Time correlations in classical statistical mechanics

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Abstract. We give a formal expansion for the time evolution of a classical many-body system. It is suggested that this new method is capable of throwing light on some of the *ad hoc* assumptions which are currently made in the theory of liquids, and on some of the unresolved problems in the understanding of time correlation functions in fluids.

1. Introduction

In classical statistical mechanics one is concerned with the evolution of correlation functions of the type $\langle A(0)B(t) \rangle$ where $A(t)$ and $B(t)$ are functions of the $3N$ coordinates and momenta (in three dimensions), $r_i(t)$, $p_i(t)$ of the particles of the system, and the angular brackets denote the infinite volume limit of a canonical or grand canonical ensemble average.

It is the purpose of this paper to develop a systematic expansion procedure for the time evolution of the system to relate the time correlation function to equilibrium configurational averages, making use of the special properties of the classical phase space distribution function of N particles, $\exp(-\beta H_N)$. Here β is $1/k_B T$, and H_N the hamiltonian for N particles

$$H_N(\{r_i, p_i\}) = \sum_{i=1}^{3N} \frac{1}{2M} p_i^2 + \Phi_N(\{r_i\}). \tag{1}$$

(In this paper, we restrict attention to particles all of the same mass and to a general N-body potential Φ_N.)

The time evolution of a classical system can be expressed in terms of an evolution operator $S_N(t)$, which in turn is a function of the Liouville operator L_N:

$$S_N(t) = \exp(L_N t) \tag{2}$$

$$L_N = \sum_{i=1}^{3N} \left(\frac{p_i}{M} \frac{\partial}{\partial r_i} - \frac{\partial \Phi}{\partial r_i} \frac{\partial}{\partial p_i} \right). \tag{3}$$

We show in the following sections that one may develop a form of cumulant expansion of $S(t)$ so that one may write

$$\langle A(0)B(t) \rangle = \langle A(\{r_i, p_i\})(S(t)B(\{r_i, p_i\})) \rangle$$
$$= \langle A(\{r_i, p_i\}) \exp \hat{L}(t) B(\{r_i, p_i\}) \rangle \tag{4}$$

where $\hat{L}(t)$ is an operator which acts on both A and B.

In the remainder of the paper we indicate how the method may be applied to the theory of transport coefficients, and to density and current correlation functions. These will be followed up in subsequent publications.

2. 'Left' and 'right' operators

The key to the expansion procedure to be developed lies in noting that, by integration by parts, we may relate averages of the form

$$\left\langle A \frac{\partial B}{\partial q} \right\rangle \qquad \text{to} \qquad \left\langle \frac{\partial A}{\partial q} B \right\rangle$$

(where q is r_i or p_i). To be precise

$$\int \exp(-\beta H) A \frac{\partial B}{\partial p_i} \, \mathrm{d}p_i = \int \exp(-\beta H)\left(\frac{\beta p_i}{M} A - \frac{\partial A}{\partial p_i}\right) B \, \mathrm{d}p_i \tag{5}$$

and

$$\int \exp(-\beta H) A \frac{\partial B}{\mathrm{d}r_i} \, \mathrm{d}r_i = \int \exp(-\beta H)\left(\beta \frac{\partial \Phi}{\partial r_i} A - \frac{\partial A}{\partial r_i}\right) B \, \mathrm{d}r_i. \tag{6}$$

Thus, if we introduce 'left' and 'right' differential operators, denoted by arrows

$$\left\langle A \frac{\vec{\partial}}{\partial q} B \right\rangle = \left\langle A \frac{\partial B}{\partial q} \right\rangle \tag{7}$$

$$\left\langle A \frac{\overleftarrow{\partial}}{\partial q} B \right\rangle = \left\langle \frac{\partial A}{\partial q} B \right\rangle \tag{8}$$

we may write, from (5) and (6)

$$\frac{\vec{\partial}}{\partial p_i} = -\frac{\overleftarrow{\partial}}{\partial p_i} + \beta \frac{p_i}{M} \tag{9}$$

$$\frac{\vec{\partial}}{\partial r_i} = -\frac{\overleftarrow{\partial}}{\partial r_i} + \beta \frac{\partial \Phi}{\partial r_i}. \tag{10}$$

Next we note that the Liouville operator (3) may be written

$$L = \beta^{-1} \sum_i \left[\left(\frac{\partial}{\partial r_i} - \beta \frac{\partial \Phi}{\partial r_i}\right)\frac{\partial}{\partial p_i} - \left(\frac{\partial}{\partial p_i} - \beta \frac{p_i}{M}\right)\frac{\partial}{\partial r_i} \right] \tag{11}$$

by adding and subtracting a term

$$\beta^{-1} \sum_i \frac{\partial}{\partial r_i} \frac{\partial}{\partial p_i}.$$

But using (9) and (10), (11) may be written (inside an ensemble average)

$$L = \beta^{-1} \sum_i \left(-\frac{\overleftarrow{\partial}}{\partial r_i} \frac{\vec{\partial}}{\partial p_i} + \frac{\overleftarrow{\partial}}{\partial p_i} \frac{\vec{\partial}}{\partial r_i} \right). \tag{12}$$

