

Quantum Corrections to Liquid Correlations

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Abstract

Sudarshan's semi-classical treatment of correlation functions is applied to the study of quantum corrections to the Van Hove function. In its generalised form, it enables one to choose the best correlation function for a given potential. Higher-order correlations are also sketched briefly and the details are similar to those considered by Oppenheim and Bloom.

1. Introduction

For scattering by a system of interacting particles the differential cross-section depends on the spatial and temporal correlations between the particle configurations. In the Born approximation this scattering cross-section can be expressed (Van Hove, 1954) in terms of Van Hove's space-time correlation function $G(\mathbf{r}, t)$. If the momentum and energy transfers are small, the phenomenon can be treated classically whereas, with large transfers, quantum effects begin to appear. These are computed as corrections to first order in \hbar through the principle of detailed balance (Schofield, 1960; Egelstaff, 1967).

In this paper the Van Hove correlation function has been related to the phase space distribution function of a semi-classical description. This procedure due to Sudarshan (1963), facilitates a classical treatment of a quantum problem. Now the quantum effects may be due to either the

statistics and/or to the uncertainties in position and momentum variables of the particles. Since it is possible to formally separate these causes (Oppenheim & Bloom, 1961), one can take for simplicity only the latter effects, and embed them entirely in the phase space distribution. In this way, we can demonstrate that $G(\mathbf{r}, t)$ is directly related to the 2-particle Wigner distribution. But the Wigner distribution gives the semi-classical description of a quantum theory in which the position and momentum operators are ordered according to Weyl's rule. But there are other rules of correspondence leading to different semi-classical descriptions (Cohen, 1966; Misra & Shankara, 1968) and these, in turn, lead to 'different quantum corrections' to the correlation function. Hence we hope, that for a given potential, we could allocate a particular correlation function from among a whole class of them, which describe the interacting system.

Further, the quantum correction to $G(\mathbf{r}, t)$ obtained by Schofield (1960) is imaginary in the first order of \hbar and $G(\mathbf{r}, t)$ itself is envisaged to be complex in quantum theory. In our treatment we will see that the complex or the real nature of it is not any inherent property, but depends only on the particular choice of the semi-classical description, or equivalently, on the correspondence of operators to the classical functions.

In the first section we indicate how $G(\mathbf{r}, t)$ could be redefined in terms of a generalised phase space distribution, which is further expressed in terms of the Wigner distribution. This leads to a method of computing the quantum corrections. Making use of these methods of averaging, we redefine $G(\mathbf{r}, t)$ in Section 3 and the quantum corrections to it are considered. The approximations necessary in its calculation are enumerated. In Section 4 the principle of detailed balance has been used to derive the constraints on the generalised semi-classical descriptions. The time-dependent pair distribution function (TDPDF) of Oppenheim & Bloom (1961) is considered in the last section as an example of a higher order correlation. We have sketched how TDPDF could be extended to arbitrary descriptions.

2. Series Expansion of the Distribution

As a preparation to redefine $G(\mathbf{r}, t)$ in the next section, we shall study now an expansion of the phase space distribution in powers of \hbar , keeping the Wigner distribution as standard.

In the Born approximation, the differential cross-section per unit solid angle and unit energy interval of the outgoing particle is given by

$$\frac{d^2 \sigma}{d\Omega d\epsilon} = AS(\mathbf{k}, w)$$

where $\hbar\mathbf{k}$ and $\hbar w$ are respectively the momentum and energy transfers. The Van Hove correlation function is defined as the Fourier transform of $S(\mathbf{k}, w)$:

$$G(\mathbf{r}, t) = (2\pi)^{-3} N^{-1} \int \exp [i(\mathbf{w}t - \mathbf{k} \cdot \mathbf{r})] S(\mathbf{k}, w) d\mathbf{k} dw \quad (2.1)$$

In the Born approximation this simplifies to

$$G(\mathbf{r}, t) = N^{-1} \left\langle \sum_{i,j} \int d\mathbf{r}' \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}_j(t)) \right\rangle \quad (2.2)$$

For a classical system this integral can be easily evaluated to obtain

$$G_{cl}(\mathbf{r}, t) = N^{-1} \left\langle \sum_{i,j} \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)) \right\rangle \quad (2.3)$$

But in the presence of quantum effects such a simple integration of (2.3) is not possible because, $\mathbf{r}_i(0)$ and $\mathbf{r}_j(t)$ are now operators which do not commute. In order to circumvent this (Sudarshan, 1963) we use a semi-classical description where operators are replaced by ordinary functions as in classical theory, but the expectation values are calculated as averages of these functions over a distribution which accounts for the quantum effects. Thus the correlation function will now be directly related to the distribution of a semi-classical picture.

