \tag{B.4}$$

gives the correct quantum mechanical momentum probability density. Equation (B.4) follows simply from (B.2) after making the substitution $\underline{q} + \frac{\underline{R}}{2} = \underline{u}$ and $\underline{q} - \frac{\underline{R}}{2} = \underline{v}$.

4. The first moment of the jth particle momentum gives the probability current density in configuration space:

$$\begin{aligned} \frac{1}{M}\int \underline{p}_j \rho_W(\underline{p},\underline{q},t)\,d\underline{p} &= \frac{1}{\mathcal{S}M} \sum_{\nu} \int d\underline{z}_j\, \psi^{\nu *}(\underline{q}_1,\dots,\underline{q}_j + \frac{\underline{z}_j}{2},\dots,\underline{q}_N) \\ &\quad (\text{x})\ \psi^{\nu}(\underline{q}_1,\dots,\underline{q}_j - \frac{\underline{z}_j}{2},\dots,\underline{q}_N) \left(\frac{1}{2\pi\hbar}\right)^{3} \int \underline{p}_j \exp\left[\frac{i}{\hbar}\,\underline{z}_j\cdot\underline{p}_j\right] d\underline{p}_j \\ &= \frac{\hbar}{i\mathcal{S}M} \sum_{\nu} \int d\underline{z}_j\, \psi^{\nu *}(\underline{q}_1,\dots,\underline{q}_j + \frac{\underline{z}_j}{2},\dots,\underline{q}_N) \\ &\quad (\text{x})\ \psi^{\nu}(\underline{q}_1,\dots,\underline{q}_j - \frac{\underline{z}_j}{2},\dots,\underline{q}_N)\, \nabla_{z_j}\delta(\underline{z}_j) \quad , \end{aligned}$$

or upon integrating by parts and noting that

$$\nabla_{z_j} \psi^{\nu *} = \frac{1}{2} \nabla_{(\underline{q}_j + \frac{\underline{z}_j}{2})} \psi^{\nu *}$$

and

$$\nabla_{z_j} \psi^{\nu} = -\frac{1}{2} \nabla_{(\underline{q}_j - \frac{\underline{z}_j}{2})} \psi^{\nu} ,$$

we get

$$\frac{1}{M}\int \underline{p}_j \rho_W(\underline{p},\underline{q},t)\, d\underline{p} = \frac{\hbar}{2iM\hbar} \sum_{\nu} \Big[\psi^{\nu *}(\underline{q}_1,\ldots,\underline{q}_N)\ \nabla_{q_j}\ \psi^{\nu}(\underline{q}_1,\ldots,\underline{q}_N) - \psi^{\nu}(\underline{q}_1,\ldots,\underline{q}_N)\ \nabla_{q_j}\ \psi^{\nu *}(\underline{q}_1,\ldots,\underline{q}_N)\Big] . \tag{B.5}$$

TIME DEVELOPMENT OF THE WIGNER DISTRIBUTION FUNCTION[58]

The time evolution of ρ_W may be obtained by differentiating Eq. (B.2) with respect to time and by noting that

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] . \tag{B.6}$$

Thus,

$$\frac{\partial \rho_W}{\partial t} = -\frac{i}{\hbar}\left(\frac{1}{2\pi\hbar}\right)^{3N} \int d\underline{R}\, \exp\left[\frac{i}{\hbar}\, \underline{R}\cdot\underline{p}\right] < \underline{q} - \frac{\underline{R}}{2} | [H, \rho] | \underline{q} + \frac{\underline{R}}{2} > . \tag{B.7}$$

Using now an argument identical to that followed in obtaining Eq. (4.54) from (4.46) leads to

$$\frac{\partial \rho_W}{\partial t} + \frac{1}{M}\, \underline{p}\cdot \nabla_q \rho_W - (2/\hbar)\, \rho_W \sin\left[\frac{\hbar}{2}\, \overleftarrow{\nabla}_p \cdot \overrightarrow{\nabla}_q\right] V(\underline{q}) = 0 , \tag{B.8}$$

or

$$\frac{\partial \rho_W}{\partial t} + \frac{2}{\hbar} H_W \sin\left[\frac{\hbar}{2}\Lambda\right]\rho_W = 0 , \qquad (B.9)$$

which is the quantum mechanical analog to Liouville's equation in classical statistical mechanics and differs from the latter only in second and higher powers of $\hbar$. For a system of harmonic oscillators, for example, the quantum mechanical and classical equations are identical because the operator $H_W\Lambda^{(2m+1)}$ vanishes for $m \geq 1$ for this case.

CANONICAL ENSEMBLE

In the case of a stationary ensemble, $\boldsymbol{\rho}$ must commute with $\boldsymbol{H}$ [see Eq. (B.6)]. Its form for a closed, isothermal, thermodynamic system is given, ex hypothesi, by

$$\boldsymbol{\rho} = \frac{1}{Z} e^{-\beta \boldsymbol{H}} \qquad (B.10)$$

where

$$Z = \mathrm{Tr}\left[e^{-\beta \boldsymbol{H}}\right] . \qquad (B.11)$$

Equation (B.2) then becomes

$$\rho_W(\underline{p},\underline{q}) = \left(\frac{1}{2\pi\hbar}\right)^{3N} \frac{1}{Z} \int d\underline{z}\, \exp\left[\frac{i}{\hbar}\, \underline{z}\cdot\underline{p}\right] < \underline{q} - \frac{\underline{z}}{2}|e^{-\beta \boldsymbol{H}}|\underline{q} + \frac{\underline{z}}{2} > . \qquad (B.12)$$

This equation can be solved for some simple systems, such as an harmonic oscillator (see Appendix C) or a system with a constant potential for which

$$< \underline{q} - \frac{\underline{z}}{2}|e^{-\beta \mathbf{H}}|\underline{q} + \frac{\underline{z}}{2} > \;=\; e^{-\beta V} < \underline{q} - \frac{\underline{z}}{2}|\exp\left[-\frac{\beta \boldsymbol{p}^2}{2M}\right]|\underline{q} + \frac{\underline{z}}{2} >$$

$$= e^{-\beta V}\int d\underline{q}'\delta(\underline{q}'-\underline{q}+\frac{\underline{z}}{2})\exp\left[\frac{\beta \hbar^2}{2M}\nabla^2_{q'}\right]\delta(\underline{q}'-\underline{q}-\frac{\underline{z}}{2})$$

$$= e^{-\beta V}\int d\underline{q}'\delta(\underline{q}'-\underline{q}+\frac{\underline{z}}{2})\left(\frac{1}{2\pi}\right)^{3N}\exp\left[\frac{\beta \hbar^2}{2M}\nabla^2_{q'}\right]\int$$

$$(x)\;\exp\left[i\underline{\sigma}\cdot(\underline{q}'-\underline{q}-\frac{\underline{z}}{2})\right]d\underline{\sigma} \qquad (B.13)$$

$$= e^{-\beta V}\int d\underline{q}'\delta(\underline{q}'-\underline{q}+\frac{\underline{z}}{2})\left(\frac{1}{2\pi}\right)^{3N}\int\exp\left[-\frac{\beta \hbar^2}{2M}\sigma^2\right]$$

$$(x)\;\exp\left[i\underline{\sigma}\cdot(\underline{q}'-\underline{q}-\frac{\underline{z}}{2})\right]d\underline{\sigma}$$

$$= \left(\frac{1}{2\pi}\right)^{3N}e^{-\beta V}\int\exp\left[-\frac{\beta \hbar^2\sigma^2}{2M}\right]e^{-i\underline{\sigma}\cdot\underline{z}}\,d\underline{\sigma}\,.$$