Now, in a time expansion of a correlation function $\langle A(0)B(t) \rangle$, one needs to evaluate terms $\langle AL^n B \rangle$. To simplify such an expression we need to rearrange the terms so that all the left operators stand on the left and all the right operators on the right. In other words we need the commutation relations for the left and right operators. Clearly, since

in the average the momentum and position integrals are separated, the p operators commute with the r operators. However for the p operators, we have

$$\left[\frac{\vec{\partial}}{\partial p_i}, \frac{\overleftarrow{\partial}}{\partial p_j}\right] = \left[\frac{\vec{\partial}}{\partial p_i}, \beta\frac{p_j}{M} - \frac{\overleftarrow{\partial}}{\partial p_j}\right] = \frac{\beta}{M}\delta_{ij} \tag{13}$$

and similarly

$$\left[\frac{\vec{\partial}}{\partial r_i}, \frac{\overleftarrow{\partial}}{\partial r_j}\right] = \beta\frac{\partial^2\Phi}{\partial r_i\partial r_j} \tag{14}$$

and in addition, one finds

$$\left[\frac{\vec{\partial}}{\partial r_i}, f(\{r_j, p_j\})\right] = \left[f(\{r_j, p_j\}), \frac{\overleftarrow{\partial}}{\partial r_i}\right] = \frac{\partial f}{\partial r_i}. \tag{15}$$

To simplify the notation, we introduce operators R_i and L_i for $(M\beta)^{-1/2}\vec{\partial}/\partial r_i$ (note that these have dimensions of inverse time) and dimensionless Bose operators z_i, z_i^+ for $(M/\beta)^{1/2}\vec{\partial}/\partial p_i$ and $(M/\beta)^{1/2}\vec{\partial}/\partial p_i$. Further, we will use bold roman **R** and **L** to denote the $3N$ vectors $\{R_i\}, \{L_i\}$. When it is necessary to distinguish particles, we will use italic vectors $\boldsymbol{R}_i$ or cartesian components R_i^α.

In terms of these operators, the Liouville operator may be written

$$\tilde{L} = \mathbf{z} \cdot \mathbf{R} - \mathbf{L} \cdot \mathbf{z}^+$$
$$= \sum_i (z_i R_i - L_i z_i^+). \tag{16}$$

z_i and z_i^+ commute with R_i and L_i, while

$$[z_i^+, z_j] = \delta_{ij} \tag{17}$$

$$[R_i, L_j] = \Phi_{i,j} \tag{18}$$

with

$$\Phi_{i,j} = \frac{1}{M}\frac{\partial^2\Phi}{\partial r_i\partial r_j}. \tag{19}$$

The comma in $\Phi_{i,j}$ is introduced because it will be necessary to distinguish derivatives which arise from right differentiation (before the comma) to left differentiation (after the comma). Thus, we shall write for example,

$$[R_i, \Phi_{j,k}] = \Phi_{ij,k}$$
$$[\Phi_{j,k}, L_i] = \Phi_{j,ki}, \tag{20}$$

although these are both equal to $(M\beta)^{-1/2}(\partial/\partial r_i)\Phi_{j,k}$, by (4).

Finally we note that the momentum of and the force on the ith degree of freedom are given by

$$p_i = (M\beta^{-1})^{1/2}(z_i + z_i^+) \tag{21}$$

$$\frac{\partial\Phi}{\partial r_i} = (M\beta^{-1})^{1/2}(L_i + R_i). \tag{22}$$

3. Ordering of operators—the cumulant expansion

In § 2, it was shown how the evolution operator $S(t)$ could be expressed in terms of the left and right operators as

$$S(t) = \exp[(\mathbf{z} \cdot \mathbf{R} - \mathbf{L} \cdot \mathbf{z}^+)t]. \tag{23}$$

To proceed, we wish now to rewrite the terms in the time expansion of $S(t)$ in an ordered fashion making use of the commutation relations. When this is done the remaining operators act only on the 'external' functions A and B. Operators acting in this way will be denoted by a zero suffix: $\mathbf{L}_0, \mathbf{z}_0$ acting on A and $\mathbf{R}_0, \mathbf{z}_0^+$ acting on B. The individual operators will be represented by hats: $\hat{L}_i$ etc.

To demonstrate the procedure, consider the first three terms in the Taylor expansion of $S(t)$:

$$S(t) = \sum_{n=0}^{\infty} \frac{1}{n!} S_n t^n. \tag{24}$$

Using the commutation relations, one finds

$$S_1 = \mathbf{z}_0 \cdot \mathbf{R}_0 - \mathbf{L}_0 \cdot \mathbf{z}_0^+ = \hat{L}_1 \tag{25}$$

$$S_2 = (\mathbf{z} \cdot \mathbf{R} - \mathbf{L} \cdot \mathbf{z}^+)^2 = \hat{L}_1^2 + \hat{L}_2 \tag{26}$$

with

$$\hat{L}_2 = -\sum_{ij} (\hat{z}_i [R_i, L_j] \hat{z}_j^+ + \hat{L}_i [z_i^+, z_j] \hat{R}_j)$$

$$= -\sum_{ij} \hat{z}_i \Phi_{i,j} \hat{z}_j^+ - \mathbf{L}_0 \cdot \mathbf{R}_0. \tag{27}$$

Similarly one finds

$$S_3 = \hat{L}_1^3 + 3\hat{L}_2 \hat{L}_1 + \hat{L}_3 \tag{28}$$

with

$$\hat{L}_3 = \sum_{i,j} \Phi_{i,j} (\hat{L}_i \hat{z}_j^+ - \hat{z}_i \hat{R}_j) + \sum_{ijk} (\hat{z}_i \Phi_{i,jk} \hat{z}_j^+ \hat{z}_k^+ - \hat{z}_i \hat{z}_j \Phi_{ij,k} \hat{z}_k^+). \tag{29}$$

These first terms suggest that $S(t)$ may be conveniently written in the cumulant expansion form

$$S(t) = \exp \hat{L}(t) \tag{30}$$

with

$$\hat{L}(t) = \sum_{n=1}^{\infty} \frac{1}{n!} \hat{L}_n t^n, \tag{31}$$

$\hat{L}_1, \hat{L}_2$ and $\hat{L}_3$ being given by (25), (27) and (29), above.

