

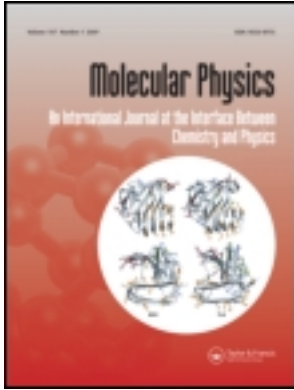
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## Inelastic neutron scattering from classical systems

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## Inelastic neutron scattering from classical systems Stationary phase approximation of the scattering law

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The scattering law for inelastic neutron scattering from classical systems is derived by treating the wavefunctions of the scattering system in the stationary phase approximation and taking the classical limit of the Wigner phase space distribution function. In this way recoil effects are properly accounted for and the scattering law fulfils the relation of detailed balance. It is shown why classical van Hove correlation functions do not properly describe neutron scattering from classical systems.

### 1. Introduction

In a famous paper [1] van Hove showed that the differential cross-section for thermal neutron scattering from condensed matter systems can be expressed in terms of quantum time correlation functions of the spatially Fourier transformed particle density. It seems natural to replace the quantum correlation functions by their classical counterparts if scattering from classical systems is considered [2]. This approach has, however, two well known deficiencies:

- (1) the resulting scattering law, also called dynamic structure factor, does not fulfil the relation of detailed balance, and
- (2) recoil effects due to the momentum transfer from the neutron on the scattering atom are neglected. The influence of recoil effects on inelastic neutron scattering spectra has been demonstrated recently by Tomkinson [3].

To account approximately for recoil and detailed balance several prescriptions have been suggested, see e.g. [4–6]. Usually they are referred to as semiclassical corrections [6–8], treating  $\hbar$  as a small quantity and recoil as a first order quantum effect [8]. Looking at simple systems, like the ideal gas and the harmonic oscillator, it becomes obvious that the validity of the various prescriptions depends on the system and the momentum transfer under consideration. Since recoil is treated as a quantum effect of first order in  $\hbar$ , none of them can be used safely in the regime of high momentum transfers  $\hbar q$  where recoil effects are dominant. Moreover, the treatment of recoil as a quantum effect shows a conceptual problem of the semiclassical corrections, since recoil can be described fully in a classical picture [9].

Recently, Evans and Ogeda [10] suggested an approach in which the scattering law is expressed in terms of the density response to a suitably chosen ‘kick’ field. For classical systems the density response is then obtained in the framework of

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classical mechanics. By construction the resulting scattering law fulfils the detailed balance relation. The authors show that the  $f$ -sum rule is fulfilled, i.e., that the first frequency moment of the dynamic structure factor is correct.

The aim of this paper is to give a rigorous description of neutron scattering from classical systems. This is achieved by writing the so-called intermediate scattering function as a Feynman path integral over closed paths along the real and imaginary time axes. The classical limit is then performed by invoking the stationary phase approximation for the Feynman propagators in real time and a carefully chosen 'high temperature' or 'short time' approximation for the propagator in imaginary time. This short time approximation is equivalent to replacing the Wigner distribution function for quantum phase space averages by the classical Boltzmann weight. The resulting dynamic structure factor is found to be always real, as it should be, and fulfils the relation of detailed balance within the validity of the classical approximation. In addition, its first four frequency moments are found to be correct.

From a practical point of view it is important that the scattering law can be calculated by molecular dynamics simulation, using perturbation schemes [10, 11]. This is useful in all cases in which the scattering system cannot be treated in the Gaussian approximation [12, 13]. In the Gaussian approximation the scattering law is determined completely by the velocity autocorrelation function of the particles. In the classical limit it can be constructed from the corresponding classical correlation function [12]. There are, however, situations where the Gaussian approximation is not valid. An example is scattering from molecular gases and liquids at high momentum transfers, a situation that is typically encountered when studying these systems with energetic neutrons produced by spallation sources or other sources for hot neutrons. This concerns in particular molecular liquids and gases containing hydrogen atoms with low effective rotational masses [14], as  $\text{CH}_4$  and  $\text{CH}_2\text{Cl}_2$  [15, 16]. Even though a classical description for such systems is in most cases adequate—giving, in principle, the possibility of realistic molecular dynamics simulations for direct comparison to neutron scattering experiments—it is impossible to obtain reliable differential neutron scattering cross-sections due to strong recoil effects.

The paper is organized as follows: In section 2 the basic quantities and relations involved in the theory of neutron scattering are introduced and briefly explained. Section 3 contains the central part in which the stationary phase approximation of the scattering law is derived. The summary and the concluding discussion are given in section 4. The appendixes contain proofs of some essential properties of the derived scattering law and a section on coherent scattering.

## 2. Basic definitions and relations

### 2.1. Correlation functions

In the following we consider a system consisting of  $N$  identical atoms, labelled by Greek characters. The double differential cross-section for the scattering of thermal neutrons reads

$$\frac{d^2\sigma}{d\Omega d\omega} = N \frac{k}{k_0} \{b_{coh}^2 S_{coh}(\mathbf{q}, \omega) + b_{inc}^2 S_{inc}(\mathbf{q}, \omega)\}. \quad (1)$$

$S_{coh}(\mathbf{q}, \omega)$  and  $S_{inc}(\mathbf{q}, \omega)$  are the coherent and incoherent dynamic structure factors,

with  $\mathbf{q}$  and  $\omega$  being the momentum and energy transfer in units of  $\hbar$ :

$$\mathbf{q} \doteq \mathbf{k}_0 - \mathbf{k}. \quad (2)$$

$$\omega \doteq \epsilon_0 - \epsilon. \quad (3)$$

Here  $\mathbf{k}_0$  and  $\epsilon_0$  are the momentum and the energy of the incident neutrons. The quantities  $b_{coh}$  and  $b_{inc}$  denote the coherent and the incoherent scattering lengths, respectively [17]. The energies are related to the corresponding momenta by the dispersion relation

$$\epsilon_{(0)} = \frac{\hbar k_{(0)}^2}{2m}, \quad (4)$$

where  $m$  is the neutron mass. Both dynamic structure factors can be expressed in terms of time correlation functions which are called intermediate scattering functions (the labels 'coh' and 'inc' are dropped if a relation applies to both coherent and incoherent scattering):

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp[-i\omega t] F(\mathbf{q}, t). \quad (5)$$

By introducing the spatially Fourier transformed particle density operators

$$\hat{\rho}(\mathbf{q}, t) \doteq \frac{1}{\sqrt{N}} \sum_{\alpha} \exp[i\mathbf{q} \cdot \hat{\mathbf{R}}_{\alpha}(t)], \quad (6)$$

$$\hat{\rho}_s(\mathbf{q}, t) \doteq \exp[i\mathbf{q} \cdot \hat{\mathbf{R}}_s(t)], \quad (7)$$

with  $\hat{\mathbf{R}}_{\alpha}$  and  $\hat{\mathbf{R}}_s$  being the position operators of atom  $\alpha$  and an arbitrarily tagged scattering atom  $s$ , the intermediate scattering functions can be written as

$$F_{coh}(\mathbf{q}, t) = \langle \hat{\rho}^{\dagger}(\mathbf{q}, 0) \hat{\rho}(\mathbf{q}, t) \rangle, \quad (8)$$

$$F_{inc}(\mathbf{q}, t) = \langle \hat{\rho}_s^{\dagger}(\mathbf{q}, 0) \hat{\rho}_s(\mathbf{q}, t) \rangle. \quad (9)$$

The brackets denote a quantum thermal average and the symbol  $\dagger$  indicates the adjoint operator. The time dependence of the particle density operators is given by the Heisenberg picture.

Finally, the van Hove correlation functions are defined as

$$G(\mathbf{r}, t) \doteq \frac{1}{(2\pi)^3} \int d^3q \exp[-i\mathbf{q} \cdot \mathbf{r}] F(\mathbf{q}, t). \quad (10)$$

If the right hand sides of equations (8) and (9) are read as classical time correlation functions they can be interpreted as conditional probabilities:  $G_{coh}(\mathbf{r}, t)$  gives the probability of finding a particle at time  $t$  at the position  $\mathbf{r}$ , given that another or the same particle was at time  $t = 0$  at the position  $\mathbf{r} = \mathbf{0}$ .  $G_{inc}(\mathbf{r}, t)$  gives the probability of finding a particle at time  $t$  at the position  $\mathbf{r}$ , given the *same* particle was at time  $t = 0$  at the position  $\mathbf{r} = \mathbf{0}$ .

## 2.2. Symmetries

From the general definition of quantum time correlation functions the following symmetry relations are readily derived:

$$F^*(\mathbf{q}, t) = F(\mathbf{q}, -t), \quad (11)$$

$$F(\mathbf{q}, t) = F(-\mathbf{q}, -t + i\beta\hbar). \quad (12)$$

Equation (11) shows that real part of  $F(\mathbf{q}, t)$  is an even function in time and the imaginary part is an odd function in time, ensuring that the dynamic structure factor is real. From equation (12) one obtains the relation of detailed balance:

$$S(\mathbf{q}, \omega) = \exp[\beta\hbar\omega]S(-\mathbf{q}, -\omega). \quad (13)$$

Combination of equations (10–12) yields

$$G^*(\mathbf{r}, t) = G(\mathbf{r}, t + i\beta\hbar), \quad (14)$$

showing that the van Hove correlation functions are complex functions in the quantum case.

If the quantum correlation functions defining the intermediate scattering functions are replaced by classical correlation functions, one obtains consistently the same symmetry relations as by setting  $\hbar$  to zero in equations (12–14) wherever it appears. The detailed balance relation is no longer fulfilled and the van Hove correlation functions are real, allowing the simple interpretation in terms of conditional probabilities mentioned above. As van Hove showed in a later paper [18], the imaginary part of  $G(\mathbf{r}, t)$  describes the local change of the particle density due to the impact of the neutrons. Therefore recoil effects are absent in the limit  $\hbar \rightarrow 0$ .

### 3. Scattering from classical systems

In the following we will discuss scattering from classical systems in terms of the incoherent intermediate scattering function. The discussion of coherent scattering or, more precisely, of *distinct* scattering which describes static and dynamic *cross*-correlations between atomic positions, is postponed to the appendix. The reason is twofold. First, from a practical point of view, distinct scattering normally can be neglected for high momentum transfers [9] where semiclassical corrections fail. If scattering from molecular liquids is considered, this applies to *intermolecular* scattering caused by cross-correlations between atoms on different molecules. Second, distinct scattering has an intrinsic quantum property [9] which is, however, apparent only in the regime of deep inelastic scattering. If cross-correlations in that regime are visible, as e.g. due to chemical bonds in molecules, they should be treated by a quantum mechanical model [19, 20] since a classical description is not appropriate.