Hence,

$$[\rho_W(\underline{p},\underline{q})]_{V=const.} = \frac{1}{Z}\left(\frac{1}{2\pi\hbar}\right)^{3N}e^{-\beta V}\exp\left[-\frac{\beta p^2}{2M}\right]. \qquad (B.14)$$

The partition function Z is derived from the above equation simply by making use of the normalization condition for ρ_W and is given by

$$Z = \left(\frac{1}{2\pi\hbar}\right)^{3N}\iint d\underline{p}d\underline{q}\;e^{-\beta V}\exp\left[-\frac{\beta p^2}{2M}\right]. \qquad (B.15)$$

For more complicated systems, however, an evaluation of (B.12) in closed form is impossible. Nonetheless, an approximate expression for ρ_W may be obtained from the stationary form of (B.8),

$$\frac{1}{M}\underline{p}\cdot\nabla_q\rho_W - \frac{2}{\hbar}\rho_W\sin\left[\frac{\hbar}{2}\overleftarrow{\nabla}_p\cdot\overrightarrow{\nabla}_q\right]V(\underline{q}) = 0, \qquad (B.16)$$

by noting that in the limit $\hbar \to 0$ this equation becomes the classical

Liouville equation which has the solution

$$\rho_w^c = \lim_{\hbar\to 0} \rho_w = f_N^c \equiv \exp \beta(F - V - \frac{p^2}{2M}) \qquad (B.17)$$

for a closed isothermal system. F is the Helmholtz free energy of the system here and is related to the partition function by

$$F = \frac{1}{\beta} \ln Z . \qquad (B.18)$$

This suggests that, for a "quasi-classical" system, ρ_w can be expressed as a series in which the dominant term is f_N^c and the remaining terms containing quantum mechanical corrections to it, i.e.,*

$$\rho_w = C f_N^c \,(1 + \hbar A_1 + \hbar^2 A_2 + \hbar^2 A_3 + \ldots) \qquad (B.19)$$

where the constant C is required for proper normalization.

The expansion coefficients may be evaluated by substituting (B.19) into (B.16) and collecting terms with equal powers of $\hbar$. This procedure leads to the following set of differential equations,

$$A_o = 1$$

$$\sum_{m=1}^{[\frac{n}{2}+1]} \frac{(-1)^{m-1}}{(2m-1)!} \frac{1}{4^{m-1}} H_w \Lambda^{2m-1} f_N^c \, A_{n-2m+2} = 0, \quad \text{for} \quad n \geq 1 . \qquad (B.20)$$

The symbol $[\frac{n}{2} + 1]$ denotes the greatest integer that does not exceed the number $\frac{n}{2} + 1$.

---

*Note the similarity between the procedure followed here and the asymptotic series expansion [Eq. (5.10)] used in Chapter V.

In particular, for n = 1

$$H_W \Lambda A_1 = 0, \tag{B.21}$$

which is Liouville's equation and thus has as a solution $A_1 = f(H_W)$ where $F(H_W)$ is an arbitrary function of H_W. For a constant potential, however, Eq. (B.19) must be equal to (B.14). Hence, it follows immediately that $C = (1/2\pi\hbar)^{3N}$ and $A_1 = 0$. The same argument leads to $A_{2m+1} = 0$ (m=1,2,3,...), since for odd values of n Eq. (B.20) will contain only odd coefficients.[9]

For n=2, Eq. (B.20) becomes

$$H_W\Lambda A_2 = \left(\frac{\underline{p}}{M}\cdot\nabla_q\right)\left[\frac{\beta^3}{24}\left(\frac{\underline{p}}{M}\cdot\vec{\nabla}_q\right)^2 V(\underline{q}) - \frac{1}{8M}\beta^2\nabla_q^2 V\right],$$

or

$$\begin{aligned} H_W\Lambda A_2 = {} & \left(\frac{\underline{p}}{M}\cdot\vec{\nabla}_q - \nabla_q V\cdot\vec{\nabla}_p\right)\left[\frac{\beta^3}{24}\left(\frac{\underline{p}}{M}\cdot\vec{\nabla}_q\right)^2 V(\underline{q}) - \frac{1}{8M}\beta^2\nabla_q^2 V\right] \\ & + \nabla_q V\cdot\vec{\nabla}_p\left[\frac{\beta^3}{24}\left(\frac{\underline{p}}{M}\cdot\vec{\nabla}_q\right)\left(\frac{\underline{p}}{M}\cdot\nabla_q V\right)\right]. \end{aligned} \tag{B.22}$$

Noting now that

$$\begin{aligned} (\nabla_q V\cdot\vec{\nabla}_p)\left(\frac{\underline{p}}{M}\cdot\vec{\nabla}_q\right)\left(\frac{\underline{p}}{M}\cdot\nabla_q V\right) &= 2\sum_{\alpha,\beta}\frac{\partial V}{\partial q_\alpha}\frac{p_\beta}{M^2}\frac{\partial^2 V}{\partial q_\alpha\partial q_\beta} \\ &= \frac{1}{M^2}\sum_{\alpha,\beta} p_\beta\frac{\partial}{\partial q_\beta}\left(\frac{\partial V}{\partial q_\alpha}\right)^2 \\ &= \frac{1}{M^2}(\underline{p}\cdot\vec{\nabla}_q)(\nabla V\cdot\nabla V) \\ &= \left(\frac{\underline{p}}{M}\cdot\vec{\nabla}_q - \nabla_q V\cdot\vec{\nabla}_p\right)\left(\frac{1}{M}\nabla V\cdot\nabla V\right) \end{aligned} \tag{B.23}$$

and substituting this result into (B.22) yields

$$H_W \Lambda A_2 = H_W \Lambda \left[\frac{\beta^3}{24} \left(\frac{\underline{p}}{M} \cdot \vec{\nabla}_q \right)^2 V(\underline{q}) - \frac{1}{8M} \beta^2 \nabla_q^2 V + \frac{\beta^3}{24M} \nabla_q V \cdot \nabla_q V \right], \quad (B.24)$$

i.e.,

$$A_2 = \frac{\beta^3}{24} \left(\frac{\underline{p}}{M} \cdot \vec{\nabla}_q \right)^2 V(\underline{q}) - \frac{\beta^2}{8M} \left(\nabla_q^2 V - \frac{\beta}{3} \nabla_q V \cdot \nabla_q V \right) . \quad (B.25)$$

The possibility of an additive constant in (B.24) has been excluded by the requirement that $A_2 = 0$ for a constant potential.

In principle, Eq. (B.20) may also be solved in a similar way for $n = 4,6$, etc.; however, the complexity of the calculations increases considerably.