We shall now show that this is indeed the case, and present the rules for obtaining the terms $\hat{L}_n$. Before doing this, we introduce a further notational device. Each term in the expansion will contain a product of derivatives of the potential Φ. If these are labelled by a dummy superscript eg $\Phi^{(a)}$, then the derivatives can be represented by operators $\mathbf{L}_a, \mathbf{R}_a$ which act solely on $\Phi^{(a)}$. Thus for example, (29) may be written

$$\hat{L}_3 = \mathbf{L}_0 \cdot \mathbf{R}_a \Phi^{(a)} \mathbf{L}_a \cdot \mathbf{z}_0^+ - \mathbf{z}_0 \cdot \mathbf{R}_a \Phi^{(a)} \mathbf{L}_a \cdot \mathbf{R}_0 + \mathbf{z}_0 \cdot \mathbf{R}_a \Phi^{(a)} (\mathbf{L}_a \cdot \mathbf{z}_0^+)^2 - (\mathbf{z}_0 \cdot \mathbf{R}_a)^2 \Phi^{(a)} (\mathbf{L}_a \cdot \mathbf{z}_0^+). \tag{32}$$

Consider a term in $S(t)$ involving I factors $\mathbf{z} \cdot \mathbf{R}$ and J factors $\mathbf{L} \cdot \mathbf{z}^+$. There are $\binom{I+J}{I}$ such terms corresponding to all possible orderings, and each has a coefficient $[(-1)^J/(I+J)!]t^{I+J}$. The ordered operator arising from such a term gives a number of terms involving $\hat{z}$, $\hat{R}$, $\hat{L}$, $\hat{z}^+$ and derivatives of the potential.

Consider first the momentum operators. Each $z_i z_j^+$ gives a term with $\hat{z}_i \hat{z}_j^+$. In addition for each pair in which z_j^+ precedes the z_i, there will be a term $\mathbf{L} \cdot \mathbf{z}^+ \mathbf{z} \cdot \mathbf{R}$ replaced by $\mathbf{L} \cdot \mathbf{R}$. Thus the result of ordering the z operators is to give a series of terms $\Pi_{i=1}^{I-K}\Pi_{j=1}^{J-K}\Pi_{k=1}^{K}\hat{z}_i\hat{z}_j^+(R_iL_jL_kR_k)_P$ where $(\quad)_P$ represents a permutation in which no R_k precedes the corresponding L_k.

Next we tackle the position operators. For each ordered pair R_iL_j, there is a term with L_jR_i plus a term with R_iL_j replaced by $\Phi_{i,j}$. Next from each triplet $R_iR_jL_k$ there is a term with this combination replaced by $\Phi_{ij,k}$. In addition to terms involving one Φ there are terms with products of Φ's. The simplest of these is $\Phi_{i,j}\Phi_{j,k}$ which arises from combinations $R_iL_jR_jL_k$, and so on. The operators which are not replaced by Φ's remain as $\hat{L}$ and $\hat{R}$ operators.

As an example consider the ordering of $R_1L_2R_3L_4L_5$. This gives:

> 5 term $\Phi_{i,j}$ from pairs (1, 2) (1, 4) (1, 5) (3, 4) (3, 5)
>
> 4 term $\Phi_{i,jk}$ from triplets (1, 24) (1, 25) (1, 45) (3, 45)
>
> 2 term $\Phi_{ij,k}$ from triplets (13, 4) (13, 5)
>
> 1 term $\Phi_{i,jkl}$ from (1, 245)
>
> 1 term $\Phi_{ij,kl}$ from (13, 45)
>
> 4 term $\Phi_{i,j}\Phi_{k,l}$ from (12, 34) (12, 35) (14, 35) (15, 34)
>
> 1 term $\Phi_{i,j}\Phi_{k,lm}$ from (12, 345).

Let us now invert this reasoning and ask what is the coefficient of a particular ordered term. First we distinguish 'linked' from 'unlinked' terms. Each term contains suffixes in pairs, one from a right operation and one from a left operation, eg $\hat{z}_i\hat{R}_i$, $\hat{z}_i\Phi_{i,j}\Phi_{j,k}R_k$, $\hat{z}_i\hat{R}_i\hat{L}_j\hat{z}_j^+$, $\hat{z}_i\hat{R}_i\hat{L}_j\Phi_{j,k}\hat{R}_k$. Linked terms are those which cannot be expressed as a product of similar terms—the first two above, for example—whereas unlinked terms (such as the second two) can be expressed in this way.

The general term can be written as a product of linked terms $(\psi_1)^{a_1}(\psi_2)^{a_2}\ldots(\psi_r)^{a_r}$, where ψ_s is a linked term arising from n_s pairs of operators $\mathbf{z} \cdot \mathbf{R}$, $\mathbf{L} \cdot \mathbf{z}^+$. Such a term has a coefficient $(1/N!)t^N$ with $N = \Sigma_{s=1}^{r}a_sn_s$, from the expansion of $S(t)$, times a coefficient giving the number of ways in which this set of suffixes can be chosen—namely

$$\frac{N!}{\Pi_{s=1}^{r}a_s!\Pi(n_s!)^{a_s}}.$$

In addition each ψ_s contains a numerical coefficient depending on its structure. This is discussed in the next section and the appendix.