#### 3.1. Wick's representation of $F(\mathbf{q}, t)$

Following Wick [9] we write  $F(\mathbf{q}, t) \equiv F_{\text{inc}}(\mathbf{q}, t)$  explicitly as

$$F(\mathbf{q}, t) = Z^{-1} \text{tr} \left\{ \exp[-\beta\hat{H}] \exp[-i\mathbf{q} \cdot \hat{\mathbf{R}}_s] \exp\left[\frac{i}{\hbar}\hat{H}t\right] \exp[i\mathbf{q} \cdot \hat{\mathbf{R}}_s] \exp\left[-\frac{i}{\hbar}\hat{H}t\right] \right\}, \quad (15)$$

using equations (7) and (9) and the general definition of quantum time correlation functions. The Hamilton operator of the system is denoted  $\hat{H}$ ,  $\beta = (k_B T)^{-1}$  and  $Z = \text{tr}\{\exp(-\beta\hat{H})\}$  is the quantum partition function of the system ('tr' stands for

'trace'). The Hamilton operator is assumed to have the standard form

$$\hat{H} = \sum_{\alpha} \frac{\hat{p}_{\alpha}^2}{2M} + V(\hat{\mathbf{R}}_1, \dots, \hat{\mathbf{R}}_N). \quad (16)$$

$M$  is the mass of an atom. Equation (15) can now be written in a different form by observing that the operators  $\exp(-i\mathbf{q} \cdot \hat{\mathbf{R}}_s)$  and  $\exp(i\mathbf{q} \cdot \hat{\mathbf{R}}_s)$  generate a translation  $\hat{p}_{\alpha} \rightarrow \hat{p}_{\alpha} + \hbar\mathbf{q}\hat{\delta}_{\alpha s}$  in the operator  $\exp[(i/\hbar)\hat{H}t]$  between them ( $\hat{\delta}_{\alpha\beta}$  is a compact notation of the Kronecker symbol  $\delta_{\alpha\beta}$  times the unit operator):

$$F(\mathbf{q}, t) = Z^{-1} \text{tr} \left\{ \exp[-\beta\hat{H}] \exp\left[\frac{i}{\hbar}\hat{H}_q t\right] \exp\left[-\frac{i}{\hbar}\hat{H}t\right] \right\}. \quad (17)$$

The 'shifted' Hamiltonian  $\hat{H}_q$  reads

$$\hat{H}_q = \sum_{\alpha} \frac{(\hat{p}_{\alpha} + \hbar\mathbf{q}\hat{\delta}_{\alpha s})^2}{2M} + V(\hat{\mathbf{R}}_1, \dots, \hat{\mathbf{R}}_N). \quad (18)$$

Equation (17) shows that the scattering system is influenced by the scattering process since the Hamiltonians appearing in the forward and backward propagators  $\exp[-(i/\hbar)\hat{H}t]$  and  $\exp[(i/\hbar)\hat{H}_q t]$  are *different*.

### 3.2. $F(\mathbf{q}, t)$ in terms of propagators

Equation (17) can be exploited further in the position space representation by inserting complete sets  $|\mathbf{R}\rangle \doteq |\mathbf{R}_1\rangle \otimes \dots \otimes |\mathbf{R}_N\rangle$  of orthonormal eigenkets of the position operators (sans serif boldface characters denote  $3N$ -dimensional vectors). Using the notation of Feynman [21] we define

$$K(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) \doteq \langle \mathbf{R}_b | \exp\left[-\frac{i}{\hbar}\hat{H}(t_b - t_a)\right] | \mathbf{R}_a \rangle, \quad (19)$$

$$K(\mathbf{R}_b, \mathbf{R}_a, -i\beta\hbar) \doteq \langle \mathbf{R}_b | \exp[-\beta\hat{H}] | \mathbf{R}_a \rangle. \quad (20)$$

$K(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a)$  and  $K(\mathbf{R}_b, \mathbf{R}_a, -i\beta\hbar)$  are the propagators of the Schrödinger equation in the position space representation for real and imaginary times. In the following they will be referred to simply as propagators. In terms of propagators the intermediate scattering function can now be written as

$$F(\mathbf{q}, t) = Z^{-1} \iint \int d^{3N}R_0 d^{3N}R'_0 d^{3N}R_t K(\mathbf{R}_0, \mathbf{R}'_0, -i\beta\hbar) K_q(\mathbf{R}'_0, \mathbf{R}_t, -t) K(\mathbf{R}_t, \mathbf{R}_0, t) \quad (21)$$

where  $K_q(\mathbf{R}'_0, \mathbf{R}_t, -t)$  is the backward propagator belonging to the Hamiltonian  $\hat{H}_q$ . The partition function reads

$$Z = \int d^{3N}R_0 K(\mathbf{R}_0, \mathbf{R}_0, -i\beta\hbar). \quad (22)$$

The real time propagators fulfil the Schrödinger equation with respect to  $(\mathbf{R}_b, t_b)$  and

the adjoint Schrödinger equation with respect to  $(\mathbf{R}_a, t_a)$  [21]:

$$i\hbar \frac{\partial}{\partial t_b} K(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) = \left\{ -\frac{\hbar^2}{2M} \left( \frac{\partial}{\partial \mathbf{R}_b} \right)^2 + V(\mathbf{R}_b) \right\} K(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a), \quad (23)$$

$$-i\hbar \frac{\partial}{\partial t_a} K(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) = \left\{ -\frac{\hbar^2}{2M} \left( \frac{\partial}{\partial \mathbf{R}_a} \right)^2 + V(\mathbf{R}_a) \right\} K(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a). \quad (24)$$

The set of Schrödinger equations belonging to the 'shifted' propagator  $K_q(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a)$  is obtained by replacing the momentum operator  $-i\hbar(\partial/\partial \mathbf{R}_s)$  of the scattering atom  $s$  by  $-i\hbar(\partial/\partial \mathbf{R}_s) + \hbar \mathbf{q}$ . To maintain a compact notation we introduce the  $3N$ -dimensional column vector  $\mathbf{Q}_s$ , defined such that its elements are zero, except for the elements corresponding to particle  $s$ , which equal  $q_x, q_y$ , and  $q_z$ , respectively:

$$\mathbf{Q}_s \doteq (0, \dots, 0, q_x, q_y, q_z, 0, \dots, 0)^T. \quad (25)$$

The symbol ' $T$ ' denotes a transposition. Using this definition the Schrödinger equations for  $K_q(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a)$  read

$$i\hbar \frac{\partial}{\partial t_b} K_q(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) = \left\{ -\frac{\hbar^2}{2M} \left( \frac{\partial}{\partial \mathbf{R}_b} + i\mathbf{Q}_s \right)^2 + V(\mathbf{R}_b) \right\} K_q(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) \quad (26)$$

$$-i\hbar \frac{\partial}{\partial t_a} K_q(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) = \left\{ -\frac{\hbar^2}{2M} \left( \frac{\partial}{\partial \mathbf{R}_a} - i\mathbf{Q}_s \right)^2 + V(\mathbf{R}_a) \right\} K_q(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a). \quad (27)$$

From these two equations and (23) and (24) follows a simple relation between the propagators  $K_q(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a)$  and  $K(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a)$ :

$$K_q(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) = K(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) \exp[-i\mathbf{Q}_s \cdot (\mathbf{R}_b - \mathbf{R}_a)]. \quad (28)$$

The intermediate scattering function as given in equation (21) can be interpreted intuitively using the path integral form of the propagators [21], especially with respect to the classical limit. The real time propagators are then written as

$$K(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) = \int \mathcal{D}[\mathbf{R}(\tau)] \exp\left(\frac{i}{\hbar} A[\mathbf{R}(\tau)]\right) \quad (29)$$

where  $\mathcal{D}[\mathbf{R}(\tau)]$  is the volume element in path space.  $A[\mathbf{R}(\tau)]$  is the action of a path  $\mathbf{R}(\tau)$  that starts at  $\mathbf{R}(t_a) = \mathbf{R}_a$  and ends at  $\mathbf{R}(t_b) = \mathbf{R}_b$ :

$$A[\mathbf{R}(\tau)] = \int_{t_a}^{t_b} d\tau L(\mathbf{R}(\tau), \dot{\mathbf{R}}(\tau)). \quad (30)$$

$L$  is the Lagrangian of the system and the dot stands for a time derivative. Assuming the standard form (16) for the Hamiltonian, the Lagrangian reads

$$L(\mathbf{R}, \dot{\mathbf{R}}) = \frac{1}{2} M \dot{\mathbf{R}}^2 - V(\mathbf{R}). \quad (31)$$

The form of the volume element  $\mathcal{D}[\mathbf{R}(\tau)]$  appearing in equation (29) is not of importance here; it is sufficient to note that the propagator is written as a 'sum over all possible paths' going from  $\mathbf{R}(t_a) = \mathbf{R}_a$  to  $\mathbf{R}(t_b) = \mathbf{R}_b$  where each path is assigned a weight  $\exp\{(i/\hbar)A[\mathbf{R}(\tau)]\}$ . Correspondingly, the path integral form of the shifted

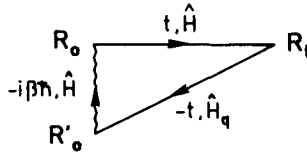


Figure 1. Diagrammatic representation of  $F(\mathbf{q}, t)$  as a sum over closed paths  $\mathbf{R}_0 \rightarrow \mathbf{R}_t \rightarrow \mathbf{R}'_0 \rightarrow \mathbf{R}_0$ . For each section the time difference between end point and initial point together with the corresponding Hamiltonian are given.

propagator is given by

$$K_q(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) = \int \mathcal{D}[\mathbf{R}(\tau)] \exp \left[ \frac{i}{\hbar} A_q[\mathbf{R}(\tau)] \right], \quad (32)$$

absorbing the argument of the exponential on the RHS of equation (28) into the action  $A_q[\mathbf{R}(\tau)]$ :

$$A_q[\mathbf{R}(\tau)] = A[\mathbf{R}(\tau)] - \hbar \mathbf{Q}_s \cdot (\mathbf{R}_b - \mathbf{R}_a) = \int_{t_a}^{t_b} d\tau L_q(\mathbf{R}(\tau), \dot{\mathbf{R}}(\tau)), \quad (33)$$

where

$$L_q(\mathbf{R}, \dot{\mathbf{R}}) = \frac{1}{2} M \dot{\mathbf{R}}^2 - V(\mathbf{R}) - \hbar \mathbf{Q}_s \cdot \dot{\mathbf{R}}. \quad (34)$$

The term  $-\hbar \mathbf{Q}_s \cdot \dot{\mathbf{R}}$  can be considered as a coupling term describing the ‘kick’  $\hbar \mathbf{q}$  transmitted to the scattering atom.