An analogous expansion in powers of $\hbar^2$ can be obtained for the configurational probability density, defined according to (B.3), by integrating Eq. (B.19) over momentum space.[13] Thus,

$$n_N = n_N^c (1 + \hbar^2 B_2 + \hbar^4 B_4 + \ldots) \quad (B.26)$$

where

$$n_N^c = \left(\frac{2\pi M}{\beta} \right)^{3N/2} \exp[\beta(F-V)] \quad (B.27)$$

is the classical density distribution function and

$$B_n = \left(\frac{\beta}{2\pi M} \right)^{3N/2} \int d\underline{p} \exp\left[-\frac{\beta p^2}{2M} \right] A_n . \quad (B.28)$$

In particular,

$$B_2 = \frac{\beta^2}{24M} (\beta \nabla_q V \cdot \nabla_q V - 2\nabla_q^2 V) . \quad (B.29)$$

For the case of two body forces, the potential of interaction may be expressed as a sum of potential energies of interaction between pairs of particles

$$V = \frac{1}{2} \sum_{i \neq k}^{N-1} \sum_{k=1}^{N} \phi_{ik} \quad . \tag{B.30}$$

In this case, reduced distribution functions may be obtained by integrating Eqs. (B.19) and (B.26) over the phase space and configuration space coordinates of N-m (m=1,2,...,N-1) particles respectively. For instance, the specific singlet space phase distribution function $f_1(\underline{p}_j,\underline{q}_j)$ can be obtained by integrating Eq. (B.19) over the phase space coordinates of all particles except one,

$$\begin{aligned} f_1(\underline{p}_j,\underline{q}_j) &= \iint \left\{ f_N^c(1+\hbar^2 A_2 + \hbar^4 A_4 + \ldots) \right\} \prod_{i \neq j}^{N} d\underline{p}_i d\underline{q}_i \\ &= \iint \left\{ f_N^c(1+\hbar^2 B_2) \right\} \prod_{i \neq j}^{N} d\underline{p}_i d\underline{q}_i \\ &+ \iint \left\{ \hbar^2 f_N^c (A_2 - B_2) \right\} \prod_{i \neq j}^{N} d\underline{p}_i d\underline{q}_i + \mathcal{O}(\hbar^4) \quad . \end{aligned} \tag{B.31}$$

Noting upon substituting Eq. (B.27) into (B.17) that

$$f_N^c = \left(\frac{\beta}{2\pi M}\right)^{3N/2} n_N^c \exp\left[-\frac{\beta p^2}{2M}\right] , \tag{B.32}$$

we get

$$f_1(\underline{p}_j,\underline{q}_j) = \left(\frac{\beta}{2\pi M}\right)^{3/2} \exp\left[-\frac{\beta p_j^2}{2M}\right] n_1(\underline{q}_j) + \hbar^2 \left(\frac{\beta}{2\pi M}\right)^{3N/2} \iint n_N^c$$

$$(x)\ \exp\left[-\frac{\beta p^2}{2M}\right](A_2-B_2) \prod_{i\neq j} d\underline{p}_i d\underline{q}_i + \mathcal{O}(\hbar^4) \tag{B.33}$$

$$= \left(\frac{\beta}{2\pi M}\right)^{3/2} \exp\left[-\frac{\beta p_j^2}{2M}\right] n_1(\underline{q}_j) + \frac{\hbar^2\beta^2}{24}\left(\frac{\beta}{2\pi M}\right)^{3N/2} \iint n_N^c$$

$$(x)\ \exp\left[-\frac{\beta p^2}{2M}\right]\left[\beta\left(\frac{\underline{p}}{M}\cdot\vec{\nabla}_q\right)^2 V - \frac{1}{M}\nabla^2 V\right] \prod_{i\neq j} d\underline{p}_i d\underline{q}_i + \mathcal{O}(\hbar^4).$$

Furthermore, since $\underline{p}_k \cdot \nabla_{q_k} = \mu_k |p_k| |\nabla_{q_k}|$,

$$\iint n_N^c \exp\left[-\frac{\beta p^2}{2M}\right] \beta\left(\frac{\underline{p}}{M}\cdot\vec{\nabla}_q\right)\left(\frac{\underline{p}}{M}\cdot\nabla_q V\right) \prod_{i\neq j} d\underline{p}_i d\underline{q}_i$$

$$= (2\pi)\beta \iint n_N^c \exp\left[-\frac{\beta p^2}{2M}\right] \sum_k \mu_k^2 \left(\frac{p_k}{M}\right)^2 (\nabla_{q_k}^2 V) p_k^2 dp_k d\mu_k d\underline{q}_k \prod_{\substack{i\neq j\\ \neq k}} d\underline{p}_i d\underline{q}_i$$

$$= \frac{\beta}{3}\sum_k \iint n_N^c \exp\left[-\frac{\beta p^2}{2M}\right]\left(\frac{p_k}{M}\right)^2 \nabla_{q_k}^2 V \prod_{i\neq j} d\underline{p}_i d\underline{q}_i . \tag{B.34}$$

Hence,

$$f_1(\underline{p}_j,\underline{q}_j) = \left(\frac{\beta}{2\pi M}\right)^{3/2} \exp\left[-\frac{\beta p_j^2}{2M}\right] n_1(\underline{q}_j)$$

$$+ \frac{\hbar^2\beta^2}{24}\left(\frac{\beta}{2\pi M}\right)^{3N/2} \sum_k \iint n_N^c \exp\left[-\frac{\beta p^2}{2M}\right]\left[\frac{\beta}{3}\left(\frac{p_k}{M}\right)^2 - \frac{1}{M}\right] \tag{B.35}$$

$$(x)\ \nabla_k^2 V \prod_{i\neq j} d\underline{p}_i d\underline{q}_i + \mathcal{O}(\hbar^4) .$$

The second term in this expression vanishes when $k \neq j$; this may be shown as follows:

$$\int \exp\left[-\frac{\beta p^2}{2M}\right]\left[\frac{\beta}{3}\left(\frac{p_k}{M}\right)^2-\frac{1}{M}\right]\prod_{i\neq j} d\underline{p}_i$$

$$= \exp\left[-\frac{\beta p_j^2}{2M}\right]\int\left[\frac{\beta}{3}\left(\frac{p_k}{M}\right)^2-\frac{1}{M}\right]\prod_{i\neq j}\exp\left[-\frac{\beta p_i^2}{2M}\right] d\underline{p}_i$$

$$= \exp\left[-\frac{\beta p_j^2}{2M}\right]\int\left[\frac{\beta}{3}\left(\frac{p_k}{M}\right)^2-\frac{1}{M}\right]\exp\left[-\frac{\beta p_k^2}{2M}\right] d\underline{p}_k\left\{\int \exp\left[-\frac{\beta p^2}{2M}\right] d\underline{p}\right\}^{N-2}$$

$$= \left(\frac{2\pi M}{\beta}\right)^{\frac{3}{2}(N-2)}\exp\left[-\frac{\beta p_j^2}{2M}\right]\int\left[\frac{\beta}{3}\left(\frac{p_k}{M}\right)^2-\frac{1}{M}\right]\exp\left[-\frac{\beta p_k^2}{2M}\right] d\underline{p}_k \tag{B.36}$$

$$= \left(\frac{2\pi M}{\beta}\right)^{\frac{3}{2}(N-2)}\frac{1}{M}\exp\left[-\frac{\beta p_j^2}{2M}\right]\left[\left(\frac{2\pi M}{\beta}\right)^{\frac{3}{2}}-\left(\frac{2\pi M}{\beta}\right)^{\frac{3}{2}}\right] = 0 .$$

Q.E.D.