But the distribution itself depends on the correspondence of operators of quantum theory to classical observables. For a classical observable $g(r, p)$ a whole class of operators $\hat{g}(\hat{r}, \hat{p})$ could be associated, where \hat{r} and \hat{p} are the usual position and momentum operators (Misra & Shankara, 1968). Thus

$$\hat{g}(\hat{r}, \hat{p}) = (2\pi)^{-2} \int g(r, p) \exp[-i(\eta r + \tau p)] \lambda_h(\eta, \tau) \exp[i(\eta \hat{r} + \tau \hat{p})] d\eta d\tau dr dp \quad (2.4)$$

where $\lambda_h(\eta, \tau)$ is any Hermitian function obeying certain conditions. This correspondence gives rise to a generalised phase space distribution

$$f(r, p) = (2\pi)^{-2} \int \exp[-i(\eta r + \tau p - \eta u)] \rho(u, \hbar\tau) \lambda_h(\eta, \tau) d\eta d\tau du \quad (2.5)$$

Here $\rho(r, \hbar\tau)$ is a certain bilinear form of the wave function of the system which appears in the Wigner distribution obtained by setting $\lambda \equiv 1$. This is also the value which gives Weyl's rule from (2.4).

We now express the generalised distribution (2.5) for an N -particle system in terms of the Wigner distribution. Using the notation (r, p) for the set $(r_1, r_2, \dots, r_{3N}, p_1, p_2, \dots, p_{3N})$ we have

$$\begin{aligned} f(r, p) &= \frac{1}{(4\pi^2)^{3N}} \prod_j \int \exp[-i(\eta_j r_j + \tau_j p_j - \eta_j u_j)] \rho(u_j, \hbar\tau_j) \lambda_h(\eta_j, \tau_j) \\ &\quad \times d\eta_j d\tau_j du_j \\ &= \frac{1}{(4\pi^2)^{3N}} \prod_j \int \lambda_h\left(i\frac{\partial}{\partial r_j}, i\frac{\partial}{\partial p_j}\right) \exp[-i\eta_j(r_j - u_j) - i\tau_j p_j] \\ &\quad \times \rho(u_j, \hbar\tau_j) d\eta_j d\tau_j du_j \\ &= \prod_j A_j f_{wj}(r, p) \end{aligned} \quad (2.6)$$

where

$$\Lambda_j = \lambda_{\hbar} \left(i \frac{\partial}{\partial r_j}, i \frac{\partial}{\partial p_j} \right)$$

and

$$f_{w_j} = (2\pi)^{-2} \int \exp(-i\tau_j p_j) \rho(r_j, \hbar\tau_j) d\tau_j$$

is the Wigner distribution.

In order to calculate meaningful quantities from the Wigner distribution (Oppenheim & Ross, 1957), it is expanded in powers of \hbar :

$$f_w = f_{cl}(1 + \hbar^2 \chi_1 + \hbar^4 \chi_2 + \dots) \quad (2.7)$$

it being well known that only even powers of \hbar should appear. f_{cl} is the classical distribution and χ_j which depend on the potential are the correction terms.

Now λ in the distribution (2.6) can be expressed as a power series in \hbar in most of the cases. Hence it is evident that an expansion of $f(r, p)$ similar to (2.7) is possible. Since λ can contain all powers of \hbar we include the possibility of corrections of any order and write

$$f = f_{cl}(1 + \hbar\phi_1 + \hbar^2\phi_2 + \dots) \quad (2.8)$$

Notice that both f and $f_w \rightarrow f_{cl}$, as they should, in the limit of $\hbar \rightarrow 0$.