The path integral form of the propagators in imaginary time reads [21]

$$K(\mathbf{R}_b, \mathbf{R}_a, -i\beta\hbar) = \int \mathcal{D}[\mathbf{R}(\tau)] \exp(-\beta \bar{H}[\mathbf{R}(\tau)]) \quad (35)$$

where  $\bar{H}[\mathbf{R}(\tau)]$  is the average energy along a path connecting  $\mathbf{R}(0) = \mathbf{R}_a$  and  $\mathbf{R}(\beta\hbar) = \mathbf{R}_b$ :

$$\bar{H}[\mathbf{R}(\tau)] = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\tau H(\mathbf{R}(\tau), \dot{\mathbf{R}}(\tau)). \quad (36)$$

Here the Hamiltonian is written in terms of coordinates and velocities:

$$H(\mathbf{R}, \dot{\mathbf{R}}) = \frac{1}{2} M \dot{\mathbf{R}}^2 + V(\mathbf{R}). \quad (37)$$

According to equation (21) the intermediate scattering function can now be interpreted as the sum over all possible *closed* paths

$$\mathbf{R}_0 \xrightarrow{\mathbf{R}(\tau)} \mathbf{R}_t \xrightarrow{\mathbf{R}'(\tau)} \mathbf{R}'_0 \xrightarrow{\mathbf{R}''(\tau)} \mathbf{R}_0$$

(see figure 1) where the different sections have the weights  $\exp \{ (i/\hbar) A[\mathbf{R}(\tau)] \}$ ,  $\exp \{ (i/\hbar) A_q[\mathbf{R}'(\tau)] \}$ , and  $\exp(-\beta \bar{H}[\mathbf{R}''(\tau)])$ , respectively.

### 3.3. Classical limit of $F(\mathbf{q}, t)$

To find the classical limit of  $F(\mathbf{q}, t)$ , we rewrite the propagator  $K(\mathbf{R}_0, \mathbf{R}'_0, i\beta\hbar)$  appearing in equation (21) in terms of the Wigner phase space distribution function. Wigner showed [22] that one can define a quantum phase space distribution



function as a generalization of the classical Boltzmann weight in order to calculate thermal averages as phase space averages. Using our notation, the Wigner distribution function reads

$$f(\mathbf{P}, \mathbf{R}) \doteq \frac{1}{(2\pi\hbar)^{3N}} \int d^{3N}y \exp\left(-\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{y}\right) K(\mathbf{R} + \mathbf{y}/2, \mathbf{R} - \mathbf{y}/2, -i\beta\hbar). \quad (38)$$

The partition function is given by

$$Z = \int d^{3N}P d^{3N}R f(\mathbf{P}, \mathbf{R}). \quad (39)$$

Inversion of Equation (38) yields

$$K(\mathbf{R} + \mathbf{y}/2, \mathbf{R} - \mathbf{y}/2, -i\beta\hbar) = \int d^{3N}P \exp\left(\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{y}\right) f(\mathbf{P}, \mathbf{R}). \quad (40)$$

Setting

$$\bar{\mathbf{R}}_0 = \frac{1}{2}(\mathbf{R}_0 + \mathbf{R}'_0), \quad (41)$$

the intermediate scattering function can be cast into the form

$$F(\mathbf{q}, t) = Z^{-1} \iiint d^{3N}P_0 d^{3N}R_0 d^{3N}R'_0 d^{3N}R_t \exp\left[\frac{i}{\hbar} \mathbf{P}_0 \cdot (\mathbf{R}_0 - \mathbf{R}'_0)\right] f(\mathbf{P}_0, \bar{\mathbf{R}}_0) \\ \times K_q(\mathbf{R}'_0, \mathbf{R}_t, -t) K(\mathbf{R}_t, \mathbf{R}_0, t). \quad (42)$$

All quantum properties of  $F(\mathbf{q}, t)$  are now concentrated in the Wigner distribution function and the real time propagators.

### 3.3.1. Stationary phase approximation

In the classical limit the actions appearing in the real time propagators according to equation (29) will be much larger than  $\hbar$ ,

$$|A| \gg \hbar. \quad (43)$$

This leads to strong oscillations of the weights  $\exp\{(i/\hbar)A[\mathbf{R}(\tau)]\}$  with even slight variations of the paths such that only the classical path survives for which the action is stationary. The real time propagators approach the form [21], [23]

$$K^{\text{cl}}(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) \propto \exp\left[\frac{i}{\hbar} A(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a)\right], \quad (44)$$

where  $A(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a)$  is the classical action

$$A(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) \doteq A[\mathbf{R}_{\text{cl}}(\tau)]. \quad (45)$$

The classical trajectory  $\mathbf{R}_{\text{cl}}(\tau)$  is a solution of the Euler–Lagrange equations [24]

$$\frac{d}{d\tau} \frac{\partial L}{\partial \dot{\mathbf{R}}} - \frac{\partial L}{\partial \mathbf{R}} = 0. \quad (46)$$

It is important to note that the Lagrangian  $L_q$  as given by equation (34) leads to the same equations of motion as the Lagrangian  $L$ . Therefore the actions  $A[\mathbf{R}(\tau)]$  and  $A_q[\mathbf{R}(\tau)]$  are minimized by the same paths and relation (28) is maintained in

the classical limit:

$$K_q^{cl}(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a) = \exp[-i\mathbf{Q}_s \cdot (\mathbf{R}_b - \mathbf{R}_a)] K^{cl}(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a). \quad (47)$$

It now follows from the representation of  $F(\mathbf{q}, t)$  given in equation (42) that the integrand is proportional to a total phase factor  $\exp[(i/\hbar)\Phi]$  in the classical limit. The phase function  $\Phi$  is given by

$$\Phi(\mathbf{P}_0, \mathbf{R}_0, \mathbf{R}_t, \mathbf{R}'_0; \hbar\mathbf{q}, t) = A(\mathbf{R}_t, \mathbf{R}_0, t) + A_q(\mathbf{R}'_0, \mathbf{R}_t, -t) + \mathbf{P}_0 \cdot (\mathbf{R}_0 - \mathbf{R}'_0) \quad (48)$$

with

$$A_q(\mathbf{R}'_0, \mathbf{R}_t, -t) = -A_q(\mathbf{R}_t, \mathbf{R}'_0, t) = -A(\mathbf{R}_t, \mathbf{R}'_0, t) + \hbar\mathbf{Q}_s \cdot (\mathbf{R}_t - \mathbf{R}'_0) \quad (49)$$

We emphasize that  $\hbar\mathbf{q}$  remains *finite* in the classical limit. Since the actions  $A(\mathbf{R}_t, \mathbf{R}_0, t)$  and  $A(\mathbf{R}_t, \mathbf{R}'_0, t)$  are large compared with  $\hbar$ , the phase factor  $\exp[(i/\hbar)\Phi]$  is a rapidly oscillating function in the arguments  $\mathbf{R}_0$ ,  $\mathbf{R}_t$ , and  $\mathbf{R}'_0$ . Therefore, starting with the integration over  $\mathbf{R}_0$ , which corresponds to the trace operation in the thermal average (equation (15)), contributions to the integral are obtained only if the integrand is smooth with respect to variations in  $\mathbf{R}_0$ . Consequently, the condition

$$\frac{\partial}{\partial \mathbf{R}_0} \Phi(\mathbf{P}_0, \mathbf{R}_0, \mathbf{R}_t, \mathbf{R}'_0; \hbar\mathbf{q}, t) = 0 \quad (50)$$

must be fulfilled. Definition (48) of  $\Phi$  shows that this relation defines  $\mathbf{R}_t$ :

$$\frac{\partial}{\partial \mathbf{R}_0} A(\mathbf{R}_t, \mathbf{R}_0, t) = -\mathbf{P}_0. \quad (51)$$

With  $\mathbf{R}_t$  now being a function of  $\mathbf{R}_0$ , the phase function  $\Phi$  varies with  $\mathbf{R}_0$  indirectly through  $\mathbf{R}_t$ . Therefore, to ensure the smoothness of the integrand with respect to the integration over  $\mathbf{R}_0$ , the additional condition

$$\frac{\partial}{\partial \mathbf{R}_t} \Phi(\mathbf{P}_0, \mathbf{R}_0, \mathbf{R}_t, \mathbf{R}'_0; \hbar\mathbf{q}, t) = 0 \quad (52)$$

must be satisfied. This equation fixes  $\mathbf{R}'_0$  and reads explicitly

$$\frac{\partial}{\partial \mathbf{R}_t} A(\mathbf{R}_t, \mathbf{R}'_0, t) = \frac{\partial}{\partial \mathbf{R}_t} A(\mathbf{R}_t, \mathbf{R}_0, t) + \hbar\mathbf{Q}_s, \quad (53)$$

using equations (48) and (49). Conditions (51) and (53) have a simple meaning. It follows from the Hamilton–Jacobi theory of classical mechanics that the derivatives of an action integral  $A(\mathbf{R}_b, \mathbf{R}_a, t_b - t_a)$  with respect to  $\mathbf{R}_b$  and  $\mathbf{R}_a$  give  $\mathbf{P}_b$  and  $-\mathbf{P}_a$ , with  $\mathbf{P}_b$  and  $\mathbf{P}_a$  being the canonical momenta at times  $t_b$  and  $t_a$ , respectively. Therefore equation (51) states that  $\mathbf{R}_t$  has to be chosen such that the initial momentum is just  $\mathbf{P}_0$ . In other words,  $\mathbf{R}_t$  is the endpoint of a classical trajectory starting with the initial coordinate  $\mathbf{R}_0$  and the initial momentum  $\mathbf{P}_0$ :

$$\mathbf{R}_t = \mathbf{R}(\mathbf{R}_0, \mathbf{P}_0, t). \quad (54)$$

Denoting the trajectory running from  $\mathbf{R}_t$  to  $\mathbf{R}'_0$  backwards in time (or, equivalently, from  $\mathbf{R}'_0$  to  $\mathbf{R}_t$  forwards in time) by  $\mathbf{R}'(\tau)$ , equation (53) can be phrased as

$$\mathbf{P}'_t = \mathbf{P}_t + \hbar\mathbf{Q}_s, \quad (55)$$

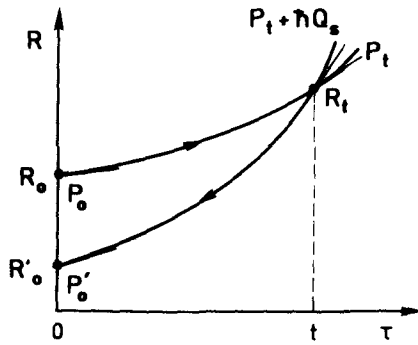


Figure 2. Classical path  $R_0 \rightarrow R_t \rightarrow R'_0$ . The slopes indicate the momenta.

which expresses the conservation of momentum. Consequently,  $R'_0$  is the endpoint of the trajectory  $R'(\tau)$  at  $\tau = 0$  that starts at  $\tau = t$  with the coordinate  $R_t$  and the momentum  $P'_t$  as given by equation (55)

$$R'_0 = R(R_t, P'_t, -t). \quad (56)$$

Combination of equations (54–56) shows that the classical path starts at  $R_0$  with a momentum  $P_0$ , evolves during a time  $t$  according to the classical equations of motion, then the scattering atom obtains a 'kick'  $\hbar q$  and the system evolves back in time arriving at  $R'_0 \neq R_0$  (see figure 2). We recall that boldface sans serif characters denote  $3N$ -dimensional vectors, specifying positions, momenta etc. for the whole system.