From the above it follows that $S(t)$ can be expressed in cumulant expansion form

$$S(t) = \exp \hat{L}(t) \tag{33}$$

where $\hat{L}(t)$ is a sum over linked terms which may be written

$$\hat{L}(t) = \sum \frac{1}{n_s!}\psi_s t^{n_s}. \tag{34}$$

4. The time expansion of $\hat{L}(t)$

In this section we consider the general term, ψ_s, of the expansion (34). This we do in three stages: (a) we consider some simple terms in detail, (b) we introduce a diagrammatic representation and (c) we consider the evaluation of the general term.

The general term ψ may be written as

$$\psi = C \prod_{i=1}^{I} \prod_{j=1}^{J} \prod_{k=1}^{K} \prod_{l=1}^{L} \prod_{m=1}^{M} \hat{z}_i \hat{L}_j \Phi(i, j, k, l, m) \hat{R}_l \hat{z}_m^+ \tag{35}$$

where $\Phi(i, j, k, l, m)$ is a product of potential derivatives containing 'right' suffixes (before the comma), i, j, left and right suffixes k and left suffixes l and m. The power of t associated with this term is equal to the number of positional suffixes, and the sign is determined by the number of left suffixes. Thus ψ of (35) has a coefficient $[(-1)^{J+K}/N!]t^N$ with $N = I + 2J + 2K + 2L + M$. In addition the coefficient C contains a combinatorial factor which gives the number of arrangements of operators in the original expansion of $S(t)$ which can contribute a term ψ.

The terms may now be classified, therefore, according to the pattern of terms in $\Phi(i, j, k, l, m)$. From § 3, we have immediately: (i) the terms independent of Φ:

$$(\mathbf{z}_0 \cdot \mathbf{R}_0 - \mathbf{L}_0 \cdot \mathbf{z}_0^+)t - \tfrac{1}{2}\mathbf{L}_0 \cdot \mathbf{R}_0 t^2$$

and (ii) the coefficient of $\Phi_{i,j}$:

$$-\frac{1}{2!}\hat{z}_i \hat{z}_j^+ t^2 + \frac{1}{3!}(\hat{L}_i \hat{z}_j^+ - \hat{z}_i \hat{R}_j)t^3 + \frac{1}{4!}\hat{L}_i \hat{R}_j t^4.$$

Higher terms rapidly become more complicated. However, for purposes of illustration we consider in detail the coefficient of $\Phi_{i,jk}$. This has terms in t^3, t^4, t^5 and t^6 according to the number of z operators. We quote the various terms, followed in parenthesis by the original orderings from which they arise:

(iii) coefficient of $\Phi_{i,jk}$

$$\hat{z}_i \hat{z}_j^+ \hat{z}_k^+ \frac{1}{3!}t^3 \qquad (R_i L_j L_k)$$

$$-\hat{L}_i \hat{z}_j^+ \hat{z}_k^+ \frac{1}{4!}t^4 \qquad (L_i R_i L_j L_k)$$

$$3\hat{z}_i \hat{z}_j^+ \hat{R}_k \frac{1}{4!}t^4 \qquad (R_i L_j L_k R_k, \; R_i L_k L_j R_k, \; R_i L_k R_k L_j)$$

$$-3\hat{L}_i \hat{R}_j \hat{z}_k^+ \frac{1}{5!}t^5 \qquad (L_i \times \text{above})$$

$$3\hat{z}_i \hat{R}_j \hat{R}_k \frac{1}{5!}t^5 \qquad (R_i L_j L_k R_j R_k, \; R_i L_j L_k R_k R_j, \; R_i L_j R_j L_k R_k)$$

$$-3\hat{L}_i \hat{R}_j \hat{R}_k \frac{1}{6!}t^6 \qquad (L_i \times \text{above}).$$

It is now natural to introduce diagrams to represent the combinations of derivatives of Φ which occur in $\Phi(i, j, k, l, m)$. This we do as follows. The diagrams consist of vertices representing the potential and directed bonds representing derivatives. In addition,

there are external bonds to represent the capped operators—'open' for $\hat{z}$ and $\hat{z}^+$ and 'closed' to represent $\hat{L}$ and $\hat{R}$.

Thus the diagrams representing (i) and (ii) (the first and second order diagrams) are

(i)   and

(ii)   ,   ,   and

while for example

    and
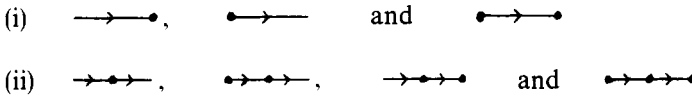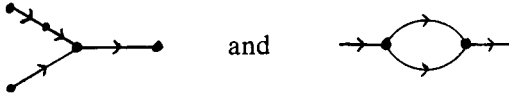
represent the fourth order terms $15\hat{L}_i\hat{L}_k\Phi_{i,j}\Phi_{jk,l}\hat{R}_l$ and $3\hat{z}_i\Phi_{i,jk}\Phi_{jk,l}\hat{z}_l^+$ respectively.

The time factor $t^N/N!$ associated with each diagram in its contribution to $\hat{L}(t)$ has N given by twice the number of closed bonds plus the number of open bonds; the sign is given by $(-1)^l$ where l is the number of occurrences of the element $\bullet\!\!\rightarrow$. In the examples above one has $(-1)^4 t^8/8!$ and $(-1)^3 t^6/6!$.

The general rule for obtaining the combinatorial factor is somewhat complex and is relegated to an appendix. The principle is to note that an element $\bullet\!\!\rightarrow$ arises from a left operation (after the comma on a Φ), and $\rightarrow\!\!\bullet$ from a right operation. One needs to calculate therefore the number of ways these operators can be ordered with all the 'right' labels to the right of the corresponding left labels. In counting these, (a) the order of the z_i determines that of the R_i so that $\hat{z}_i\hat{z}_jR_iR_j$ is not distinct from $\hat{z}_i\hat{z}_jR_jR_i$, and likewise for L_i and z_i^+ and (b) in terms with L_iR_i, the order of either the L's or the R's is fixed so that (fixing L), $L_iL_jR_iR_j$ and $L_iL_jR_jR_i$ are distinct but $L_iL_jR_iR_j$ and $L_jL_iR_iR_j$ are not distinct.