A few comments about the quantum corrections to thermodynamic quantities would be relevant (Imre *et al.*, 1967; Nienhuis, 1970). The partition function is

$$Z = \int f_{cl}(1 + \hbar\phi_1 + \hbar^2\phi_2 + \dots) dr dp$$

and hence the quantum corrections to Z_{cl} are obtained by

$$Z = Z_{cl}(1 + \hbar C_1 + \hbar^2 C_2 + \dots)$$

where

$$C_j = \frac{\int \phi_j f_{cl} dr dp}{\int f_{cl} dr dp}$$

Using the expansion (2.6) the partition function also becomes

$$\begin{aligned} Z &= \int f(r, p) dr dp \\ &= (\lambda(0, 0))^{3N} \int f_w(r, p) dr dp \\ &= (\lambda(0, 0))^{3N} \int f_{cl}(1 + \hbar^2 \chi_1 + \hbar^4 \chi_2 + \dots) dr dp \end{aligned}$$

from the expansion (2.7). Comparing the classical terms on both sides we get $\lambda(0, 0) = 1$. Incorporating this value and comparing other powers of \hbar we obtain $\langle \phi_{2r} \rangle_{cl} = \langle \chi_r \rangle_{cl}$ and $\langle \phi_{2r+1} \rangle_{cl} = 0$. Thus,

$$Z = Z_w = \int f_{cl}(1 + \hbar^2 \chi_1 + \hbar^4 \chi_2 + \dots) dr dp$$

i.e., all partition functions obtained by different distributions coincide with the one obtained by Wigner's distribution.

Inserting (2.7) and (2.8) in the relation (2.6) between f and f_w we have

$$f_{cl}(1 + \hbar\phi_1 + \hbar^2\phi_2 + \dots) = \prod_j \lambda_{\hbar} \left(i \frac{\partial}{\partial r_j}, i \frac{\partial}{\partial p_j} \right) f_{cl}(1 + \hbar^2\chi_1 + \hbar^4\chi_2 + \dots) \tag{2.9}$$

Since the expressions for χ_1, χ_2, \dots on the right side of this equation have been calculated, (Oppenheim & Ross, 1957) we can make use of them to derive expressions for ϕ_1, ϕ_2, \dots by comparing the coefficients of equal powers of \hbar . (It must be remembered that in general λ may also contain \hbar .) We skip these straight-forward steps and only list the first non-vanishing quantum corrections to the distribution for a few well-known orderings.†

Correspondence	$\lambda_{\hbar}(\eta, \tau)$	ϕ_1 or ϕ_2
Symmetrisation	$\cos(\frac{1}{2}\hbar\eta\tau)$	$\phi_1 = 0$ $\phi_2 = \chi_1 - \frac{1}{8f_{cl}} \sum_j \frac{\partial^2}{\partial r_j^2} \frac{\partial^2}{\partial p_j^2} f_{cl}$
Born-Jordan	$\frac{\sin(\frac{1}{2}\hbar\eta\tau)}{\frac{1}{2}\hbar\eta\tau}$	$\phi_1 = 0$ $\phi_2 = \chi_1 - \frac{1}{24f_{cl}} \sum_j \frac{\partial^2}{\partial r_j^2} \frac{\partial^2}{\partial p_j^2} f_{cl}$
Standard	$\exp(-\frac{1}{2}i\hbar\eta\tau)$	$\phi_1 = \frac{1}{f_{cl}} \left[\frac{i}{2} \sum_j \frac{\partial}{\partial r_j} \frac{\partial}{\partial p_j} f_{cl} \right]$
Anti-standard	$\exp(\frac{1}{2}i\hbar\eta\tau)$	$\phi_1 = -\frac{1}{f_{cl}} \left[\frac{i}{2} \sum_j \frac{\partial}{\partial r_j} \frac{\partial}{\partial p_j} f_{cl} \right]$
Normal	$\exp[\frac{1}{4}\hbar(\eta^2 + \tau^2)]$	$\phi_1 = -\frac{1}{4f_{cl}} \left[\sum_j \left(\frac{\partial^2}{\partial r_j^2} + \frac{\partial^2}{\partial p_j^2} \right) f_{cl} \right]$
Anti-normal	$\exp[-\frac{1}{4}\hbar(\eta^2 + \tau^2)]$	$\phi_1 = \frac{1}{4f_{cl}} \left[\sum_j \left(\frac{\partial^2}{\partial r_j^2} + \frac{\partial^2}{\partial p_j^2} \right) f_{cl} \right]$

It is interesting to note that the last four rules give rise to corrections even to first order in \hbar . Also the corrections in all the cases are real except with standard and antistandard orderings, where it is imaginary. It is because, in these two cases, λ is not Hermitian and so they do not yield Hermitian operators.