### 3.3.2. Classical limit of the Wigner distribution function

According to Wigner [22]  $f(\mathbf{P}, \mathbf{R})$  can be written as an expansion in even powers of  $\hbar$ ,

$$f(\mathbf{P}, \mathbf{R}) \propto \exp[-\beta H(\mathbf{P}, \mathbf{R})](1 + \hbar^2 g_2(\mathbf{P}, \mathbf{R}) + \hbar^4 g_4(\mathbf{P}, \mathbf{R}) + \dots), \quad (57)$$

with the Boltzmann factor as the leading term and the Hamilton function  $H(\mathbf{P}, \mathbf{R}) = (\mathbf{P}^2/2M) + V(\mathbf{R})$ . The functions  $g_{2n}(\mathbf{P}, \mathbf{R})$  contain the quantum corrections which can be neglected if

$$\beta \hbar \omega_0 \ll 1 \quad (58)$$

where the frequency  $\omega_0$  is given by the curvature of the potential function, i.e., by  $\omega_0^2 = M^{-1}V''(x)$  in the case of a one-dimensional harmonic oscillator. For many-body systems described by a pairwise additive potential energy this translates into

$$\lambda_T \ll \sigma, \quad (59)$$

with  $\lambda_T = \hbar(2\pi\beta/M)^{1/2}$  being the thermal wavelength and  $\sigma$  the typical interparticle distance.

Keeping in mind that the limit ' $\hbar \rightarrow 0$ ' is meant in the sense of expressions (58) and (59), it follows from expression (57) that the classical limit of the Wigner distribution function is just the Boltzmann weight,

$$f^{cl}(\mathbf{P}, \mathbf{R}) \propto \exp[-\beta H(\mathbf{P}, \mathbf{R})]. \quad (60)$$

This follows also from path integral representation (35) of the propagator in imaginary time and definition (38) of  $f(\mathbf{P}, \mathbf{R})$  if one approximates

$$\int_0^{\beta\hbar} d\tau V(\mathbf{R}(\tau)) \approx \beta\hbar V[(\mathbf{R}_b + \mathbf{R}_a)/2]. \quad (61)$$

This means that the curvature of the potential can be neglected for motion on the time scale  $\beta\hbar$  in imaginary time ('short time approximation').

### 3.3.3. The resulting formula for the intermediate scattering function

Making use now of the stationary phase approximation, i.e., retaining only the total weight  $\exp[(i/\hbar)\Phi]$  of the classical path  $\mathbf{R}_0 \rightarrow \mathbf{R}_t \rightarrow \mathbf{R}'_0$ , and taking the classical limit of the Wigner distribution function, it follows from equation (42) that

$$\begin{aligned} \tilde{F}^{cl}(\mathbf{q}, t) = Z_{cl}^{-1} \iint d^{3N}P_0 d^{3N}R_0 \exp \left[ -\beta \left( \frac{P_0^2}{2M} + V[\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t)] \right) \right] \\ \times \exp \left[ \frac{i}{\hbar} \Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t) \right] \end{aligned} \quad (62)$$

is the classical limit of  $F(\mathbf{q}, t)$ .  $\bar{\mathbf{R}}_0$  and the phase  $\Phi$  are determined entirely by the initial momenta and coordinates  $(\mathbf{P}_0, \mathbf{R}_0)$ , the time  $t$ , and the momentum transfer  $\hbar\mathbf{q}$ .  $Z_{cl}$  is the classical partition function. The tilde on the left-hand of equation (62) indicates the classical limit of  $F(\mathbf{q}, t)$  in the sense of expressions (43), (58) and (59).

To express  $\tilde{F}^{cl}(\mathbf{q}, t)$  as a classical thermal average and to clarify its relation to the intermediate scattering function  $F^{cl}(\mathbf{q}, t)$ , defined as the classical time correlation function, we introduce the quantities

$$\Delta V(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t) \doteq V[\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t)] - V(\mathbf{R}_0) \quad (63)$$

and

$$\Delta\Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t) \doteq \Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t) - \hbar\mathbf{Q}_s \cdot (\mathbf{R}_t - \mathbf{R}_0) \quad (64)$$

$$= A(\mathbf{R}_t, \mathbf{R}_0, t) - A(\mathbf{R}_t, \mathbf{R}'_0, t) + (\mathbf{P}_0 + \hbar\mathbf{Q}_s) \cdot (\mathbf{R}_0 - \mathbf{R}'_0). \quad (65)$$

We recall that  $\mathbf{R}_t$  and  $\mathbf{R}'_0$  are defined by expressions (54) and (56), respectively. Using the explicit expression for  $\mathbf{R}_t$ ,  $\tilde{F}^{cl}(\mathbf{q}, t)$  can be rewritten as

$$\begin{aligned} \tilde{F}^{cl}(\mathbf{q}, t) = Z_{cl}^{-1} \iint d^{3N}P_0 d^{3N}R_0 \exp[-\beta H(\mathbf{P}_0, \mathbf{R}_0)] \exp[-\beta \Delta V(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t)] \\ \times \exp \left[ \frac{i}{\hbar} \Delta\Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t) \right] \exp(i\mathbf{Q}_s \cdot [\mathbf{R}(\mathbf{P}_0, \mathbf{R}_0, t) - \mathbf{R}_0]). \end{aligned} \quad (66)$$

This is the central result of this paper. The intermediate scattering function is entirely expressed in classical variables. Planck's constant enters in  $\Delta V$  and  $\Delta\Phi$  through the momentum transfer  $\hbar\mathbf{q}$ . The classical intermediate scattering function  $F^{cl}(\mathbf{q}, t)$  can be retrieved by taking the formal limit  $\hbar \rightarrow 0$  of  $\tilde{F}^{cl}(\mathbf{q}, t)$ , as will be shown now. Since  $\mathbf{R}'_0$  approaches  $\mathbf{R}_0$  if  $\hbar$  and consequently the momentum transfer  $\hbar\mathbf{q}$  go to zero, it

follows immediately that

$$\lim_{\hbar \rightarrow 0} \Delta V(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t) = 0, \quad (67)$$

$$\lim_{\hbar \rightarrow 0} \Delta \Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t) = 0. \quad (68)$$

In the limit  $\hbar \rightarrow 0$  the phase factor  $\exp [(i/\hbar)\Delta\Phi]$  approaches an expression of the type  $\exp [0/0]$  and therefore the right-hand side of the identity

$$\lim_{\hbar \rightarrow 0} \frac{\Delta\Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t)}{\hbar} = \lim_{\hbar \rightarrow 0} \frac{\partial}{\partial \hbar} \Delta\Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t) \quad (69)$$

must be examined. The phase function  $\Delta\Phi$ , as given in equation (64), depends directly on  $\hbar$  and indirectly through  $\mathbf{R}'_0$  on  $\hbar$  (see expressions (55) and (56)). Using that  $(\partial/\partial \mathbf{R}'_0)A(\mathbf{R}_t, \mathbf{R}'_0, t) = -\mathbf{P}'_0$  one obtains

$$\lim_{\hbar \rightarrow 0} \frac{\partial}{\partial \hbar} \Delta\Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t) = \lim_{\hbar \rightarrow 0} \left\{ (\mathbf{P}'_0 - \mathbf{P}_0) \cdot \frac{\partial \mathbf{R}'_0}{\partial \hbar} + \mathbf{Q}_s \cdot (\mathbf{R}_0 - \mathbf{R}'_0) - \hbar \mathbf{Q}_s \cdot \frac{\partial \mathbf{R}'_0}{\partial \hbar} \right\} = 0, \quad (70)$$

since for  $\hbar \mathbf{q} \rightarrow \mathbf{0}$  the forwards and the backwards trajectories become identical and therefore  $\mathbf{R}'_0 \rightarrow \mathbf{R}_0$  and  $\mathbf{P}'_0 \rightarrow \mathbf{P}_0$ . Consequently,  $\lim_{\hbar \rightarrow 0} \exp [(i/\hbar)\Delta\Phi] = 1$ , and the intermediate scattering function as given by expression (66) approaches the usual classical form

$$\begin{aligned} \lim_{\hbar \rightarrow 0} \tilde{F}^{cl}(\mathbf{q}, t) &= Z_{cl}^{-1} \iint d^{3N} P_0 d^{3N} R_0 \exp [-\beta H(\mathbf{P}_0, \mathbf{R}_0)] \\ &\quad \times \exp [i\mathbf{Q}_s \cdot (\mathbf{R}(\mathbf{P}_0, \mathbf{R}_0, t) - \mathbf{R}_0)] \\ &\equiv F^{cl}(\mathbf{q}, t). \end{aligned} \quad (71)$$

It is now clear that taking the formal limit  $\lim_{\hbar \rightarrow 0}$  in  $F(\mathbf{q}, t)$  means to neglect  $\Delta V$  and  $\Delta\Phi$  resulting from the 'kick'  $\hbar \mathbf{q}$  which the scattering atom receives from the neutron.  $\Delta V$  and  $\Delta\Phi$  represent the *influence* of the neutron on the sample.

As shown in the appendixes, the dynamic structure factor  $\tilde{S}^{cl}(\mathbf{q}, \omega)$  corresponding to  $\tilde{F}^{cl}(\mathbf{q}, t)$  is always real and fulfils the relation of detailed balance, given that the scattering system can be described well by classical mechanics. Under the same condition the first four frequency moments of the dynamic structure factor are correct.

Another important property of  $\tilde{F}^{cl}(\mathbf{q}, t)$  is that the corresponding van Hove correlation function  $\tilde{G}^{cl}(\mathbf{r}, t)$  is *complex*, as for scattering from quantum systems. In the light of the above considerations a simple interpretation in terms of a conditional probability as described in section 2.1 is possible only if the influence of the neutron on the sample can be neglected, i.e. for sufficiently small momentum transfers.