To illustrate this we consider the two elements:

The first gives a contribution $6!/(2!)^3 3!$ from the ways of choosing three pairs LR from six operators and fixing the order of the three L operators; the second gives $14!/8!6! \cdot 4!/2^2 2!$, the first factor being the number of ways of putting down the eight and six operators in the lower and upper routes between the two ends, while the second represents the number of ways of obtaining the loop in the upper half.

These are diagrams which may be simply reduced by successively partitioning sets of operators. An example of a diagram which cannot be treated in this way is
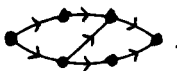
The combinatorial factor for the general diagram is derived in the appendix. This may be specified by $(T+1)$ ordered vertices, those labelled 0 and $T+1$ representing the external functions A and B on which the $\hat{L}$ and $\hat{R}$ operate, and N bonds of which these are $n_{r,s}$ between internal vertices r and s, l_s and m_s left acting open and closed external bonds

and p_r and q_r right acting external bonds. The contribution of this diagram to $\hat{L}(t)$ is

$$\frac{(-1)^Q}{N!} t^N \prod \mathscr{C}_{r,s} \cdot \mathscr{N} \prod_{s=1}^{T} (\mathbf{z}_0 \cdot \mathbf{R}_s)^{l_s} (\mathbf{L}_0 \cdot \mathbf{R}_s)^{m_s}$$

$$\times \prod_{s=2}^{T} \prod_{r=1}^{S=1} (\mathbf{L}_r \cdot \mathbf{R}_s)^{n_{r,s}} \prod_{r=1}^{S} (\mathbf{R}_r \cdot \mathbf{L}_0)^{p_s} (\mathbf{R}_r \cdot \mathbf{z}_0^+)^{q_s} \prod_{s=1}^{T} \Phi^{(s)}$$

where $\mathscr{C}_{r,s}$, $\mathscr{N}$, Q and N are as given in the appendix.

In the next section, we show how $\hat{L}(t)$ may be written more compactly as an expansion in the interaction Φ, by summing sets of diagrams and removing the apparent complexity of the combinatorial factors.

5. Potential expansion of $\hat{L}(t)$

It will now be shown that the formal expansion of $\hat{L}(t)$ may be more compactly written in terms of a different set of diagrams, achieved by summing over multiple connections between two vertices. That is, we write

$$\tag{36}$$

for internal bonds, while for external bonds we write

$$\tag{37}$$

In addition, we introduce 'optional' bonds denoted by broken lines, to include the possibility of no direct link between two vertices or externally: for example

$$\tag{38}$$

In terms of these diagrams $\hat{L}(t)$ may be represented up to third order in the potential by
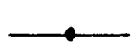

$$\tag{39}$$

It is shown in the appendix that the operator functions associated with these diagrams can be constructed from functions $g_{ab}(t)$ for internal bonds, and $g_a(t)$, $g_b^+(t)$ for external left and right bonds:

$$g_{ab}(t) = \exp(-\tfrac{1}{2}\mathbf{L}_a \cdot \mathbf{R}_b t^2) \tag{40}$$

$$g_a(t) = \exp(\mathbf{z}_0 \cdot \mathbf{R}_a t - \tfrac{1}{2}\mathbf{L}_0 \cdot \mathbf{R}_a t^2) \tag{41}$$

$$g_b^+(t) = \exp(-\mathbf{L}_b \cdot \mathbf{z}_0^+ t - \tfrac{1}{2}\mathbf{L}_b \cdot \mathbf{R}_0 t^2). \tag{42}$$
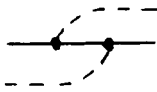
Thus the first order term is

$$\text{———} \!\!\bullet\!\!\text{———} = \int_0^t dt_1 \frac{d}{dt_1} g_1(t-t_1)\Phi^{(1)} \int_0^{t_1} dt_2 \frac{d}{dt_2} g_1^+(t_1-t_2)$$

$$= \frac{d}{dt} \int_0^t dt_1 [g_1(t-t_1)-1]\Phi^{(1)}[g_1^+(t_1)-1] \tag{43}$$

and the second term is (after some rearrangement)

$$\text{———} \!\!\bullet\!\!\text{——}\!\!\!\!\rightarrow = \int_0^t dt_1 \dot{g}_1(t-t_1)\Phi^{(1)}g_1^+(t_1)$$

$$\times \int_0^{t_1} dt_2 g_2(t-t_2)[g_2(t_1-t_2)-1]\Phi^{(2)}\dot{g}_2^+(t_2). \tag{44}$$

6. The calculation of correlation functions

At this stage we should consider precisely what has been achieved by formally writing the evolution operator in the cumulant form (30). Essentially what has been done is (i) to average the correlation functions over the initial Maxwell velocity distribution and (ii) to reduce the configurational average to a canonical form in which all first derivatives of the potential have been integrated out. Thus the correlation function of two functions A and B which are functions of position only is reduced directly to the evaluation of a configurational average (of the function obtained after setting z and z^+ equal to zero). Functions of velocity are similarly reduced after the operation of the $\hat{z}$ and $\hat{z}^+$ operators. Thus, for example the velocity autocorrelation function $\langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle$ is the configurational average of the coefficient of $\mathbf{z}_i \cdot \mathbf{z}_i^+$ in the expansion of $S(t)$ in the external operators.