† Equation (2.6) connecting f and f_w can also be used to study the time and temperature dependences of f keeping those of f_w as standard.

3. Semi-Classical Redefinition of $G(\mathbf{r}, t)$

In this section we shall redefine the quantum mechanical correlation function using the methods of averaging outlined in the previous section.

The Van Hove correlation function is the expectation value of the integral

$$N^{-1} \sum_{i,j} \int d\mathbf{r}' \delta(\mathbf{r} + \mathbf{r}_i - \mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}_j(t)) \quad (2.2)$$

Here, $\mathbf{r}_i = \mathbf{r}_i(0)$ and $\mathbf{r}_j(t)$ are operators which do not commute. But in a passage to a semi-classical description we shall treat them as commuting functions, but transfer the quantum effects to the generalised phase space distribution over which the average value of the integral is taken. Thus,

$$G(\mathbf{r}, t) = N^{-1} \int f(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) \times \sum_{i,j} \delta(\mathbf{r} + \mathbf{r}_i - \mathbf{r}_j(t)) d\mathbf{r}_1 \dots, d\mathbf{r}_N, d\mathbf{p}_1 \dots, d\mathbf{p}_N \quad (3.1)$$

where $f(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$ is the same as (2.6). As we are considering an assembly of identical particles (3.1) integrates to

$$G(\mathbf{r}, t) = \frac{N^{-1}}{2} \int f^{2/N}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) \sum_{\substack{i,j=1 \\ i \neq j}}^2 \delta(\mathbf{r} + \mathbf{r}_i - \mathbf{r}_j(t)) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 \quad (3.2)$$

where

$$f^{2/N} = \frac{N!}{(N-2)!} \int f^N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^{N-2} d\mathbf{p}^{N-2}$$

is the 2-particle distribution. The considerations of the previous section now enable us to calculate $G(\mathbf{r}, t)$ once λ and the potential of the system have been specified. In fact the advantage of this unified approach is that one can obtain the best approximation for G (or equivalently, the best operator correspondence) for a given potential. Further, since the phase space distribution could be extended to include spin (Kaplan & Summerfield, 1969), the calculations with G for spinning particles could also be done classically.

In the actual calculation of G certain approximations are made depending on the nature of the system. These are very well enumerated by Oppenheim & Bloom (1961) in their calculation of the TDPDF. With the same approximations we will indicate the calculation of the Van Hove function, taking the standard ordering as an example. This is an interesting case as the quantum correction is to the first order in \hbar and is also imaginary, like the one obtained by Schofield and Egelstaff. However, it does not obey their dispersion relation.

To compute these corrections we first note that the classical correlation function is also given by (3.2) with $f^{2/N}$ replaced by the classical 2-particle distribution: viz.,

$$f_{cl}^{2/N}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) = \zeta^2 \left(\frac{\beta}{2\pi m} \right)^3 \exp \left[-\beta \left\{ \frac{|\mathbf{p}_1|^2 + |\mathbf{p}_2|^2}{2m} - V(|r_1 - r_2|) \right\} \right] \quad (3.3)$$

where $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the temperature of the assembly, m mass of the molecule, ζ the density of the system and $V(|\mathbf{r}_1 - \mathbf{r}_2|)$ is the intermolecular potential.

Now from the table given in the previous section we have for the standard ordering

$$\begin{aligned} f_{\text{std}}^{2/N} &= f_{\text{cl}}^{2/N} \left\{ 1 + \frac{1}{f_{\text{cl}}^{2/N}} \frac{i\hbar}{2} \left(\frac{\partial}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} + \frac{\partial}{\partial \mathbf{r}_2} \cdot \frac{\partial}{\partial \mathbf{p}_2} \right) f_{\text{cl}}^{2/N} \right\} \\ &= f_{\text{cl}}^{2/N} + \frac{i\hbar \beta^2}{2m} \{ (\mathbf{p}_2 - \mathbf{p}_1) \cdot \nabla_{\mathbf{r}_2} V \} f_{\text{cl}}^{2/N} \end{aligned} \quad (3.4)$$