Thus, we now have

$$f_1(\underline{p}_j,\underline{q}_j) = \left(\frac{\beta}{2\pi M}\right)^{\frac{3}{2}}\exp\left[-\frac{\beta p_j^2}{2M}\right] n_1(\underline{q}_j) + \frac{\hbar^2\beta^2}{24}\left(\frac{\beta}{2\pi M}\right)^{\frac{3}{2}}\exp\left[-\frac{\beta p_j^2}{2M}\right]$$

$$(x)\left[\frac{\beta}{3}\left(\frac{p_j}{M}\right)^2-\frac{1}{M}\right]\int n_N^c \nabla_j^2 V\prod_{i\neq j} d\underline{q}_i + \mathcal{O}(\hbar^4) . \tag{B.37}$$

Moreover, from Eq. (B.30) we get

$$\nabla_j^2 V = \frac{1}{2}\sum_{k\neq j}^{N-1}\left[\nabla_j^2 \phi_{jk} + \nabla_j^2 \phi_{kj}\right] , \tag{B.38}$$

and since

$$\nabla_j^2 \phi(\underline{q}_j - \underline{q}_k) = \nabla_{r_k}^2 \phi(\underline{r}_k)$$

$$\nabla_j^2 \phi(\underline{q}_k - \underline{q}_j) = \nabla_{(-r_k)}^2 \phi(-\underline{r}_k) = \nabla_{r_k}^2 \phi(\underline{r}_k) \tag{B.39}$$

where $\underline{r}_k = \underline{q}_j - \underline{q}_k$, it follows that

$$\nabla_j^2 V = \sum_{k\neq j}^{N-1}\nabla_{r_k}^2 \phi(\underline{r}_k) . \tag{B.40}$$

Hence,

$$\int n_N^c \nabla_j^2 V \prod_{i\neq j} d\underline{q}_i = \sum_{k\neq j}^{N-1} \int n_N^c \nabla_{r_k}^2 \phi(\underline{r}_k) \prod_{i\neq j} d\underline{q}_i$$

$$= \sum_{k\neq j}^{N-1} \int n_2^c(\underline{q}_k, \underline{q}_j) \nabla_{r_k}^2 \phi(\underline{r}_k) d\underline{q}_k \qquad (B.41)$$

$$= (N-1) \int n_2^c(\underline{q}_j, \underline{q}_j + \underline{r}) \nabla_r^2 \phi(\underline{r}) d\underline{r} \ .$$

Finally, substituting this result into (B.37) yields

$$f_1(\underline{p}_j, \underline{q}_j) = \left(\frac{\beta}{2\pi M}\right)^{\frac{3}{2}} \exp\left[-\frac{\beta p_j^2}{2M}\right] \left\{ n_1(\underline{q}_j) + \frac{\hbar^2\beta^2}{24M} \left[\frac{\beta}{3} \frac{p_j^2}{M} - 1\right] \right. \qquad (B.42)$$

$$\left. (x) \ (N-1) \int n_2^c(\underline{q}_j, \underline{q}_j + \underline{r}) \nabla_r^2 \phi(\underline{r}) d\underline{r} \right\} + \mathcal{O}(\hbar^4) \ .$$

APPENDIX C

THE WIGNER DISTRIBUTION FUNCTION FOR AN ISOTROPIC HARMONIC OSCILLATOR

It was shown in Appendix B that when $V(\underline{q})$ is an harmonic oscillator potential Eq. (B.8) reduces to the classical Liouville equation

$$\frac{\partial\rho_W}{\partial t} + \frac{1}{M}\,\underline{p}\cdot\nabla_q\,\rho_W - \rho_W\,\overleftarrow{\nabla}_p\cdot\overrightarrow{\nabla}_q\,V(\underline{q}) = 0\ . \tag{C.1}$$

For thermodynamical equilibrium, this equation has the canonical solution

$$\rho_W = C_1\,\exp\left[-\alpha\left(\frac{p^2}{2M} + \frac{M\omega^2q^2}{2}\right)\right] \tag{C.2}$$

where C_1 and α are constants to be determined.

C_1 can be obtained directly in terms of α by making use of the normalization condition

$$\int \rho_W\,d\underline{p}d\underline{q} = 1 = C_1\iint d\underline{p}d\underline{q}\,\exp\left[-\alpha\left(\frac{p^2}{2M} + \frac{M\omega^2q^2}{2}\right)\right] \tag{C.3}$$

and is given by

$$C_1 = \left(\frac{\alpha\omega}{2\pi}\right)^3 . \tag{C.4}$$

To evaluate α, we substitute (C.2) into the Fourier inverse of Eq. (B.2) and get

$$< \underline{q} - \frac{\underline{z}}{2}\,|\rho|\,\underline{q} + \frac{\underline{z}}{2} > = C_1\int \exp\left[-\frac{i}{\hbar}\,\underline{z}\cdot\underline{p}\right]\exp\left[-\alpha\left(\frac{p^2}{2M} + \frac{M\omega^2q^2}{2}\right)\right]d\underline{p}\ . \tag{C.5}$$

Setting $\underline{z} = 0$ in the above equation and performing the indicated integration yields

$$< \underline{q}|\rho|\underline{q} > \;=\; \left(\frac{\alpha M\omega^2}{2\pi}\right)^{\frac{3}{2}} \exp\left[-\frac{\alpha M\omega^2 q^2}{2}\right] . \qquad (C.6)$$

The term in the left side of Eq. (C.6) is the diagonal element of the density matrix in the coordinate representation. It may be conveniently expressed in terms of energy eigenfunctions by making the transformation

$$\rho^{(\underline{q})} \;=\; S^{\dagger}\rho^{(H)}S \qquad (C.7)$$

where the superscripts indicate in which representation ρ is expressed and S is a unitary matrix. Thus,

$$< \underline{q}|\rho^{(\underline{q})}|\underline{q} > \;=\; \sum_{k,\ell} < \underline{q}|S^{+}|k > < k|\rho^{(H)}|\ell > < \ell|S|\underline{q} > . \qquad (C.8)$$

If $|k >$ and $|\ell >$ are energy eigenvectors, then

$$< k|\rho^{(H)}|\ell > \;=\; \frac{1}{Z}\, e^{-\beta E_\ell}\, \delta_{k\ell} \qquad (C.9)$$

and Eq. (C.8) becomes

$$< \underline{q}|\rho^{(\underline{q})}|\underline{q} > \;=\; \frac{1}{Z} \sum_{\ell} < \underline{q}|S^{\dagger}|\ell > e^{-\beta E_\ell} < \ell|S|\underline{q} > . \qquad (C.10)$$

The matrix elements of S can be readily obtained from the closure property of the energy eigenfunctions:

$$\delta(\underline{q}-\underline{q}') \;=\; \sum_{\ell} U_\ell^{*}(\underline{q})U_\ell(\underline{q}') \qquad (C.11)$$

and are given by

$$< \ell | S | \underline{q} > \ = \ U^*_\ell(\underline{q}) \qquad (C.12)$$

and

$$< \underline{q} | S^\dagger | \ell > \ = \ U_\ell(\underline{q}) \ . \qquad (C.13)$$