Of course, the utility of the formalism depends on the ability to use it to calculate properties of the system—in particular the transport coefficients, density and current correlation functions etc—which require the extrapolation from short time to long time behaviour. We shall demonstrate the utility of the method in this respect in a second paper. Here we content ourselves with a number of general remarks.

6.1. Free particles

If there is no interaction, then $S(t)$ reduces to

$$S_0(t) = \exp\!\left(\sum_i (\hat{\mathbf{z}}_i \cdot \hat{\mathbf{R}}_i - \hat{\mathbf{L}}_i \cdot \hat{\mathbf{z}}_i^+)t - \tfrac{1}{2}\hat{\mathbf{L}}_i \cdot \hat{\mathbf{R}}_i t^2 \right) \tag{45}$$

giving no coupling between different particles. To demonstrate that this is correct, consider the correlation of $A(\mathbf{r})$ and $B(\mathbf{r})$, with Fourier transforms $\tilde{A}(\mathbf{K})$, $\tilde{B}(\mathbf{K})$:

$$\langle A(0)B(t) \rangle = \int d\mathbf{R} \int\!\!\int \exp[i(\mathbf{K}+\mathbf{K}') \cdot \mathbf{R}] A(\mathbf{K})B(\mathbf{K}') \langle \exp(i\mathbf{K} \cdot \mathbf{v}t) \rangle \, d^3\!K \, d^3\!K'$$

$$= \int dK A(K) \exp[-\tfrac{1}{2}K^2(kTt^2/M)] B(K) \tag{46}$$

which is precisely what one obtains directly from (45).

6.2. Functions of position only

If A and B are functions of position only, then the general expression for $\hat{L}(t)$ simplifies considerably. First since $\hat{z}$ and $\hat{z}^+$, can be set equal to zero, and second since if A and B are represented by their Fourier coefficients $A(K)$, $B(K')$ where K represents the $3N$ coordinates K_i^α, $\hat{L}(t)$ reduces to a function of K, t and the coordinates of the system. Thus from (41) $g_a(t)$ is replaced by

$$g_a(K, t) = \exp(-\tfrac{1}{2}i\tilde{K} \cdot \mathbf{R}_a t^2) \tag{47}$$

$$g_b^+(K', t) = \exp(\tfrac{1}{2}i\mathbf{L}_b \cdot \tilde{K}' t^2) \tag{48}$$

with

$$\tilde{K} = \left(\frac{kT}{M}\right)^{1/2} K.$$

In particular we may write the single particle density correlation function

$$\langle \exp i K \cdot (\mathbf{r}_0(t) - \mathbf{r}_0(0)) \rangle = \langle \exp \hat{L}_{00}(K, t) \rangle \tag{49}$$

and the density–density correlation function

$$\langle \mathbf{n}_K(0)\mathbf{n}_K(t) \rangle = \left\langle \sum_{ab} \exp[iK \cdot (\mathbf{r}_a - \mathbf{r}_b)] \exp \hat{L}_{ab}(K, t) \right\rangle \tag{50}$$

where $\hat{L}_{ab}(K, t)$ is the function derived from $\hat{L}(t)$ on setting

$$\hat{R}_a = -iK\left(\frac{kT}{M}\right)^{1/2} \qquad \hat{L}_b = iK\left(\frac{kT}{M}\right)^{1/2}$$

and all other external operators zero:

$$\hat{L}_{ab}(K, t) = -\tilde{K}^2 \left[\frac{1}{2}\delta_{ab}t^2 - \frac{1}{4!}\Phi_{ab}t^4 + \frac{1}{6!}\left(\sum_i \Phi_{ai}\Phi_{ib} - 3i\tilde{K}(\Phi_{abb} - \Phi_{aab})\right)t^6 \right.$$

$$-\frac{1}{8!}\left(\sum_{i,j}(\Phi_{ai}\Phi_{ij}\Phi_{jb} + 3\Phi_{aij}\Phi_{ijb}) - i\tilde{K}\sum_j(3\Phi_{aaj}\Phi_{jb} - 15\Phi_{abj}\Phi_{jb} + 15\Phi_{aj}\Phi_{jab}$$

$$\left. -3\Phi_{aj}\Phi_{jbb}) - \tilde{K}^2(15\Phi_{aaab} - 9\Phi_{aabb} + 15\Phi_{abbb})\right)t^8\right] + O(t^{10}). \tag{51}$$

(Note that after the counting has been done, the commas on the Φ may be dropped.) (51) represents in compact form, the expression from which the 'sum rules' for the scattering functions may be calculated (Schofield 1968).

6.3. Pair potentials

If the potential $\Phi(\{\mathbf{r}_i\})$ can be expressed as a sum of pair potentials $\frac{1}{2}\Sigma_{i \neq j}\phi(\mathbf{r}_{ij})$, further reduction is necessary. To illustrate this we give the contribution of an element of the

diagrams of § 5 :

$$\Phi(g(t)-1)\Phi$$

$$= \tfrac{1}{4} \sum_{i \neq j} \phi(\mathbf{r}_{ij}) \left[\exp\left(-\tfrac{1}{2} \sum_{k} \mathbf{L}_k \cdot \mathbf{R}_k t^2 \right) - 1 \right] \sum_{l \neq m} \phi(\mathbf{r}_{lm})$$

$$= \tfrac{1}{2} \sum_{i \neq j} \phi(\mathbf{r}_{ij}) \bigg([\exp(-\mathbf{L}_{ij} \cdot \mathbf{R}_{ij} t^2) - 1] \phi(\mathbf{r}_{ij})$$

$$+ 2 \sum_{k \neq i,j} [\exp(-\tfrac{1}{2}\mathbf{L}_{ij} \cdot \mathbf{R}_{ik} t^2) - 1] \phi(\mathbf{r}_{ik}) \bigg) . \tag{52}$$