In the case of dilute systems, $\mathbf{r}_j(t)$ appearing in (3.2) may be given a Taylor expansion using classical dynamics limiting the number of terms by the 'constant acceleration approximation'. Thus

$$\mathbf{r}_j(t) = \mathbf{r}_j + \frac{\mathbf{p}_j t}{m} - \frac{t^2}{2m} \nabla_j V \quad (3.5)$$

Hence the correlation function in standard ordering assumes the form

$$\begin{aligned} G_{\text{std}}(\mathbf{r}, t) &= \frac{N^{-1}}{2} \int f_{\text{std}}^{2/N} \sum_{i \neq j}^2 \delta \left(\mathbf{r} + \mathbf{r}_i - \mathbf{r}_j - \frac{\mathbf{p}_j t}{m} + \frac{t^2}{2m} \nabla_j V \right) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 \\ &= \frac{N^{-1}}{2} \int f_{\text{cl}}^{2/N} \left\{ 1 + \frac{i\hbar}{2m} \beta^2 (\mathbf{p}_2 - \mathbf{p}_1) \cdot \nabla_2 V \right\} \\ &\quad \times \left\{ \delta \left(\mathbf{r} + \mathbf{r}_1 - \mathbf{r}_2 - \frac{\mathbf{p}_2 t}{m} + \frac{t^2}{2m} \nabla_2 V \right) \right. \\ &\quad \left. + \delta \left(\mathbf{r} + \mathbf{r}_2 - \mathbf{r}_1 - \frac{\mathbf{p}_1 t}{m} + \frac{t^2}{2m} \nabla_1 V \right) \right\} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 \end{aligned} \quad (3.6)$$

This last expression can be readily calculated once the potential is specified. This function is complex and the imaginary part is also the quantum mechanical part as with the usual Van Hove function.

In the case of dense systems (Oppenheim & Bloom, 1961) there will be many particle interactions and we should make use of the Langevin's equation to compute $\mathbf{r}_j(t)$ in the argument of the δ function in (3.2). Obviously this would give rise to a more complicated form for $G_{\text{std}}(\mathbf{r}, t)$.

For other orderings, the correlation function is obtained in an identical fashion.

4. Constraints on λ

From our general treatment of the quantum mechanical correlation function, we have seen that the real or complex nature of it depends only on the operator correspondence chosen. For a complex G , Schofield has used the principle of detailed balance and obtained a dispersion relation connecting the imaginary part to the real part. On the other hand, instead of obtaining a dispersion relation, we shall make use of the principle of

detailed balance to derive conditions on the operator correspondences which should conform to the principle. These conditions must be satisfied over and above the algebraic conditions on λ referred to after equation (2.6).

The principle of detailed balance for the scattering cross-section implies that

$$S(\mathbf{k}, -w) = \exp\left(-\frac{\hbar w}{k_B T}\right) S(\mathbf{k}, w) \quad (4.1)$$

Since $G(\mathbf{r}, t)$ is the Fourier transform of $S(\mathbf{k}, w)$ the dispersion relation of Schofield viz.,

$$\begin{aligned} \text{Im } G(\mathbf{r}, t) &= -\tan\left(\frac{\hbar}{2k_B T} \frac{\partial}{\partial t}\right) \text{Re } G(\mathbf{r}, t) \\ &\cong \frac{\hbar}{2k_B T} \frac{\partial}{\partial t} \text{Re } G(\mathbf{r}, t) \end{aligned}$$

to the first order in \hbar , is a direct consequence of (4.1). But we shall regard (4.1) as a constraint imposed on the correlation function as a consequence of the thermal equilibrium of the system. This, in turn, gives rise to restrictions on the set of operator correspondences which would allow semi-classical descriptions of correlation phenomena.