Finally, substituting these results into Eq. (C.10) yields

$$<\underline{q}|\rho|\underline{q}> \ = \ \frac{1}{Z} \sum_\ell e^{-\beta E_\ell} |U_\ell(\underline{q})|^2 \ = \ \left(\frac{\alpha M\omega^2}{2\pi}\right)^{\frac{3}{2}} \exp\left[-\frac{\alpha M\omega^2 q^2}{2}\right] \ . \qquad (C.14)$$

SCHRÖDINGER'S METHOD OF FACTORIZATION[59,60]

In order to obtain α from Eq. (C.14) explicitly, it is convenient to consider first some properties of the complex operators

$$A_{(+)} \ = \ P_x + iM\omega R_x \ , \qquad (C.15)$$

and

$$A_{(-)} \ = \ P_x - iM\omega R_x \qquad (C.16)$$

which obey the commutator relations:

$$[H_x, A_{(+)}] \ = \ \hbar\omega A_{(+)} \qquad (C.17)$$

and

$$[H_x, A_{(-)}] \ = \ -\hbar\omega A_{(-)} \ . \qquad (C.18)$$

In the above equations, R_x and P_x are the components of $\underline{R}$ and $\underline{P}$ along the $\underline{x}$-axis and $H_x = \frac{P_x^2}{2M} + \frac{M\omega^2}{2} R_x^2$.

Making use of Eqs. (C.17) and (C.18), together with the fact that for an isotropic oscillator the eigenfunctions are separable into a product of components along each axis, we have

$$A_{(+)} H_x U_n(x) = E_n A_{(+)} U_n(x)$$

or

$$H_x A_{(+)} U_n(x) = (E_n + \hbar\omega) A_{(+)} U_n(x) ,$$

i.e.,

$$A_{(+)} U_n(x) = N_n^{(+)} U_{n+1}(x) . \qquad (C.19)$$

Similarly,

$$H_x A_{(-)} U_n(x) = (E_n - \hbar\omega) A_{(-)} U_n(x) ,$$

and

$$A_{(-)} U_n(x) = N_n^{(-)} U_{n-1}^{(-)}(x) . \qquad (C.20)$$

Moreover, since there are no eigenfunctions with eigenvalues smaller than $(E_n)_{minimum}$,

$$A_{(-)} U_o(x) = 0 ,$$

$$(A_{(+)} A_{(-)}) U_o(x) = 2M[H_x - \frac{\hbar\omega}{2}] U_o(x) = 0 ,$$

and

$$H_x U_o(x) = \frac{\hbar\omega}{2} U_o(x) .$$

That is,

$$(E_n)_{min} = \frac{\hbar\omega}{2} \tag{C.21}$$

and

$$E_n = (n + \frac{1}{2})\hbar\omega . \tag{C.22}$$

The normalization constant $N_n^{(-)}$ may be obtained from the norm of (C.20). Thus,

$$|N_n^{(-)}|^2 = \int A_{(-)} U_n(x) [A_{(-)} U_n(x)]^* dx$$

$$= \int A_{(-)} U_n(x) [A_{(+)}^{\dagger} U_n(x)]^* dx$$

$$= < n|A_{(+)} A_{(-)}|n >$$

$$= < n|2M(H_x - \frac{\hbar\omega}{2})|n > = 2Mn\hbar\omega ,$$

or

$$N_n^{(-)} = (2M\hbar\omega n)^{\frac{1}{2}} . \tag{C.23}$$

$N_n^{(+)}$ follows readily from

$$< n|A_{(-)} A_{(+)}|n > = N_n^{(+)} N_{n+1}^{(-)}$$

and

$$< n|A_{(-)} A_{(+)}|n > = < n|2M(H_x + \frac{\hbar\omega}{2})|n > = 2M\hbar\omega(n+1) ,$$

i.e.,

$$N_n^{(+)} = \frac{2M\hbar\omega(n+1)}{N_{n+1}^{(-)}} = \frac{2M\hbar\omega(n+1)}{[2M\hbar\omega(n+1)]^{\frac{1}{2}}} = [2M\hbar\omega(n+1)]^{\frac{1}{2}} . \tag{C.24}$$

EVALUATION OF α

We now return to the problem of calculating α from (C.14) explicitly. To this end, note that

$$
\begin{aligned}
<\underline{q}|\rho|\underline{q}> &= \frac{1}{Z}\sum_{\ell} e^{-\beta E_\ell}|U_\ell(\underline{q})|^2 \\
&= \frac{1}{Z}\sum_{\ell=n+m+j} e^{-\beta E_\ell}|U_m(y)U_j(z)|^2\,|U_n(x)|^2 .
\end{aligned}
\tag{C.25}
$$

Making use of the operators introduced in the previous section, we obtain

$$
\begin{aligned}
\frac{\partial}{\partial x}<\underline{q}|\rho|\underline{q}> &= \frac{1}{Z}\sum_{\ell} e^{-\beta E_\ell}|U_mU_j|^2\left[U_n^*\frac{\partial U_n}{\partial x}+U_n\frac{\partial U_n^*}{\partial x}\right] \\
&= \frac{i}{2\hbar Z}\sum_{\ell} e^{-\beta E_\ell}|U_mU_j|^2\left[U_n^*(A_{(+)}+A_{(-)})U_n-U_n(A_{(+)}+A_{(-)})^*U_n^*\right] \\
&= \frac{i}{2\hbar Z}\sum_{\ell=0} e^{-\beta E_\ell}|U_mU_j|^2N_n^{(+)}[U_n^*U_{n+1}-U_nU_{n+1}^*] \\
&+ \frac{i}{2\hbar Z}\sum_{\ell=1} e^{-\beta E_\ell}|U_mU_j|^2N_n^{(-)}[U_n^*U_{n-1}-U_nU_{n-1}^*] .
\end{aligned}
\tag{C.26}
$$

Now changing the index of notation ($n\to n+1$) in the second term of the above equation and taking into account Eq. (C.22) yields

$$
\begin{aligned}
\frac{\partial}{\partial x}<\underline{q}|\rho|\underline{q}> = \frac{i}{2\hbar Z}\sum_{\ell=0} e^{-\beta E_\ell}|U_mU_j|^2\Big\{N_n^{(+)}[U_n^*U_{n+1}-U_nU_{n+1}^*] \\
+ e^{-\beta\hbar\omega}N_{n+1}^{(-)}[U_{n+1}^*U_n-U_{n+1}U_n^*]\Big\} ,
\end{aligned}
$$

or since $N_n^{(+)} = N_{n+1}^{(-)}$,

$$\frac{\partial}{\partial x} < \underline{q}|\rho|\underline{q} > = \frac{i}{2\hbar Z}(1-e^{-\beta\hbar\omega})\sum_{\ell=0} e^{-\beta E_\ell}|U_m U_j|^2 N_n^{(+)} [U_n^* U_{n+1} - U_n U_{n+1}^*] \ . \tag{C.27}$$