Thus each bond gives rise to a two-body interaction, represented by the first term in (52), and an interaction involving three particles from the second term. Similarly the operation of an external bond, $(g_a(t) - 1)$ from a single particle function $A(\mathbf{r}_0, \mathbf{p}_0)$ gives

$$A(g_a(t)-1)\Phi$$

$$= A(\mathbf{r}_0, \mathbf{p}_0)[\exp(z_0 \cdot \mathbf{R}t - \tfrac{1}{2}\mathbf{L}_0 \cdot \mathbf{R}_0 t^2) - 1]\tfrac{1}{2} \sum_{i \neq j} \phi(\mathbf{r}_{ij})$$

$$= A(\mathbf{r}_0, \mathbf{p}_0) \sum_i [\exp(z_0 \cdot \mathbf{R}_{0i}t - \tfrac{1}{2}\mathbf{L}_0 \cdot \mathbf{R}_{0i}t^2) - 1]\phi(\mathbf{r}_{0i}). \tag{53}$$

7. Discussion

In this paper we have presented a formal method of evaluation of time dependent correlation functions in classical statistical mechanics; the usefulness of the method has yet to be demonstrated, and this will be done in forthcoming papers, the first of which will deal with the binary 'hard-core' collision contribution to transport coefficients. To conclude this paper we make some general remarks concerning the method.

In the compact form of § 5, the theory is expressed in terms of the operators $g_{ab}(t)$, which play the role of propagators. It is perhaps a weakness of the formalism that these operators do not have a clear cut physical interpretation. They may be regarded, however, as in some sense representing velocity averaged propagators. We hope to demonstrate, however, in future work that this weakness is compensated by ease of computation.

Because we work with velocity averaged quantities, it is not obvious how our work relates to other formulations of the classical many-body problem (for example, Prigogine 1962, and more recently Gross 1972, Martin *et al* 1973). The connections will, no doubt, emerge in time.

A second important comment should be made regarding the convergence of the expansion of § 5. It is apparent from the form of the operator functions $g_{ab}(t)$ that there are convergence problems with the expansion (39). For instance if the potential is Fourier transformable, then the expansion contains terms like $\exp(-\tfrac{1}{2}\mathbf{K} \cdot \mathbf{K}'t^2)$ which diverge for $\mathbf{K} \cdot \mathbf{K}' < 0$. The means by which this may be resolved in general is not yet completely clear. Indeed, one would not expect this to be simple since the conditions on the potential for dynamical stability of the system are quite severe. For repulsive differentiable potentials (eg inverse power potentials) the problem does not arise since these $\mathbf{L}$ and $\mathbf{R}$ acting on Φ have the same sign.

The major potential advantage of the method (apart from the trivial one of simplifying the calculation of 'sum rules', or the Taylor expansion of correlation functions) arises from the fact that it is not a density expansion, and therefore should be directly applicable at liquid densities. It will be shown, for example, that the various 'kinetic' and 'configurational' contributions to transport coefficients correspond to fairly simple sets of diagrams representing configurational averages whose symmetries and similar time dependence relate the numerical contributions to different coefficients.

Appendix. Combinatorial factors for diagrams

Consider a diagram with T vertices, labelled from left to right $1 \ldots T$. In addition, we may regard an external bond as terminating in a vertex labelled 0 (on the left) or $(T+1)$ (on the right). Let $n_{r,s}$ be the number of bonds connecting vertex r to vertex s, and denote the set of L and R operators which give rise to these bonds by $\{r, s\}$. The number required is the number of ways of arranging these operators subject to (i) all R_i operators associated with vertex s must appear before any L_j associated with vertex s and (ii) any R_k associated with vertex s must appear after the L_k associated with vertex $r (<s)$.

We consider the problem in two parts, first the number of ways of arranging the sets of operators, and second the number of ways the operators in each set may be ordered.

Let $n_{r,s}^x (r < x < s)$ denote the number of operators of the set $\{r, s\}$, in any allowed arrangement, which occur before the last operator of any set $\{u, x\}$ but after the last of any set $\{u, x-1\}$; let $n_{r,x}^x$ be the number between vertices r and x after the last of any set $\{u, x-1\}$.

Thus

$$\sum_x n_{r,s}^x = 2n_{r,s} \qquad (1 \leqslant r < s \leqslant T) \tag{A.1}$$

$$\sum_x n_{0,s}^x = l_s + 2m_s \qquad (1 \leqslant s \leqslant T) \tag{A.2}$$

$$\sum_x n_{r,T+1}^x = 2p_r + q_r \qquad (1 \leqslant r \leqslant T) \tag{A.3}$$

where l_s, q_s are the number of open external bonds and m_s and p_s the number of closed external bonds.

The number of ways of arranging the sets in the interval x is a product of two factors (i) the number of ways of arranging the elements of the sets $\{r, s\}$ for $s \neq x$ with the union of the sets $\{r, x\}$, excluding the last element and (ii) the number of ways of arranging the sets $\{r, x\}$:

$$\mathscr{N}_x = \frac{(\sum_{r=0}^{x-1} \sum_{s=x}^{T+1} n_{r,s}^x - 1)!}{(\sum_{r=0}^{x-1} n_{r,x}^x - 1)! \prod_{r=0}^{x-1} \prod_{s=x+1}^{T+1} n_{r,s}^x!} \frac{(\sum_{r=0}^{x-1} n_{r,x}^x)!}{\prod_{r=0}^{x-1} (n_{r,x}^x)!}. \tag{A.4}$$

The total number of ways of arranging the sets is therefore

$$\mathscr{N} = \sum_P \prod_{x=1}^{T+1} \mathscr{N}_x. \tag{A.5}$$

The sum of P is over the number of ways of dividing the operators into the subsets x, subject to (A.1–3).