In the constant acceleration approximation we have

$$\begin{aligned} S(\mathbf{k}, w) &= (2\pi)^{-1} N \int G(\mathbf{r}, t) \exp[i(\mathbf{k} \cdot \mathbf{r} - wt)] d\mathbf{r} dt \\ &= \frac{1}{4\pi} \int f^{2/N} \exp[i(\mathbf{k} \cdot \mathbf{r} - wt)] \left\{ \delta\left(\mathbf{r} + \mathbf{r}_1 - \mathbf{r}_2 - \frac{\mathbf{p}_2 t}{m} + \frac{t^2}{2m} \nabla_2 V\right) \right. \\ &\quad \left. + \delta\left(\mathbf{r} + \mathbf{r}_2 - \mathbf{r}_1 - \frac{\mathbf{p}_1 t}{m} + \frac{t^2}{2m} \nabla_1 V\right) \right\} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r} dt \\ &= \frac{1}{4\sqrt{\pi}} \int f^{2/N} \left[\left(\frac{i\mathbf{k} \cdot \nabla_2 V}{2m}\right)^{-1/2} \exp\left\{i\mathbf{k} \cdot (\mathbf{r}_2 - \mathbf{r}_1) + i\frac{2m(w - \mathbf{k} \cdot \mathbf{p}_2/m)^2}{4\mathbf{k} \cdot \nabla_2 V}\right\} \right. \\ &\quad \left. + \left(\frac{i\mathbf{k} \cdot \nabla_1 V}{2m}\right)^{-1/2} \exp\left\{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2) + i\frac{2m(w - \mathbf{k} \cdot \mathbf{p}_1/m)^2}{4\mathbf{k} \cdot \nabla_1 V}\right\} \right] \\ &\quad \times d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 \end{aligned}$$

Replacing w by $-w$ on the right-hand side we obtain the corresponding expression for $S(\mathbf{k}, -w)$. Further,

$$\begin{aligned} f^{2/N}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) &= \frac{1}{(4\pi^2)^6} \int \lambda(\boldsymbol{\eta}_1, \boldsymbol{\tau}_1) \lambda(\boldsymbol{\eta}_2, \boldsymbol{\tau}_2) \rho(\mathbf{u}_1, \mathbf{u}_2, \boldsymbol{\tau}_1, \boldsymbol{\tau}_2) \\ &\quad \times \exp[-i(\boldsymbol{\eta}_1 \cdot \mathbf{r}_1 + \boldsymbol{\eta}_2 \cdot \mathbf{r}_2 + \boldsymbol{\tau}_1 \cdot \mathbf{p}_1 + \boldsymbol{\tau}_2 \cdot \mathbf{p}_2 - \boldsymbol{\eta}_1 \cdot \mathbf{u}_1 - \boldsymbol{\eta}_2 \cdot \mathbf{u}_2)] \\ &\quad \times d\boldsymbol{\eta}_1 d\boldsymbol{\eta}_2 d\boldsymbol{\tau}_1 d\boldsymbol{\tau}_2 d\mathbf{u}_1 d\mathbf{u}_2] \\ &= \frac{1}{(4\pi^2)^4} \int R(\boldsymbol{\eta}_1, \boldsymbol{\eta}_2, \mathbf{p}_1, \mathbf{p}_2, \mathbf{u}_1, \mathbf{u}_2) \\ &\quad \times \exp[-i\{\boldsymbol{\eta}_1 \cdot (\mathbf{r}_1 - \mathbf{u}_1) + \boldsymbol{\eta}_2 \cdot (\mathbf{r}_2 - \mathbf{u}_2)\}] d\boldsymbol{\eta}_1 d\boldsymbol{\eta}_2 d\mathbf{u}_1 d\mathbf{u}_2] \end{aligned}$$

where

$$R = \frac{1}{(4\pi^2)^2} \int \lambda(\boldsymbol{\eta}_1, \boldsymbol{\tau}_1) \lambda(\boldsymbol{\eta}_2, \boldsymbol{\tau}_2) \rho(\mathbf{u}_1, \mathbf{u}_2, \boldsymbol{\tau}_1, \boldsymbol{\tau}_2) \exp [i(\boldsymbol{\tau}_1 \cdot \mathbf{p}_1 + \boldsymbol{\tau}_2 \cdot \mathbf{p}_2)] d\boldsymbol{\tau}_1 d\boldsymbol{\tau}_2$$