Similarly, noting that

$$A_{(+)} U_n U_n^* = U_n^* A_{(+)} U_n + U_n A_{(+)} U_n^* - iM\omega x U_n^* U_n \tag{C.28}$$

and

$$A_{(-)} U_n U_n^* = U_n^* A_{(-)} U_n + U_n A_{(-)} U_n^* + iM\omega x U_n^* U_n \ , \tag{C.29}$$

we get

$$\begin{aligned}(A_{(+)}-A_{(-)}) < \underline{q}|\rho|\underline{q} > &= 2iM\omega x < \underline{q}|\rho|\underline{q} > = \frac{1}{Z}\sum_{\ell} e^{-\beta E_\ell}|U_m U_j|^2 \\ &\quad (x)\ (A_{(+)}-A_{(-)}) U_n U_n^* \\ &= \frac{1}{Z}\sum_{\ell} e^{-\beta E_\ell}|U_m U_j|^2 [U^*(A_{(+)}-A_{(-)}) U_n \\ &\quad + U_n (A_{(+)}-A_{(-)}) U_n^* - 2iM\omega x < \underline{q}|\rho|\underline{q} > \ ,\end{aligned} \tag{C.30}$$

i.e.,

$$\begin{aligned}-2M\omega w < \underline{q}|\rho|\underline{q} > &= \frac{i}{2Z}\sum_{\ell=0} e^{-\beta E_\ell}|U_m U_j|^2 N_n^{(+)} [U_n^* U_{n+1} - U_n U_{n+1}^*] \\ &\quad - \frac{i}{2Z}\sum_{\ell=1} e^{-\beta E_\ell}|U_m U_j|^2 N_n^{(-)} [U_n^* U_{n-1} - U_n U_{n-1}^*] \ .\end{aligned} \tag{C.31}$$

Direct comparison of this result with Eqs. (C.26) and (C.27) leads to:

$$-2M\omega x < \underline{q}|\rho|\underline{q} > = \frac{i}{2Z}(1+e^{-\beta\hbar\omega})\sum_{\ell=0} e^{-\beta E_\ell}|U_m U_j|^2 N_n^{(+)} [U_n^* U_{n+1} - U_n U_{n+1}^*] \ . \tag{C.32}$$

Substituting this expression into (C.27) results in the differential equation

$$\frac{\partial}{\partial x} < \underline{q}|\rho|\underline{q} > \;=\; -\frac{2M\omega x}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right) < \underline{q}|\rho|\underline{q} > . \qquad (C.33)$$

Evaluating now $\frac{\partial}{\partial x} < \underline{q}|\rho|\underline{q} >$ from the right side of Eq. (C.14) and inserting the result into (C.33) yields

$$\alpha M\omega^2 x < \underline{q}|\rho|\underline{q} > \;=\; \frac{2M\omega x}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right) < \underline{q}|\rho|\underline{q} > ,$$

or

$$\alpha \;=\; \frac{2}{\hbar\omega}\tanh\left(\frac{\beta\hbar\omega}{2}\right) . \qquad (C.34)$$

In summary, we then have for an isotropic harmonic oscillator

$$\rho_W \;=\; \left(\frac{\alpha\omega}{2\pi}\right)^3 \exp\left[-\alpha\left(\frac{p^2}{2M} + \frac{M\omega^2 q^2}{2}\right)\right] \qquad (C.35)$$

with α given by (C.34).*

In the classical limit ($\beta\hbar\omega \ll 1$),

$$\alpha \;\approx\; \beta$$

and ρ_W becomes identical with the classical phase space distribution function. This, of course, could be expected since in this case the distribution of energy levels can be regarded as practically continuous and quantisation ceases to have any effect.

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*Except for the normalization constant, the same result was obtained by Wells[61] by making use of Feynman's path integral techniques. See also Landau and Lifshitz[62] for a derivation of the marginal distributions by a device similar to the one used here.

APPENDIX D

ASYMPTOTIC FORM OF $G_s(\underline{r},t)$, THE "CLASSICAL" LIMIT $G_s^c(\underline{r},t)$, AND VINEYARD'S APPROXIMATION FOR THE IDEAL MONATOMIC GAS

The purpose of this section is dual:

1. To derive an asymptotic expression for the space-time correlation $G_s(\underline{r},t)$.

2. To show in the case of the ideal monatomic gas that the time displaced pair distribution function $G_s^c(\underline{r},t)$, obtained by letting $\hbar \to 0$ in $G_s(\underline{r},t)$, yields the incorrect classical limit for the scattering function $S_s(\underline{\Delta p},\epsilon)$.

Our first objective may be attained by Fourier inverting Eq. (5.34) to get

$$G_s(\underline{r},t) = \left(\frac{1}{2\pi\hbar}\right)^3 \int d\underline{\Delta p}\, \exp\left[-\frac{\beta\Delta p^2}{8M}\right] < \exp\left[-\frac{i\underline{\Delta p}}{\hbar}\cdot\underline{s}\right] >_{TC} + \mathcal{O}(\hbar^2) \tag{D.1}$$

where

$$\underline{s} = \underline{r} + \underline{q}_j - \underline{q}_j(t) + \frac{i\beta\hbar}{2M}\,\underline{p}_j \quad . \tag{D.2}$$

Completing now the squares in Eq. (D.1) and defining a new vector $\underline{v}$ by

$$\underline{v} = \left(\frac{\beta}{2M}\right)^{1/2}\left[\frac{\underline{\Delta p}}{2} - \underline{p}_j\right] + i\underline{\gamma} \tag{D.3}$$

with

$$\underline{\gamma} = \frac{1}{\hbar}\left(\frac{2M}{\beta}\right)^{1/2}\left(\underline{s} - \frac{i\beta\hbar}{2M}\,\underline{p}_j\right) = (\underline{r}+\underline{q}_j-\underline{q}_j(t))\,\frac{1}{\hbar}\left(\frac{2M}{\beta}\right)^{1/2} \tag{D.4}$$

yields

$$G_s(\underline{r},t) = \left(\frac{2M}{\beta}\right)^{3/2}\left(\frac{1}{\pi\hbar}\right)^3 < \exp\left[-\frac{2Ms^2}{\beta\hbar^2}\right]\int d\underline{v}\ \exp[-v^2] >_{TC} + \mathcal{O}(\hbar^2)\ . \tag{D.5}$$

If $\underline{\gamma}$ is chosen along the z-axis, then

$$v_x = \left(\frac{\beta}{2M}\right)^{1/2}\left(\frac{\Delta p}{2} - \underline{p}_j\right)_x$$