### 3.4. Short time behaviour of $\tilde{F}^{cl}(\mathbf{q}, t)$

The following useful relation for the phase  $\Phi$  follows from equation (A. 20) in the appendixes.

$$\Phi(t) = (E_q(0) - E)t + O(t^2, \nabla V(\mathbf{R}_0)). \quad (72)$$

$\nabla V(\mathbf{R}_0)$  denotes the gradient of the potential at  $\mathbf{R}_0$ .  $E$  is the energy of the forward path and  $E_q(0)$  is the energy of the backward path, the 'reversal time'  $t$  being zero.

We emphasize that, in general,

$$E_q(t) = \frac{(\mathbf{P}(t) + \hbar\mathbf{Q}_s)^2}{2M} + V(\mathbf{R}(t)) \equiv E + \frac{\hbar\mathbf{Q}_s \cdot (\hbar\mathbf{Q}_s + 2\mathbf{P}(t))}{2M} \quad (73)$$

depends on the reversal time  $t$ , which should not be confused with the parameter  $\tau$  describing the time evolution.  $E_q$  is, of course, constant along the backward trajectory as  $E$  is constant on the forward trajectory. Since  $E_q(0) - E = [\hbar\mathbf{Q}_s \cdot (\hbar\mathbf{Q}_s + 2\mathbf{P}_0)/2M]$  does not depend on the potential, equation (72) states that the short time behaviour of  $\Phi$  is determined by inertial effects. For sufficiently small times one can truncate Taylor expansion (72) for  $\Phi(t)$  after the term  $\propto t$ . According to equation (A 22) one can write in the same approximation

$$\exp[-\beta V(\bar{\mathbf{R}}(t))] \approx \exp[-\beta V(\mathbf{R}_0)] \left[ 1 + \beta \frac{\hbar\mathbf{Q}_s \cdot \nabla V(\mathbf{R}_0)}{2M} t \right]. \quad (74)$$

Inserting expressions (72) and (74) into (62) for  $\tilde{F}^{cl}(\mathbf{q}, t)$  and assuming that the potential is even in  $\mathbf{R}_0$  yields

$$\lim_{t \rightarrow 0} \tilde{F}^{cl}(\mathbf{q}, t) = F_{id.gas}(\mathbf{q}, t). \quad (75)$$

$F_{id.gas}(\mathbf{q}, t)$  is the *exact* expression for the intermediate scattering function of an ideal Maxwell-Boltzmann gas:

$$F_{id.gas}(\mathbf{q}, t) = \exp \left[ -\frac{q^2 t(t - i\beta\hbar)}{2M\beta} \right]. \quad (76)$$

Relation (75) is just the impulse approximation of the intermediate scattering function [17] for high temperatures where the quantum thermal average can be replaced by a classical one. As shown in section 2.4 of appendix A, the first two frequency moments of the dynamic structure factor are the same as in the general quantum case. The first moment is known as recoil-moment and vanishes, as do all other odd moments, in the usual classical calculation where  $\hbar$  is put to zero and the dynamic structure factor is symmetric. Explicit expressions for the first four moments are listed in the table. Differences between quantum and classical systems appear only if

The coefficients  $C_{n,2k}$  as defined in equation (A 46).  $\gamma$  is the recoil coefficient  $\hbar/2M$ ,  $\langle \dots \rangle$  denotes a classical thermal average, and  $V^{(n)}$  and  $n$ th derivative of the potential  $V$  with respect to the  $z$  coordinate of the position of the scattering atom with  $\mathbf{q}$  being parallel to the  $z$  axis.  $\delta C_{4,2}$  and  $\delta C_{4,4}$  are negligible, as discussed in the text.

$n$	$2k$			
	2	4	6	8
1	$\gamma$	—	—	—
2	$\frac{1}{M\beta}$	$\gamma^2$	—	—
3	$\gamma \frac{\langle V^{(2)} \rangle}{M}$	$\gamma \frac{3}{M\beta}$	$\gamma^3$	—
4	$\frac{\langle V^{(2)} \rangle}{M^2\beta} + \delta C_{4,2}$	$\frac{3}{(M\beta)^2} + 4\gamma^2 \frac{\langle V^{(2)} \rangle}{M} + \delta C_{4,4}$	$\gamma^2 \frac{6}{M\beta}$	$\gamma^4$

interparticle forces are involved. For an ideal Maxwell-Boltzmann gas, where no interparticle forces are present, the stationary phase approximation for the scattering law is exact.

It is interesting to note that  $\tilde{F}_{id.gas}^{cl}(\mathbf{q}, t) \equiv F_{id.gas}(\mathbf{q}, t)$  can be obtained from the corresponding classical time correlation function by replacing  $t^2$  with  $t(t - i\beta\hbar)$ . This prescription has been suggested by Egelstaff as a general rule to correct classical scattering laws for recoil and detailed balance [5]. For the ideal gas this rule is equivalent to the prescription of Aamodt *et al.* [6].

### 3.5. An example

To illustrate the stationary phase approximation of the scattering law for a simple model system where the scattering atom moves under the influence of a position-dependent force we consider the case of a harmonic oscillator with a potential  $V(\mathbf{r}) = \frac{1}{2}M\omega_0^2|\mathbf{r}|^2$ , where  $\omega_0$  is the frequency of the oscillator. The problem can be solved by treating the motions along the  $x$ ,  $y$ , and  $z$  axes separately. Considering the motion along the  $x$  axis and observing conditions (54–56), the solution of the equations of motion yields

$$x(\tau) = x_0 \cos \omega_0 \tau + \frac{p_0}{M\omega_0} \sin \omega_0 \tau, \quad (77)$$

$$x'(\tau) = x_t \cos \omega_0(\tau - t) + \frac{p_t + \hbar q_x}{M\omega_0} \sin \omega_0(\tau - t), \quad (78)$$

with  $x_t = x(t)$  and  $p_t = M\dot{x}(t)$ . The position  $x'_0$  (see figure 2 and equation (56)) is given by

$$x'_0 = x'(0) = x_0 - \frac{\hbar q_x}{M\omega_0} \sin \omega_0 t. \quad (79)$$

Straightforward calculation yields the total phase (see equation (48))

$$\begin{aligned} \Phi(p_0, x_0; \hbar q_x, t) &= p_0 \frac{\hbar q_x}{M\omega_0} \sin \omega_0 t + x_0 \hbar q_x (\cos \omega_0 t - 1) \\ &+ (2 - \cos \omega_0 t) \frac{\hbar^2 q_x^2}{2M\omega_0} \sin \omega_0 t. \end{aligned} \quad (80)$$

The potential at  $\bar{x}_0$  reads

$$V(\bar{x}_0(p_0, x_0; \hbar q_x, t)) = \frac{1}{2}M\omega_0^2 \left( x_0 - \frac{\hbar q_x}{2M\omega_0} \sin \omega_0 t \right)^2. \quad (81)$$

Insertion of equation (80) and (81) into the general expression (62) yields  $\tilde{F}^{cl}(\mathbf{q}_x, t)$  after two integrations over Gaussian integrals. We give immediately the result for the three-dimensional case:

$$\tilde{F}^{cl}(\mathbf{q}, t) = \exp \left[ i \frac{\hbar q^2}{2M\omega_0} \sin \omega_0 t \right] \exp \left[ - \frac{q^2}{M\beta\omega_0^2} (1 - \cos \omega_0 t) \right]. \quad (82)$$

Comparison of  $\tilde{F}^{cl}(q, t)$  with the full quantum expression, given by [17]

$$F(q, t) = \exp \left[ i \frac{\hbar q^2}{2M\omega_0} \sin \omega_0 t \right] \exp \left[ -\frac{\hbar q^2}{2M\omega_0} \coth \frac{\beta \hbar \omega_0}{2} (1 - \cos \omega_0 t) \right], \quad (83)$$

shows that  $\tilde{F}^{cl}(q, t)$  is the high temperature limit of  $F(q, t)$ , which allows us to approximate  $\coth(\beta \hbar \omega_0 / 2) \approx 2 / \beta \hbar \omega_0$ . The formal limit  $\hbar \rightarrow 0$  gives the classical time correlation function  $F^{cl}(q, t)$ .

$$F(q, t) \xrightarrow{\beta \hbar \omega_0 \ll 1} \tilde{F}^{cl}(q, t), \quad (84)$$

$$F(q, t) \xrightarrow{\hbar \rightarrow 0} F^{cl}(q, t). \quad (85)$$

The following relation can be derived from the expression of the dynamic structure factor  $S(q, \omega)$  [17, 19]:

$$S(q, \omega) \xrightarrow{\beta \hbar \omega_0 \ll 1} \tilde{S}^{cl}(q, \omega) = \exp \left[ \frac{\beta \hbar \omega}{2} \right] S^{cl}(q, \omega). \quad (86)$$

Reading the right-hand side as a prescription to correct the classical scattering law for recoil and detailed balance shows that one obtains the Schofield correction [4].

#### 4. Summary and conclusion

The derivation of the scattering law for inelastic neutron scattering from classical systems as presented in previous sections shows that it is possible to describe this type of scattering for arbitrary momentum and energy transfers staying completely in the picture of classical dynamics with respect to the scattering system. As shown in the appendixes, an exception is deep inelastic distinct scattering, since the uncertainty relation between momentum and position of the scattering particle becomes important for this scattering process and a classical picture is not appropriate. The intermediate scattering function  $\tilde{F}^{cl}(q, t)$  can be written as a time dependent thermal average in which recoil effects and the detailed balance relation are maintained. The usual classical form  $F^{cl}(q, t)$  is obtained by performing the limit  $\hbar \rightarrow 0$  in a formal sense. The limit  $\hbar \rightarrow 0$  means effectively neglecting the influence of the neutron on the scattering system which results from the ‘kick’  $\hbar q$  transmitted to the scattering atom. In general, this influence cannot be taken into account by a simple correction rule but instead by a system-dependent correction of the phase space function to be averaged to obtain  $\tilde{F}^{cl}(q, t)$ . It is important to note that the expression for the intermediate scattering function contains only functions and functionals depending on classical phase space trajectories. Therefore the scattering law can be calculated by classical molecular dynamics simulation. The general form of  $\tilde{F}^{cl}(q, t)$  suggests a perturbation scheme as discussed in [11]. Here it should be pointed out that the assumption of a small perturbation, which is implicit in any approach using linear response theory, was not made for the derivation of the scattering law. For practical purposes, however, the energy transmitted from the neutron to the simulated system should be much smaller than the total energy of the system.

It has been shown that the stationary phase approximation of the scattering law for self-scattering is strictly correct in the short time limit, which implies that the



scattering law for an ideal Maxwell–Boltzmann gas is the same as found from a quantum mechanical treatment. The reason for the latter is simply that the reaction of an ideal gas to the impact of the neutron is determined completely by the mass of the scattering atom and its momentum before and after scattering, since no forces between the particles are present. Comparing the scattering laws of the ideal gas and the harmonic oscillator with their counterparts in the usual classical limit  $\hbar \rightarrow 0$  shows that one obtains, for these examples, well-known semiclassical corrections.