The number of ways of arranging the elements within each set is

$$\mathscr{C}_{r,s} = \frac{(2n_{r,s})!}{2^{n_{r,s}}(n_{r,s})!} \qquad (1 \leqslant r < s \leqslant T)$$

$$\mathscr{C}_{0,s} = \frac{(l_s + 2m_s)!}{l_s!(2m_s)!} \frac{(2m_s)!}{2^{m_s}m_s!} \qquad (s \leqslant T) \tag{A.6}$$

$$\mathscr{C}_{s,T+1} = \frac{(2p_s + q_s)!}{q_s!(2p_s)!} \frac{(2p_s)!}{2^{p_s}p_s} \qquad (1 \leqslant s).$$

Finally, we require the time dependence of the diagram in its contribution to $\hat{L}(t)$ which, from the main text, is $(-1)^Q t^N / N!$ with

$$Q = \sum m_s + \sum p_s + \sum n_{r,s}$$
$$N = \sum (l_s + 2m_s + 2n_{r,s} + 2p_s + q_s). \tag{A.7}$$

To perform the sum over multiple bonds, as discussed in § 5 of the paper, we have to sum the diagrams in $\hat{L}(t)$ over $n_{r,s}$, m_s, p_s, l_s and q_s with the appropriate power of t. This may be done by generalizing the beta function integral

$$\int_0^1 (1-\tau)^{y-1} \tau^x \, d\tau = \frac{x!(y-1)!}{(x+y)!}. \tag{A.8}$$

The generalization we require is

$$\int_0^t dt_1 (t-t_1)^{x_1-1} \int_0^{t_1} dt_2 (t_1 - t_2)^{x_2 - 1} \dots \int_0^{t_{n-1}} dt_n (t_{n-1} - t_n)^{x_n}$$

$$= \frac{\Pi_{r=1}^n (x_r - 1)!}{(\Sigma x_r)!} t^{\Sigma x_r} = \beta(t; x_1 \dots x_n). \tag{A.9}$$

It follows directly from (A.4, A.5) that

$$\mathscr{N} t^N = \frac{N! \Sigma_P \Pi_x \Sigma_{r=0}^{x-1} n_{r,x}^x}{\Pi_{r=0}^{x-1} \Pi_{s=x}^{T+1} n_{r,s}^x!} \beta(t; s_1 \dots s_{T+1}) \tag{A.10}$$

with

$$s_x = \sum_{r=0}^{x-1} \sum_{s=x}^{T+1} n_{r,s}^x. \tag{A.11}$$

But

$$\prod_x \sum_{r=0}^{x-1} n_{r,x}^x \beta(t; s_1 \dots s_{T+1}) \tag{A.12}$$

is just the integral of the form (A.9) with $(t_{x-1} - t_x)^{s_x - 1}$ replaced by

$$(t_{x-1} - t_x)^{s_x - v_x} \left(-\frac{d}{dt_x} \right) (t_{x-1} - t_x)^{v_x}$$

where

$$v_x = \sum_{r=0}^{x-1} n_{r,x}^x. \tag{A.13}$$

Next we note that $(\Sigma_{x=r+1}^{s} n_{r,s}^{x})!$ divided by the denominator of (A.10) is just the coefficient in the multinominal expansion of $(t_r - t_s)^{\Sigma}$ as $\overline{(t_r - t_{r-1} + t_{r-1} - t_{r-2} \cdots - t_s)^{\Sigma}}$. Therefore the sum over P can be performed, yielding

$$\mathcal{N}\bar{t}^N = N! \left(\prod_{r<s} \prod (2n_{r,s})! \prod_{s} (l_s + 2m_s)! \prod_{r} (2p_r + q_r)! \right)^{-1} G(t; l_s, m_s, n_{r,s}, p_r, q_r) \tag{A.14}$$

where

$$G = \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_T} dt_{T+1} \left(-\frac{d}{dt_1} \right)(t - t_1)^{2m_1 + l_1}$$

$$\times \prod_{s=2}^{T} \left[\left(-\frac{d}{dt_s} \right)(t - t_s)^{2m_s + l_s} \prod_{r=1}^{s-1} (t_r - t_s)^{2n_{r,s}} \right]$$

$$\times \left(-\frac{d}{dt_{T+1}} \right) \prod_{r=1}^{T} (t_r - t_{T+1})^{2p_r + q_r}. \tag{A.15}$$

Finally one may sum over all values of the indices, after multiplying by the combinatorial factors $\mathcal{C}_{r,s}$ and the sign $(-1)^{Q}$ to obtain the result quoted in § 5, namely that the contribution to $\hat{L}(t)$ of a diagram with T vertices may be written (in the notation of § 5)

$$\hat{L}_T(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_T} dt_{T+1} \left(-\frac{d}{dt_1} \right) f_{01}(t - t_1) \Phi^{(1)}$$

$$\times \prod_{s=2}^{T} \left[\left(-\frac{d}{dt_s} \right) f_{0s}(t - t_s) \prod_{r=1}^{s-1} f_{rs}(t_r - t_s) \right] \Phi^{(s)} \left(-\frac{d}{dt_{t+1}} \right)$$

$$\times \prod_{r=1}^{T} f_{r0}^{+}(t_r - t_{T+1}) \tag{A.16}$$

where $f_{ab}(t) = g_{ab}(t)$ or $g_{ab}(t) - 1$ according to whether the bond between a and b is optional or not.

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