Substituting these expressions for $S(\mathbf{k}, w)$, $S(\mathbf{k}, -w)$, $f^{2/N}$ and noting that $\nabla_2 V = -\nabla_1 V$ and setting

$$\frac{2m}{4\mathbf{k} \cdot \nabla_1 V} = a_1, \quad \frac{\mathbf{k} \cdot \mathbf{p}_i}{m} = b_i, \quad \mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}$$

and comparing the integrands resulting from (4.1) we get,

$$\begin{aligned} R(-k, k) i \exp [-ia_1(b_2 + w)^2 - ik \cdot \mathbf{r}] + R(k, -k) \exp [ia_1(b_1 + w)^2 + ik \cdot \mathbf{r}] \\ = \exp \left(-\frac{\hbar w}{k_B T} \right) [i \exp \{-ia_1(b_2 - w)^2 - ik \cdot \mathbf{r}\} R(-k, k) \\ + \exp \{ia_1(b_1 - w)^2 + ik \cdot \mathbf{r}\} R(k, -k)] \end{aligned} \quad (4.2)$$

This is a functional equation in R and may be considered as a general constraint on λ imposed by thermal equilibrium of the system.

5. Generalised TDPDF

From the general standpoint of statistical mechanics we shall consider, in this section, higher order correlation functions which become significant with many particle interactions. The one higher-order correlation function to which some attention has been paid is the time dependent pair distribution function TDPDF of Oppenheim & Bloom (1961), viz.,

$$G(\mathbf{r}^2, \mathbf{r}'^2, t) = \int f^{2/N}(\mathbf{r}^2, \mathbf{p}^2) \delta(\mathbf{r}'^2 - \mathbf{r}_t^2(\mathbf{r}^2, \mathbf{p}^2)) d\mathbf{p}^2 \quad (5.1)$$

Here r^2 and p^2 stand for the coordinates and momenta of two particles at $t = 0$ and the δ function is a product of six δ functions. Equation (5.1) is the simultaneous probability per unit volume that two particles have positions between $\mathbf{r}_1, \mathbf{r}_1 + d\mathbf{r}_1$ and $\mathbf{r}_2, \mathbf{r}_2 + d\mathbf{r}_2$ at time 0 and between $\mathbf{r}'_1, \mathbf{r}'_1 + d\mathbf{r}'_1$ and $\mathbf{r}'_2, \mathbf{r}'_2 + d\mathbf{r}'_2$ at time t . As before, $R_t^2(r^2, p^2)$ is determined by ordinary dynamical methods in the case of dilute systems or by stochastic methods in the case of dense systems. The quantum effects are assumed to reside in the 2-particle distribution $f^{2/N}$.

For the classical case,

$$\begin{aligned} G_{cl}(\mathbf{r}^2, \mathbf{r}'^2, t) = \zeta^2 \left(\frac{\beta}{2\pi m} \right)^3 \left(\frac{m}{t} \right)^6 \exp \left\{ -\left[\frac{\beta\mu}{2t^2} (\mathbf{r}' - \mathbf{r})^2 + \frac{\beta M}{2t^2} (\mathbf{r}'_c - \mathbf{r}_c)^2 \right] \right. \\ \left. \times [g_{cl}(\mathbf{r})]^{1/2} [g_{cl}(\mathbf{r}')]^{1/2} \right\} \end{aligned} \quad (5.2)$$

where \mathbf{r}, \mathbf{r}' are relative coordinates, $\mathbf{r}_c, \mathbf{r}'_c$: centre of mass coordinates, $\beta = (k_B T)^{-1}$, μ : reduced mass, M : sum of the masses, $m^2 = \mu M$, $g_{cl}(\mathbf{r}) = \exp(-\beta V)$: the radial distribution function.

For the quantum case Oppenheim & Bloom (1961) have discussed (5.1) using the Weyl ordering; i.e., using the Wigner distribution for f in (5.1). With constant acceleration approximation it has the form

$$G_w(\mathbf{r}^2, \mathbf{r}'^2, t) = G_{cl}(\mathbf{r}^2, \mathbf{r}'^2, t) [1 + \hbar^2 \{D_1(\mathbf{r}, \mathbf{r}', t) + D_2(\mathbf{r}, \mathbf{r}')\}] \quad (5.3)$$