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## Appendix A

### Properties of $\tilde{F}^{cl}(\mathbf{q}, t)$

#### A.1. Taylor expansions of the dynamical variables

To check the essential properties of  $\tilde{F}^{cl}(\mathbf{q}, t)$ , such as the detailed balance relation and the first sum rules, one makes use of the fact that the total phase function  $\Phi$  introduced in section 3.3.1 (equation (48)) can be expressed as a functional of the forward and backward trajectory, which is itself entirely determined by the initial coordinates and momenta, the momentum transfer  $\hbar\mathbf{q}$ , and the time  $t$ . To show this we write it in the form

$$\begin{aligned} \Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t) = & A(\mathbf{R}_t, \mathbf{R}_0, t) - \mathbf{P}_0 \cdot (\mathbf{R}_t - \mathbf{R}_0) + A(\mathbf{R}'_0, \mathbf{R}_t, -t) \\ & - (\mathbf{P}_0 + \hbar\mathbf{Q}_s) \cdot (\mathbf{R}'_0 - \mathbf{R}_t), \end{aligned} \quad (\text{A } 1)$$

rearranging the term  $\mathbf{P}_0 \cdot (\mathbf{R}_0 - \mathbf{R}'_0)$  on the right-hand side of equation (48) as

$$\mathbf{P}_0 \cdot (\mathbf{R}_0 - \mathbf{R}'_0) = -\mathbf{P}_0 \cdot (\mathbf{R}_t - \mathbf{R}_0) - \mathbf{P}_0 \cdot (\mathbf{R}'_0 - \mathbf{R}_t). \quad (\text{A } 2)$$

$\mathbf{R}_t$  and  $\mathbf{R}'_0$  are given by equations (54) and (56). Introducing the functions  $F(\mathbf{P}, \mathbf{R})$  and  $F_q(\mathbf{P}, \mathbf{R})$ , defined as

$$F(\mathbf{P}, \mathbf{R}) \doteq L(\mathbf{P}, \mathbf{R}) - \frac{\mathbf{P}_0 \cdot \mathbf{P}}{M}, \quad (\text{A } 3)$$

$$F_q(\mathbf{P}, \mathbf{R}) \doteq L(\mathbf{P}, \mathbf{R}) - \frac{(\mathbf{P}_0 + \hbar\mathbf{Q}_s) \cdot \mathbf{P}}{M}, \quad (\text{A } 4)$$

with  $L(\mathbf{P}, \mathbf{R}) = \mathbf{P}^2/2M - V(\mathbf{R})$  being the Lagrangian in terms of the phase space variables  $\mathbf{P}$  and  $\mathbf{R}$ ,  $\Phi$  can be written as

$$\Phi(t) = \int_0^t d\tau F(\mathbf{P}(\tau), \mathbf{R}(\tau)) + \int_t^0 d\tau F_q(\mathbf{P}'(\tau), \mathbf{R}'(\tau)). \quad (\text{A } 5)$$

We use the shorthand notation  $\Phi(t) \equiv \Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t)$  since only the time dependence is of interest for the moment.  $(\mathbf{P}(\tau), \mathbf{R}(\tau))$  is the forward phase space trajectory starting at  $\tau = 0$  with the initial conditions  $\mathbf{P}(0) = \mathbf{P}_0$  and  $\mathbf{R}(0) = \mathbf{R}_0$ . Correspondingly,  $(\mathbf{P}'(\tau),$

$\mathbf{R}'(\tau)$  is the backward trajectory starting at  $\tau = t$  with the initial conditions  $\mathbf{P}'(t) = \mathbf{P}(t) + \hbar\mathbf{Q}_s$  and  $\mathbf{R}'(t) = \mathbf{R}(t)$ . The abbreviations  $\mathbf{P}(t) \equiv \mathbf{P}_t$  and  $\mathbf{R}(t) \equiv \mathbf{R}_t$  will be used below.  $F$  and  $F_q$  may now be expanded in a Taylor series around  $\tau = 0$  and  $\tau = t$ , respectively. To emphasize the time dependence we write them as functions of  $\tau$ , suppressing again the variables  $\mathbf{P}_0$ ,  $\mathbf{R}_0$ , and  $\mathbf{q}$ :

$$F(\tau) = \sum_{v=0}^{\infty} \frac{\tau^v}{v!} F^{(v)}(0), \quad (\text{A } 6)$$

$$F_q(\tau) = \sum_{v=0}^{\infty} \frac{(\tau - t)^v}{v!} F_q^{(v)}(t). \quad (\text{A } 7)$$

$F^{(v)}$  is the  $v$ th time derivative of  $F$ . The total time derivative of an arbitrary function  $f(\mathbf{P}(\tau), \mathbf{R}(\tau), \tau)$  can be expressed in  $\mathbf{R}$  and  $\mathbf{P}$  only,

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{\mathbf{P}} \cdot \frac{\partial f}{\partial \mathbf{P}} + \dot{\mathbf{R}} \cdot \frac{\partial f}{\partial \mathbf{R}} = \frac{\partial f}{\partial t} + \{H, f\}, \quad (\text{A } 8)$$

eliminating  $\dot{\mathbf{P}}$  and  $\dot{\mathbf{R}}$  by virtue of the Hamiltonian equations of motion. The symbol  $\{H, f\}$  is the Poisson bracket:

$$\{H, f\} \doteq \frac{\partial H}{\partial \mathbf{P}} \cdot \frac{\partial f}{\partial \mathbf{R}} - \frac{\partial H}{\partial \mathbf{R}} \cdot \frac{\partial f}{\partial \mathbf{P}}. \quad (\text{A } 9)$$

In terms of Poisson brackets  $F$  and  $F_q$  read

$$F(\tau) = \sum_{v=0}^{\infty} \frac{\tau^v}{v!} \{H, F\}^{(v)}(\mathbf{P}_0, \mathbf{R}_0) \quad (\text{A } 10)$$

$$F_q(\tau) = \sum_{v=0}^{\infty} \frac{(\tau - t)^v}{v!} \{H, F_q\}^{(v)}(\mathbf{P}_t + \hbar\mathbf{Q}_s, \mathbf{R}_t). \quad (\text{A } 11)$$

$\{H, F\}^{(v)}$  is the  $v$ -fold Poisson bracket,

$$\{H, F\}^{(v)} \doteq \{H, \{H, \dots \{H, F\} \dots\}\}. \quad (\text{A } 12)$$

The notation  $\{H, F\}^{(v)}(\dots)$  means that the  $v$ -fold Poisson bracket has to be evaluated at the arguments given in the parentheses, e.g., at  $\mathbf{P}(0) = \mathbf{P}_0$  and  $\mathbf{R}(0) = \mathbf{R}_0$ . Using equation (A5) the phase function  $\Phi$  takes the form

$$\Phi(t) = \sum_{v=0}^{\infty} \frac{t^{v+1}}{(v+1)!} \{H, F\}^{(v)}(\mathbf{P}_0, \mathbf{R}_0) + \sum_{v=0}^{\infty} \frac{(-t)^{v+1}}{(v+1)!} \{H, F_q\}^{(v)}(\mathbf{P}_t + \hbar\mathbf{Q}_s, \mathbf{R}_t). \quad (\text{A } 13)$$

$\mathbf{P}_t$  and  $\mathbf{R}_t$  are themselves Taylor series in  $t$ :

$$\mathbf{P}_t = \sum_{v=0}^{\infty} \frac{t^v}{v!} \{H, \mathbf{P}\}^{(v)}(\mathbf{P}_0, \mathbf{R}_0), \quad (\text{A } 14)$$

$$\mathbf{R}_t = \sum_{v=0}^{\infty} \frac{t^v}{v!} \{H, \mathbf{R}\}^{(v)}(\mathbf{P}_0, \mathbf{R}_0). \quad (\text{A } 15)$$

The time dependence of  $V(\bar{\mathbf{R}}_0(t))$  in equation (62), explicitly written as

$$V(\bar{\mathbf{R}}_0(t)) = V((\mathbf{R}'_0(t) + \mathbf{R}_0)/2), \quad (\text{A } 16)$$

is determined by

$$\mathbf{R}'_0(t) = \sum_{v=0}^{\infty} \frac{(-t)^v}{v!} \{H, \mathbf{R}\}^{(v)}(\mathbf{P}_t + \hbar \mathbf{Q}_s, \mathbf{R}_t). \quad (\text{A } 17)$$

Using now the Poisson-bracket formalism one obtains explicitly

$$\mathbf{R}'_0(t) = \mathbf{R}_0 - \frac{\hbar \mathbf{Q}_s}{M} t + \frac{\nabla \nabla V(\mathbf{R}_0) \hbar \mathbf{Q}_s}{6M^2} t^3 + O(t^4), \quad (\text{A } 18)$$

$$\mathbf{P}'_0(t) = (\mathbf{P}_0 + \hbar \mathbf{Q}_s) - \frac{\nabla \nabla V(\mathbf{R}_0) \hbar \mathbf{Q}_s}{2M} t^2 + O(t^3), \quad (\text{A } 19)$$

$$\Phi(t) = \frac{\hbar \mathbf{Q}_s \cdot (\hbar \mathbf{Q}_s + 2\mathbf{P}_0)}{2M} t - \frac{\hbar \mathbf{Q}_s \cdot \nabla V(\mathbf{R}_0)}{2M} t^2 + O(t^3), \quad (\text{A } 20)$$

$$\Delta \Phi(t) = \frac{\hbar^2 \mathbf{Q}_s^2}{2M} t + \frac{\hbar \mathbf{Q}_s \cdot \nabla \nabla V(\mathbf{R}_0) \hbar \mathbf{Q}_s}{6M^2} t^3 + O(t^4), \quad (\text{A } 21)$$

$$V(\bar{\mathbf{R}}(t)) = V(\mathbf{R}_0) - \frac{\hbar \mathbf{Q}_s \cdot \nabla V(\mathbf{R}_0)}{2M} t + O(t^2). \quad (\text{A } 22)$$

The notation ' $\nabla V(\mathbf{R}_0)$ ' indicates the gradient of the potential at  $\mathbf{R}_0$  and ' $\nabla \nabla V(\mathbf{R}_0)$ ' the matrix formed by the second derivatives  $\partial_{ij}^2 V$  at  $\mathbf{R}_0$ . The above Taylor expansions have been obtained with the computer algebra program MAPLE V [25].