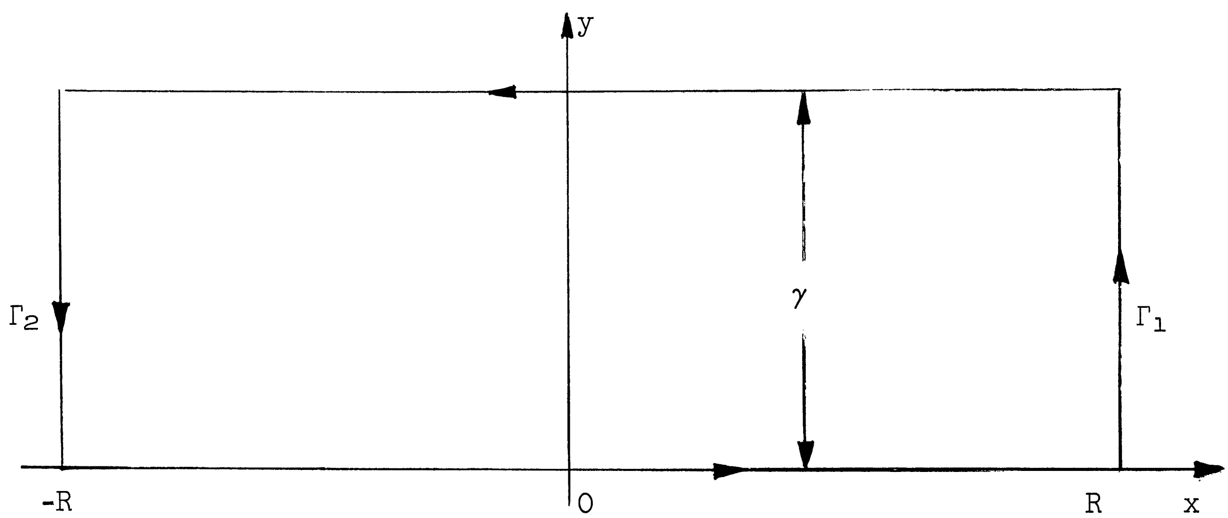
$$v_y = \left(\frac{\beta}{2M}\right)^{1/2}\left(\frac{\Delta p}{2} - \underline{p}_j\right)_y$$

$$v_z = \left(\frac{\beta}{2M}\right)^{1/2}\left(\frac{\Delta p}{2} - \underline{p}_j\right)_z + i\gamma\ ,$$

and

$$\begin{aligned}\int d\underline{v}\ \exp[-v^2] &= \left\{\int_{-\infty}^{\infty} dv_x\ \exp[-v_x^2]\right\}^2 \int_{-\infty+i\gamma}^{\infty+i\gamma} dv_z\ \exp[-v_z^2] \\ &= \pi\int_{-\infty+i\gamma}^{\infty+i\gamma} dv_z\ \exp[-v_z^2]\ .\end{aligned} \tag{D.6}$$

In order to perform the above integration, consider the following contour in the complex plane:



Since $\exp[-z^2]$ is an entire function,

$$\oint dz\, e^{-z^2} = 0 = \int_{-R}^{R} e^{-x^2}\, dx + I_{\Gamma_1} + I_{\Gamma_2} + \int_{R+i\gamma}^{-R+i\gamma} e^{-z^2} dz \;, \quad \text{(D.7)}$$

or

$$\lim_{R\to\infty} \int_{-R+i\gamma}^{R+i\gamma} e^{-z^2} dz = (\pi)^{1/2} + \lim_{R\to\infty} (I_{\Gamma_1} + I_{\Gamma_2}) \;. \quad \text{(D.8)}$$

Furthermore,

$$I_{\Gamma_1} = \int_{R}^{R+i\gamma} \exp[-(x^2-y^2+2ixy)]\,(dx+idy)$$

$$= \int_{R}^{R+i\gamma} e^{-(x^2-y^2)} [\cos(2xy) - i \sin(2xy)](dx+idy)$$

$$= \int_{R}^{R} e^{-(x^2-y^2)} \cos(2xy)\, dx + i\int_{0}^{\gamma} e^{-(R^2-y^2)} \cos(2Ry)\, dy$$

$$- i\int_{R}^{R} e^{-(x^2-y^2)} \sin(2xy)\, dx + \int_{0}^{\gamma} e^{-(R^2-y^2)} \sin(2Ry)\, dy \;,$$

i.e.,

$$I_{\Gamma_1} = ie^{-R^2} \int_{0}^{\gamma} e^{+y^2} \cos(2Ry)\, dy + e^{-R^2} \int_{0}^{\gamma} e^{y^2} \sin(2Ry)\, dy \;. \quad \text{(D.9)}$$

Both integrals in (D.9) are finite. Therefore,

$$\lim_{R\to\infty} I_{\Gamma_1} = 0 \;.$$

Similarly,

$$\lim_{R\to\infty} I_{\Gamma_2} = 0$$

and Eq. (D.8) becomes

$$\int_{-\infty+i\gamma}^{\infty+i\gamma} e^{-z^2} dz = (\pi)^{1/2} . \tag{D.10}$$

In view of Eqs. (D.10) and (D.6), Eq. (D.5) goes into

$$G_s(\underline{r},t) = \left(\frac{2M}{\beta\pi\hbar^2}\right)^{\frac{3}{2}} < \exp\left[-\frac{2Ms^2}{\beta\hbar^2}\right] >_{TC} + \mathcal{O}(\hbar^2) . \tag{D.11}$$

The limit as $\hbar \to 0$ of this expression may be obtained by noting that if in Eq. (D.1) we make the dummy variable transformation

$$\underline{\Delta p}/\hbar = \underline{\kappa} ,$$

then

$$G_s(\underline{r},t) = \left(\frac{1}{2\pi}\right)^3 \int d\underline{\kappa} \exp\left[-\frac{\beta\hbar^2\kappa^2}{8M}\right] < \exp[-i\underline{\kappa}\cdot\underline{s}] >_{TC} + \mathcal{O}(\hbar^2)$$

and

$$\begin{aligned} \lim_{\hbar\to 0} G_s(\underline{r},t) &= \left(\frac{1}{2\pi}\right)^3 \int d\underline{\kappa} < \exp\{-i\underline{\kappa}\cdot[\underline{r}+\underline{q}_j-\underline{q}_j(t)]\} >_{TC} \\ &= < \delta[\underline{r}+\underline{q}_j-\underline{q}_j(t)] >_{TC} = G_s^c(\underline{r},t) . \end{aligned} \tag{D.12}$$

In actual fact, this limit is meaningless since we have kept $\underline{\kappa}$ finite, and hence, implied zero momentum transfer.

IDEAL MONATOMIC GAS

As will be seen below, this case is particularly convenient for comparing the scattering functions obtained from (D.11) and (D.12) and to show that although

$$\lim_{\hbar\to 0} G_s(\underline{r},t) = G_s^c(\underline{r},t)$$

$$\lim_{\hbar\to 0} S_s(\underline{\Delta p},\epsilon) \neq S_{sv}(\underline{\Delta p},\epsilon) .$$

For this purpose, note that

$$\underline{s} = \underline{r} + \underline{p}_j\left(\frac{i\beta\hbar}{2M} - t\right)$$

and

$$\frac{\beta p_j^2}{2M} + \frac{2Ms^2}{\beta\hbar^2} = \frac{2M}{\beta\hbar^2}\left[\left(\frac{i\beta\hbar}{2} - t\right)^2 + \frac{\beta^2\hbar^2}{4}\right]\left\{\frac{\underline{p}_j}{M} + \frac{\underline{r}\,(\frac{i\beta\hbar}{2} - t)}{\left[(\frac{i\beta\hbar}{2} - t)^2 + \frac{\beta^2\hbar^2}{4}\right]}\right\}^2 + \frac{r^2\beta M}{2\left[(\frac{i\beta\hbar}{2} - t)^2 + \frac{\beta^2\hbar^2}{4}\right]} \quad . \tag{D.13}$$