where

$$\begin{aligned} D_1 &= \frac{\beta^3}{24t^2} \left[(\mathbf{r}' - \mathbf{r})^2 + \{\mathbf{r} \cdot (\mathbf{r}' - \mathbf{r})\}^2 \frac{1}{r} \frac{d}{dr} \right] \frac{1}{r} \frac{dV}{dr} \\ D_2 &= -\frac{\beta^2}{8\mu} \nabla_r^2 V + \frac{\beta^3}{24\mu} (\nabla_r V)^2 + \frac{\beta^3}{24\mu} \left[(\mathbf{r}' - \mathbf{r}) \cdot \nabla_r V \right. \\ &\quad \left. + \{\mathbf{r} \cdot (\mathbf{r}' - \mathbf{r})\} \{\mathbf{r} \cdot \nabla_r V\} \right] \frac{1}{r} \frac{d}{dr} \frac{1}{r} \frac{dV}{dr} \end{aligned} \quad (5.4)$$

It has been shown that this can be incorporated as a correction to the radial distribution which now becomes,

$$g_w(r) = \exp(-\beta V) \left[1 + \hbar^2 \left\{ -\frac{\beta^2}{12\mu} \nabla_r^2 V + \frac{\beta^3}{24\mu} (\nabla_r V)^2 \right\} \right] \quad (5.4)$$

Along similar lines we can obtain corrections for arbitrary orderings. For example, using the methods of Section 3, we get for the Born–Jordan distribution the corrections corresponding to (5.4), viz.,

$$\begin{aligned} D_1' &= D_1 - \frac{\beta^3}{72\mu^2} \left[\frac{\mu}{t} (\mathbf{r}' - \mathbf{r}) + \frac{t}{2} \nabla_r V \right]^2 [\beta (\nabla_r V)^2 - \nabla_r^2 V] \\ D_2' &= D_2 + \frac{\beta^2}{24\mu} [\beta (\nabla_r V)^2 - \nabla_r^2 V] \end{aligned}$$

This can in turn be incorporated as Born–Jordan corrections to the radial distribution:

$$g_{BJ}(r) = \exp(-\beta V) \left[1 + \hbar^2 \left\{ -\frac{\beta^2}{9\mu} \nabla_r^2 V + \frac{\beta^3}{12\mu} (\nabla_r V)^2 \right\} \right]$$

Such corrections to correlation functions for different orderings may be of help in the calculation of quantities, such as the nuclear spin relaxation time, which have a direct dependence on the value of $g(\mathbf{r})$. Though some of the indicated corrections may be too small for experimental detection, some others are definitely more pronounced. Hence, it is our belief that a unified treatment of the quantum corrections such as above is useful from the point of view of experiment and also useful in its own right.

6. Conclusion

In the quantum theory of liquid correlations the traditional Van Hove function is complex. This is not any inherent property of it, but only a result of a certain choice of averaging that is employed. There could be different

choices, and they all lead to different semi-classical descriptions. If we start with a given potential, they lead to a class of correlation functions specified by a parameter λ . By fixing this parameter, it is possible to pick up the most accurate $G(\mathbf{r}, t)$ from among a whole class of correlation functions. There are some algebraic restrictions on λ [which may be found in Cohen (1966) or Misra & Shankara (1968)] and besides, the principle of detailed balance imposes a constraint on it which is expressed as a functional equation in Section 4. Higher order correlations could also be considered along similar lines, and such a treatment is sketched in the last section.

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References

- Cohen, L. (1966). *Journal of Mathematical Physics*, **7**, 781.
Egelstaff, P. A. (1967). *An Introduction to the Liquid State*. Academic Press.
Imre, K., Ozizmir, E., Rosenbaum, M. and Zweifel, P. F. (1967). *Journal of Mathematical Physics*, **8**, 1097.
Kaplan, D. M. and Summerfield, G. C. (1969). *Physical Review*, **187**, 639.
Misra, S. P. and Shankara, T. S. (1968). *Journal of Mathematical Physics*, **9**, 299.
Nienhuis, G. (1970). *Journal of Mathematical Physics*, **11**, 239.
Oppenheim, I. and Ross, J. (1957). *Physical Review*, **107**, 28.
Oppenheim, I. and Bloom, M. (1961). *Canadian Journal of Physics*, **39**, 845.
Schofield, P. (1960). *Physical Review Letters*, **4**, 239.
Sudarshan, E. C. G. (1963). *Physical Review Letters*, **10**, 277.
Van Hove, L. (1954). *Physical Review*, **95**, 249.