## A.2. Symmetries of $\tilde{F}^{cl}(\mathbf{q}, t)$

### A.2.1. Inversion symmetry

In the following the assumption

$$V(-\mathbf{R}) = V(\mathbf{R}) \quad (\text{A } 23)$$

is made. We change now

$$\mathbf{q} \rightarrow -\mathbf{q} \quad (\text{A } 24)$$

in  $\tilde{F}^{cl}(\mathbf{q}, t)$  as defined in equation (62) and perform at the same time a change in the integration variables on the right-hand side of equation (62)

$$\mathbf{P}_0 \rightarrow -\mathbf{P}_0, \mathbf{R}_0 \rightarrow -\mathbf{R}_0. \quad (\text{A } 25)$$

Using the symmetry properties of Poisson brackets and the Taylor series for  $\Phi$ ,  $\mathbf{P}_t$ ,  $\mathbf{R}_t$ , and  $\mathbf{R}'_0$  in terms of Poisson brackets, one finds that

$$\Phi(-\mathbf{P}_0, -\mathbf{R}_0; -\hbar \mathbf{q}, t) = \Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t), \quad (\text{A } 26)$$

$$\bar{\mathbf{R}}_0(-\mathbf{P}_0, -\mathbf{R}_0; -\hbar \mathbf{q}, t) = -\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t), \quad (\text{A } 27)$$

$$V(\bar{\mathbf{R}}_0(-\mathbf{P}_0, -\mathbf{R}_0; -\hbar \mathbf{q}, t)) = V(\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t)). \quad (\text{A } 28)$$

Noting that the kinetic energy weight  $\exp[-\beta(\mathbf{P}_0^2/2M)]$  in equation (62) as well as the integrations over  $\mathbf{P}_0$  and  $\mathbf{R}_0$  remain invariant under the variable change, one

finds that

$$\tilde{F}^{cl}(-\mathbf{q}, t) = \tilde{F}^{cl}(\mathbf{q}, t). \quad (\text{A } 29)$$

This must, of course, result since the potential is assumed to be symmetric in  $\mathbf{R}$ . Relation (A 29) should therefore be considered as a formal check.

### A.2.2. $S(\mathbf{q}, \omega)$ is a real function

As a second operation we change

$$\mathbf{q} \rightarrow -\mathbf{q}, t \rightarrow -t \quad (\text{A } 30)$$

and the integration variables as

$$\mathbf{P}_0 \rightarrow -\mathbf{P}_0, \mathbf{R}_0 \rightarrow \mathbf{R}_0. \quad (\text{A } 31)$$

The symmetries of  $\Phi$ ,  $\bar{\mathbf{R}}_0$ , and  $V(\bar{\mathbf{R}}_0)$  are now

$$\Phi(-\mathbf{P}_0, \mathbf{R}_0; -\hbar\mathbf{q}, -t) = -\Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t), \quad (\text{A } 32)$$

$$\bar{\mathbf{R}}_0(-\mathbf{P}_0, \mathbf{R}_0; -\hbar\mathbf{q}, -t) = \bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t), \quad (\text{A } 33)$$

$$V(\bar{\mathbf{R}}_0(-\mathbf{P}_0, \mathbf{R}_0; -\hbar\mathbf{q}, -t)) = V(\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t)). \quad (\text{A } 34)$$

Again, the kinetic energy weight  $\exp[-\beta(\mathbf{P}_0^2/2M)]$  in equation (62) as well as the integrations over  $\mathbf{P}_0$  and  $\mathbf{R}_0$  remain effectively unchanged and one finds that

$$\tilde{F}^{cl}(-\mathbf{q}, -t) = \tilde{F}^{cl*}(\mathbf{q}, t). \quad (\text{A } 35)$$

Together with equation (A 29) it follows that

$$\tilde{F}^{cl*}(\mathbf{q}, t) = \tilde{F}^{cl}(\mathbf{q}, -t) \quad (\text{A } 36)$$

ensuring that the dynamic structure factor is always real (see equation (11)).

### A.2.3. Detailed balance

Since the classical limit of the scattering law considered in this paper is not a mathematical limit, the detailed balance relation  $F(\mathbf{q}, t) = F(-\mathbf{q}, -t + i\beta\hbar)$  cannot be expected to hold formally for  $\tilde{F}^{cl}(\mathbf{q}, t)$ . One can, however, show that it holds in the classical limit defined by the relations (43), (58) and (59). We start from equation (17) and replace  $\mathbf{q}$  by  $-\mathbf{q}$  and  $t$  by  $-t + i\beta\hbar$ . Cyclic permutation of operators under the trace yields

$$F(-\mathbf{q}, -t + i\beta\hbar) = Z^{-1} \text{tr} \left\{ \exp[-\beta\hat{H}_{-q}] \exp\left[-\frac{i}{\hbar}\hat{H}_{-q}t\right] \exp\left[\frac{i}{\hbar}\hat{H}t\right] \right\}. \quad (\text{A } 37)$$

Performing now the stationary phase approximation and at the same time the

variable substitution  $\mathbf{P}_0 \rightarrow -\mathbf{P}_0$  gives

$$\begin{aligned}
 \tilde{F}^{cl}(-\mathbf{q}, -t + i\beta\hbar) &= Z_{cl}^{-1} \iint d^{3N} P_0 d^{3N} R_0 \\
 &\quad \times \exp \left[ -\beta \left( \frac{(\mathbf{P}_0 + \hbar \mathbf{Q}_s)^2}{2M} + V(\bar{\mathbf{R}}_0(-\mathbf{P}_0, \mathbf{R}_0; -\hbar \mathbf{q}, -t)) \right) \right] \\
 &\quad \times \exp \left[ \frac{i}{\hbar} \Phi(-\mathbf{P}_0, \mathbf{R}_0; -\hbar \mathbf{q}, -t) \right] \\
 &= Z_{cl}^{-1} \iint d^{3N} P_0 d^{3N} R_0 \\
 &\quad \times \exp \left[ -\beta \left( \frac{(\mathbf{P}_0 + \hbar \mathbf{Q}_s)^2}{2M} + V(\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t)) \right) \right] \\
 &\quad \times \exp \left[ -\frac{i}{\hbar} \Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t) \right]. \tag{A 38}
 \end{aligned}$$

Writing  $\tilde{F}^{cl}(-\mathbf{q}, -t + i\beta\hbar) = \tilde{F}^{cl}(-\mathbf{q}, -[t - i\beta\hbar])$  and using that  $\tilde{F}^{cl}(-\mathbf{q}, -t) = \tilde{F}^{cl*}(\mathbf{q}, t)$ , one obtains from equation (62)

$$\begin{aligned}
 \tilde{F}^{cl}(-\mathbf{q}, -t + i\beta\hbar) &= Z_{cl}^{-1} \iint d^{3N} P_0 d^{3N} R_0 \\
 &\quad \times \exp \left[ -\beta \left( \frac{\mathbf{P}_0^2}{2M} + V(\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t - i\beta\hbar)) \right) \right] \\
 &\quad \times \exp \left[ -\frac{i}{\hbar} \Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t - i\beta\hbar) \right]. \tag{A 39}
 \end{aligned}$$

Since, according to the classical limit of the Wigner phase space distribution function, the curvature of the potential with respect to motion in imaginary time can be neglected (see equation (61)), one can put

$$V(\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t - i\beta\hbar)) \approx V(\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar \mathbf{q}, t)). \tag{A 40}$$

With equation (A 5) one has correspondingly

$$\begin{aligned}
 \Phi(t - i\beta\hbar) &= \int_0^{t-i\beta\hbar} d\tau F(\mathbf{P}(\tau), \mathbf{R}(\tau)) + \int_{t-i\beta\hbar}^0 d\tau F_q(\mathbf{P}'(\tau), \mathbf{R}'(\tau)) \\
 &= \Phi(t) + \int_t^{t-i\beta\hbar} d\tau \{F(\mathbf{P}(\tau), \mathbf{R}(\tau)) - F_q(\mathbf{P}'(\tau), \mathbf{R}'(\tau))\} \\
 &\approx \Phi(t) - i\beta\hbar (F(\mathbf{P}(t), \mathbf{R}(t)) - F_q(\mathbf{P}(t) + \hbar \mathbf{Q}_s, \mathbf{R}(t))). \tag{A 41}
 \end{aligned}$$

Inspection of the term  $F(\dots) - F_q(\dots)$  shows that one can write

$$\Phi(t - i\beta\hbar) \approx \Phi(t) - i\beta\hbar \left( \frac{(\mathbf{P}_0 + \hbar \mathbf{Q}_s)^2}{2M} - \frac{\mathbf{P}_0^2}{2M} \right). \tag{A 42}$$

If this is now inserted into equation (A 39) together with (A 40), one obtains

consistently the same expression as by performing the limit  $F(-\mathbf{q}, -t + i\beta\hbar) \rightarrow \tilde{F}^{cl}(-\mathbf{q}, -t + i\beta\hbar)$  (see equation (A 38)). Approximation (A 42) could be obtained alternatively by replacing  $t \rightarrow t - i\beta\hbar$  only in the first term of the Taylor series for  $\Phi$  (see equation (A 20)), but not in the following terms which depend on the derivatives of the potential energy that are assumed to be zero with respect to motion in imaginary time.

#### A.2.4. Sum rules

The evaluation of the first moments of the dynamic structure factor provides another important test of the validity of the stationary phase approximation of  $F(\mathbf{q}, t)$ . The general definition of the  $n$ th moment reads

$$\langle \omega^n \rangle \doteq \int_{-\infty}^{+\infty} d\omega \omega^n S(\mathbf{q}, \omega). \quad (\text{A } 43)$$

More convenient for practical purposes is the relation

$$\langle \omega^n \rangle = (-i)^n \left. \frac{\partial^n}{\partial t^n} F(\mathbf{q}, t) \right|_{t=0}, \quad (\text{A } 44)$$

which shows that the moments are essentially the coefficients of the Taylor series of  $F(\mathbf{q}, t)$  with respect to  $t$ . Its short time behaviour is obviously described by the first few moments.

As a trivial consequence of equations (A 20) and (A 22), which show that  $\lim_{t \rightarrow 0} \Phi = 0$  and  $\lim_{t \rightarrow 0} V(\tilde{\mathbf{R}}_0) = V(\mathbf{R}_0)$ , the zeroth moment is found to be correct:

$$\langle 1 \rangle = \tilde{F}^{cl}(\mathbf{q}, 0) = 1. \quad (\text{A } 45)$$

For  $n \geq 1$  the  $n$ th moment for the quantum case is known to have the general form of a polynomial of order  $n$  in  $q^2$  [8],

$$\langle \omega^n \rangle := \sum_{k=1}^n C_{n,2k} q^{2k}, \quad (\text{A } 46)$$

whereas it is a polynomial of order  $n/2$  in the usual classical approximation, with all odd moments being zero. Inserting general formula (62) for  $\tilde{F}^{cl}(\mathbf{q}, t)$  into the right-hand side of equation (A 44) allows us to calculate the moments of  $\tilde{S}^{cl}(\mathbf{q}, \omega)$  by making use of Taylor expansions (A 13) and (A 17). With  $\langle V^{(2)} \rangle = \beta \langle (V^{(1)})^2 \rangle$  and  $H(-\mathbf{P}, -\mathbf{R}) = H(\mathbf{P}, \mathbf{R})$  one finds explicitly the coefficients  $C_{n,2k}$  shown in the table for the first four moments. Comparison with the corresponding coefficients resulting from a full quantum calculation [8] shows that (i) the powers of  $\gamma \doteq \hbar/(2M)$  survive, and (ii) quantum thermal averages are replaced by classical thermal averages.