Thus,

$$G_s(\underline{r},t) = \exp\left\{-\frac{\beta M r^2}{2\left[(\frac{i\beta\hbar}{2} - t)^2 + \frac{\beta^2\hbar^2}{4}\right]}\right\}\int d\underline{p}_j \exp\left[-\frac{2M}{\beta\hbar^2}\left[(\frac{i\beta\hbar}{2} - t)^2 + \frac{\beta^2\hbar^2}{4}\right]\left\{\frac{\underline{p}_j}{M} + \frac{\underline{r}(\frac{i\beta\hbar}{2} - t)}{\left[(\frac{i\beta\hbar}{2} - t)^2 - \frac{\beta^2\hbar^2}{4}\right]}\right\}^2\right] \quad , \tag{D.14}$$

and after following a procedure entirely analogous to that used to evaluate the integral in (D.1), we get

$$G_s(\underline{r},t) = \left[\frac{M\beta}{2\pi t(t - i\beta\hbar)}\right]^{3/2}\exp\left[-\frac{Mr^2\beta}{2t(t - i\beta\hbar)}\right] \tag{D.15}$$

and

$$\begin{aligned} S_s(\underline{\Delta p},\epsilon) &= \frac{1}{2\pi\hbar}\int d\underline{r}\int dt \exp\left[\frac{i}{\hbar}(\underline{\Delta p}\cdot\underline{r} - \epsilon t)\right] G_s(\underline{r},t) \\ &= \frac{1}{2\pi\hbar}\int dt \exp\left[-\frac{i\epsilon t}{\hbar}\right]\exp\left[-\frac{\Delta p^2 t}{2M\hbar^2\beta}(t - i\beta\hbar)\right] \\ &= \exp\left[\frac{\beta\epsilon}{2}\right]\exp\left[-\frac{\beta\Delta p^2}{8M}\right]\left(\frac{\beta M}{2\pi\Delta p^2}\right)^{1/2}\exp\left[-\frac{M\epsilon^2\beta}{2\Delta p^2}\right] \quad . \end{aligned} \tag{D.16}$$

Equations (D.15) and (D.16) are exact because the correction terms of $\mathcal{O}(\hbar^2)$ in (D.11), containing the potential of interaction between particles of the system, vanish for an ideal gas.

The classical equivalent of (D.15) obtained according to (D.12) is

$$G_s^c(\underline{r},t) = \left[\frac{M\beta}{2\pi t^2}\right]^{3/2} \exp\left[-\frac{Mr^2\beta}{2t^2}\right], \tag{D.17}$$

and inserting this result into Eq. (5.31) gives

$$\begin{aligned} S_{sv}(\underline{\Delta p},\epsilon) &= \frac{1}{2\pi\hbar}\left(\frac{M\beta}{2\pi}\right)^{3/2}\int d\underline{r}\ \exp\left[\frac{i}{\hbar}\ \underline{\Delta p}\cdot\underline{r}\right]\int_{-\infty}^{\infty} dt\ \frac{e^{-i\epsilon t}}{t^3}\ \exp\left[-\frac{Mr^2\beta}{2t^2}\right] \\ &= \frac{1}{2\pi\hbar}\int dt\ e^{-i\epsilon t}\ \exp\left[-\frac{\Delta p^2 t^2}{\hbar^2 2M\beta}\right] \\ &= \left(\frac{\beta M}{2\pi\Delta p^2}\right)^{1/2}\exp\left[-\frac{M\epsilon^2\beta}{2\Delta p^2}\right] . \end{aligned} \tag{D.18}$$

Moreover, Eq. (D.16) is entirely classical containing no powers of $\hbar$ at all. Hence,

$$\begin{aligned} S_s(\underline{\Delta p},\epsilon)_{I.g.} = \lim_{\hbar\to 0} S_s(\underline{\Delta p},\epsilon)_{I.g.} &= \exp\left[\frac{\beta\epsilon}{2}\right]\exp\left[-\frac{\beta\Delta p^2}{8M}\right] S_{sv}(\underline{\Delta p},\epsilon) \\ &\neq S_{sv}(\underline{\Delta p},\epsilon) , \end{aligned} \tag{D.19}$$

i.e., the Fourier transform of the time displaced pair distribution function $G_s^c(\underline{r},t)$ does not give the correct classical limit for the scattering function $S_s(\underline{\Delta p},\epsilon)$. Q.E.D. This discrepancy disappears, of course, when $\underline{\Delta p}\to 0$.

APPENDIX E

THE ASYMPTOTIC EXPANSION OF THE INTERMEDIATE SCATTERING FUNCTION

In Chapter V [Eq. (5.10)] we have obtained an asymptotic series expansion in powers of $\hbar$ for the function $\Omega_W(\underline{p},\underline{q},\tau)$. In order to have a similar power series for the intermediate scattering function $\chi(\underline{\Delta}p,\hbar\tau)$, there is the additional requirement that the thermal averages

$$< \exp\left[-\frac{i}{\hbar}\underline{\Delta}p\cdot\underline{q}_i\right]\exp\left[\frac{1}{2}\underline{\Delta}p\cdot\vec{\nabla}_{p_i}\right]f(\tau) >_{TC} \qquad (E.1)$$

and

$$< \exp\left[-\frac{i}{\hbar}\underline{\Delta}p\cdot\underline{q}_i\right]\exp\left[\frac{1}{2}\underline{\Delta}p\cdot\vec{\nabla}_{p_i}\right]F_n(\tau)f(\tau) >_{TC}, \quad \text{for} \quad n \geq 3 \qquad (E.2)$$

in Eq. (5.18) be of the same order in $\hbar$.

For the diagonal component (i=j) of $\chi(\underline{\Delta}p,\hbar\tau)$, this follows immediately since the essential singularity inside the thermal average bracket is only apparent and disappears when $f(\tau)$ is expanded in a Maclaurin series. Thus, Eqs. (E.1) and (E.2) are both, in this case, of order $\hbar^0$.

For $i\neq j$, however, the essential singularity is real and a Maclaurin expansion of $f(\tau)$ in (E.1) and (E.2) yields

$$< \exp\left[-\frac{i}{\hbar}\,\underline{\Delta p}\cdot\underline{q}_i\right]\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_i}\right]\,F_n(\tau)f(\tau) >_{\substack{TC \\ i\neq j}}$$

$$= \;< \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot(\underline{q}_j-\underline{q}_i)\right]\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_i}\right]\,F_n(\tau)\exp\left[\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right] \qquad (E.3)$$

$$(x)\;\;[1 + \mathcal{O}(\hbar)\,] >_{\substack{TC \\ i\neq j}}\;,$$

and

$$< \exp\left[\frac{i}{\hbar}\,\underline{\Delta p}\cdot(\underline{q}_j-\underline{q}_i)\right]\exp\left[\frac{1}{2}\,\underline{\Delta p}\cdot\vec{\nabla}_{p_i}\right]\;\exp\left[\frac{i\tau}{M}\,\underline{\Delta p}\cdot\underline{p}_j\right][1 + \mathcal{O}(\hbar)\,] >_{\substack{TC \\ i\neq j}}\,, \qquad (E.4)$$

respectively.

Because of the additional factor $F_n(\tau)$, it is not clear that (E.3) is of the same order in $\hbar$ as (E.4) and, consequently, that an asymptotic expansion for the interference part of $\chi(\underline{\Delta p},\hbar\tau)$ exists.

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