The terms  $\delta C_{4,2}$  and  $\delta C_{4,4}$  appearing in the last row of the table vanish in the classical limit where the thermal wavelength  $\lambda_T$  is much smaller than the typical interparticle distance  $\sigma$ ,

$$\delta C_{4,2} \propto \gamma \left( \frac{\lambda_T}{\sigma} \right) \approx 0, \quad (\text{A } 47)$$

$$\delta C_{4,4} \propto \gamma^2 \left( \frac{\lambda_T}{\sigma} \right)^2 \approx 0. \quad (\text{A } 48)$$

It should be mentioned that  $\delta C_{4,2}$  and  $\delta C_{4,4}$  are exactly zero for a harmonic potential.

As a trivial consequence of  $\gamma$  not going to zero, as would have been the case in the formal limit  $\hbar \rightarrow 0$ , the recoil moment is found to be correct ('*f* sum rule'):

$$\langle \omega \rangle = \frac{\hbar q^2}{2M}. \quad (\text{A } 49)$$

This is meaningful since the occurrence of  $\hbar$  in the recoil moment is merely a consequence of using  $\hbar$  as a *unit* for the momentum transfer. The second moment, not depending on the forces acting on the scattering atom either, is also identical to that obtained from a full quantum calculation. It can be checked easily that none of the well known semiclassical correction methods give this general result for arbitrary systems [4–6]. The interparticle forces enter at the third moment. As outlined in section 3.3.2, quantum thermal averages can be replaced by their classical counterparts in the classical limit. Since, by definition, scattering from classical systems is considered, the third moment is correct. The same applies to the fourth moment since  $\delta C_{4,2}$  and  $\delta C_{4,4}$  can be neglected, as outlined above.

Taking the above considerations into account shows that, at least up to the fourth order, the classical moments—in the sense of the classical limit as discussed in this paper—are obtained by replacing quantum thermal averages by classical thermal averages, keeping, however, the powers of recoil moment, which would vanish in the usual classical limit.

Comparing the moments  $\langle \omega^n \rangle'$ , obtained from  $\tilde{F}^{cl}(-\mathbf{q}, -t + i\beta\hbar)$  by using general definition (A 44) and approximations (A 40) and (A 42), with the corresponding moments  $\langle \omega^n \rangle$ , obtained from  $\tilde{F}^{cl}(\mathbf{q}, t)$ , one finds that

$$\langle \omega^n \rangle' = \langle \omega^n \rangle, \quad n = 1, 2, 3, \quad (\text{A } 50)$$

$$\langle \omega^4 \rangle' = \langle \omega^4 \rangle + 2\delta C_{4,2} q^2. \quad (\text{A } 51)$$

The coefficient  $\delta C_{4,2}$  can be neglected according to the above discussion (see equation (A 47)). This confirms that approximations (A 40) and (A 42), which were made to derive the detailed balance relation, are consistent with the stationary phase approximation of the intermediate scattering function.

## Appendix B

### Coherent scattering

Formally, the stationary phase approximation of the scattering law for coherent scattering can be handled in exactly the same way as for incoherent scattering. However, in the deep inelastic regime, or equivalently for short times, it does not give meaningful results for the distinct part, i.e., from the contribution arising from cross-correlations. To see this, let us for the moment include distinct scattering in the quantum intermediate scattering function  $F(\mathbf{q}, t)$ , i.e.,

$$F(\mathbf{q}, t) = \frac{1}{N} \sum_{\alpha, \gamma} F_{\alpha\gamma}(\mathbf{q}, t) \quad (\text{B } 1)$$

where  $F_{\alpha\gamma}(\mathbf{q}, t)$  is given by

$$F_{\alpha\gamma}(\mathbf{q}, t) = Z^{-1} \text{tr} \left\{ \exp[-\beta\hat{H}] \exp[-i\mathbf{q}\cdot\hat{\mathbf{R}}_\alpha] \exp\left[\frac{i}{\hbar}\hat{H}t\right] \exp[i\mathbf{q}\cdot\hat{\mathbf{R}}_\gamma] \exp\left[-\frac{i}{\hbar}\hat{H}t\right] \right\}. \quad (\text{B } 2)$$

Following Wick as in section 3.1,  $F_{\alpha\gamma}(\mathbf{q}, t)$  can be rewritten as

$$F_{\alpha\gamma}(\mathbf{q}, t) = Z^{-1} \text{tr} \left\{ \exp[-\beta\hat{H}] \exp[-i\mathbf{q}\cdot(\hat{\mathbf{R}}_\gamma - \hat{\mathbf{R}}_\alpha)] \exp\left[\frac{i}{\hbar}\hat{H}_{q\gamma}t\right] \exp\left[-\frac{i}{\hbar}\hat{H}t\right] \right\}. \quad (\text{B } 3)$$

Here  $\hat{H}_{q\gamma}$  is the Hamiltonian where the momentum of atom  $\gamma$  has been shifted by  $\hbar\mathbf{q}$ . Taking now the classical limit according to expressions (43), (58) and (59) yields

$$\begin{aligned} \tilde{F}_{\alpha\gamma}^{cl}(\mathbf{q}, t) &= Z_{cl}^{-1} \iint d^{3N} P_0 d^{3N} R_0 \exp \left[ -\beta \left( \frac{\mathbf{P}_0^2}{2M} + V(\bar{\mathbf{R}}_0(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}_\gamma, t)) \right) \right] \\ &\times \exp [i(\mathbf{Q}_\gamma - \mathbf{Q}_\alpha) \cdot \mathbf{R}'_0(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}, t)] \exp \left[ \frac{i}{\hbar} \Phi(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}_\gamma, t) \right], \quad (\text{B } 4) \end{aligned}$$

which is the equivalent to expression (62).  $\mathbf{Q}_\alpha$  and  $\mathbf{Q}_\gamma$  are defined according to equation (25) with  $s$  replaced by  $\alpha$  and  $\gamma$ , respectively. The notation  $\hbar\mathbf{q}_\gamma$  for the momentum transfer expresses that atom  $\gamma$  is the scattering atom.

In the case of deep inelastic scattering the impulse approximation can be invoked, i.e., one can write

$$\exp \left[ \frac{i}{\hbar} \hat{H}_{q\gamma} t \right] \exp \left[ -\frac{i}{\hbar} \hat{H} t \right] \approx \exp \left[ \frac{i}{\hbar} (\hat{H}_{q\gamma} - \hat{H}) t \right] = \exp \left[ i \frac{\mathbf{q} \cdot (\hbar\mathbf{q} + 2\mathbf{p}_\gamma)}{2M} t \right]. \quad (\text{B } 5)$$

Using the Wigner phase space distribution function, as defined in equation (38), this can be cast into the form

$$\begin{aligned} F_{\alpha\gamma}(\mathbf{q}, t) &\approx \exp \left[ i\delta_{\alpha\gamma} \frac{\hbar q^2}{2M} t \right] Z^{-1} \iint d^{3N} P_0 d^{3N} R_0 f(\mathbf{P}_0, \mathbf{R}_0) \\ &\times \exp [i(\mathbf{Q}_\gamma - \mathbf{Q}_\alpha) \cdot \mathbf{R}_0] \exp \left[ i \frac{\mathbf{Q}_\gamma \cdot \mathbf{P}_0}{M} t \right]. \quad (\text{B } 6) \end{aligned}$$

Note that the strongly time dependent recoil factor in front of the integral vanishes for distinct scattering. The corresponding expression resulting from the stationary phase approximation reads

$$\begin{aligned} \tilde{F}_{\alpha\gamma}^{cl}(\mathbf{q}, t) &\approx \exp \left[ i(2\delta_{\alpha\gamma} - 1) \frac{\hbar q^2}{2M} t \right] Z_{cl}^{-1} \iint d^{3N} P_0 d^{3N} R_0 f_{cl}(\mathbf{P}_0, \mathbf{R}_0) \\ &\times \exp [i(\mathbf{Q}_\gamma - \mathbf{Q}_\alpha) \cdot \mathbf{R}_0] \exp \left[ i \frac{\mathbf{Q}_\gamma \cdot \mathbf{P}_0}{M} t \right]. \quad (\text{B } 7) \end{aligned}$$

For the self-terms with  $\gamma = \alpha$  this expression is correct. It is just the high temperature



limit of  $F_{\alpha\alpha}(\mathbf{q}, t)$ , and gives the scattering law of an ideal Maxwell-Boltzmann gas (see equation (75)). For the distinct terms expression (B 7) does not give the correct scattering law. The reason is that deep inelastic distinct scattering looks at the same time at the momenta *and* the positions of the scattering particles, as is clear from relations (B 6), and therefore the uncertainty relation between position and momentum plays a vital role in this type of scattering. This effect, of course, cannot be accounted for if the particles are described in terms of classical phase space trajectories [9].

One has, however, to keep in mind that distinct scattering contributes only little in the deep inelastic regime and the above considerations are therefore not of practical interest. Performing the same steps as in appendix section A 2 one can show easily that the scattering law for distinct scattering in the stationary phase approximation is always real, as for self-scattering, and obeys also the relation of detailed balance if the interference term  $\exp [i(\mathbf{Q}_\gamma - \mathbf{Q}_\alpha) \cdot \mathbf{R}'_0(\mathbf{P}_0, \mathbf{R}_0; \hbar\mathbf{q}_\gamma, t)]$  in equation (B 4) can be replaced by  $\exp [i(\mathbf{Q}_\gamma - \mathbf{Q}_\alpha) \cdot \mathbf{R}_0]$ , i.e., if the spatial information is not influenced by the impact of the scattered neutron. This is true not only in the trivial case of very small momentum transfers, but also for large momentum transfers if the time  $t$  is sufficiently long and the perturbation caused by the scattering process has dissipated. Then the return positions  $\mathbf{R}'_0$  are representative equilibrium configurations covering exactly this part of the configuration space which contributes significantly to the thermal average and may therefore be replaced with  $\mathbf{R}_0$  which covers the whole configuration space.

### References

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