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A new approach to the calculation of thermodynamics and structure for classical one-dimensional systems with pairwise additive potentials in an external field

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Abstract. A new approximation scheme has been derived for classical statistical mechanics of one-dimensional systems with pairwise additive potentials in an external field. It enables both the thermodynamic functions and the static correlation functions to be obtained. The analysis depends on combining the recurrence relation of Baxter with an extension of the analysis of functional differential equations started by Volterra.

1. Introduction

There have been many one-dimensional models in classical statistical mechanics from which exact results for the correlation functions and thermodynamic properties have been obtained. By this I mean results which give a practical procedure for the numerical evaluation of these properties. For a review of much of this work for the uniform case, i.e. in the absence of an external field, see the first chapter of Lieb and Mattis [1]. A lot of work has also been done on non-uniform fluids, much of which has been summarised by Percus [2]. This includes the rigorous treatment of the ideal gas and the gas of hard rods in an external field.

In this work I have been trying to use the idea Baxter first put forward [3] which is to derive a recurrence relation for the configuration integrals by differentiating them with respect to the length of the system, combined with an extension of the work on functionals and functional differential equations which has been compiled by Volterra [4], to proceed as far as possible with the exact analysis of the class of systems for which Baxter's recurrence relation holds, namely one-dimensional systems with a pairwise additive potential and an external field. To this end I have had partial success in that I have had to make one approximation but the theory is otherwise exact and general. It is also encouraging to find that the resulting approximation scheme for the uniform fluid is simple to use but a systematic study of the accuracy of the method by comparing it with other approximations and with Monte Carlo calculations remains to be done.

The arrangement of this paper is as follows. In § 2 the definitions and notation are briefly stated and an expression for the pressure is obtained from a grand canonical average and it is indicated how all the thermodynamic functions can be obtained from this. In § 3 a general argument is used, which is essentially equivalent to the one given by Baxter, to derive an equation for the grand partition function. The criterion that any approximation to this gives the correct pressure follows easily. One approximation is suggested for which a plausible argument suggested that it might give correct results in the thermodynamic limit but it turned out to be false. However the fact that this approximation, a functional differential equation (FDE), turned out to have a remarkably simple solution and that other approximations could lead to other FDE led me to investigate in § 4 the general treatment of FDE of the first order. A subset of these is identified which has a particularly simple solution which is developed in detail in § 5. In § 6 a special case of this is used to solve the approximation mentioned above and equations are derived from this for calculating the pressure and the correlation functions n_1 and n_2. Further simplifications arise from assumptions made about the behaviour of these functions in the thermodynamic limit. This results in simple expressions for the pressure and the radial distribution function. Finally in § 7 some concluding remarks are given.

2. Definitions including a general expression for the pressure

The grand partition function for the one-dimensional classical gas is

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int_{-\infty}^{\infty} \mathrm{d}p_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}p_N \int_0^L \mathrm{d}L_1 \ldots \int_0^L \mathrm{d}L_N \frac{1}{h^N} \exp[\beta(N\mu - H_N)] \tag{2.1}$$

where the system has length L with the N-particle Hamiltonian H_N, the chemical potential μ and h is Planck's constant. Also the standard notation $\beta = 1/k_B T$ is used with T the absolute temperature and k_B is Boltzmann's constant. Assume that

$$H_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V_N(L_1 \ldots L_N) \tag{2.2}$$

where V_N is symmetric and p_i and L_i are respectively the momentum and position of particle i and m is the mass of the particles. Then it follows that

$$\langle p_1^2 \rangle = m/\beta \tag{2.3}$$

in general and integration over momenta gives

$$\Xi = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_0^L \mathrm{d}L_1 \ldots \int_0^L \mathrm{d}L_N \exp[-\beta V_N(L_1 \ldots L_N)] \tag{2.4}$$

where z is the fugacity given by

$$\mathrm{e}^{\beta\mu} \left(\frac{2\pi m}{\beta h^2} \right)^{1/2}. \tag{2.5}$$

The grand canonical average of a function $g(N, L_1 \ldots L_N, x)$ is

$$\langle g \rangle_{\mathrm{GCE}} = \frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_0^L \mathrm{d}L_1 \ldots \int_0^L \mathrm{d}L_N\, g(N, L_1 \ldots L_N, x) \exp[-\beta V_N(L_1 \ldots L_N)]. \tag{2.6}$$

In order to calculate the pressure P, i.e. the force on the right-hand wall, it is convenient to avoid the singularity by replacing V_N by V_{NL} which contains terms which describe the interaction of the particles with the wall at $x = L$. This will typically be a short-ranged repulsive potential but it is not necessary to specify it explicitly. Finally the limit will be taken in which this extra potential goes to zero, the hard wall case, and the original potential is recovered.

Let $V_{NL}(L_1 \ldots L_N)=\infty$ except when $0<L_i<L$ for all i and in particular $V_{NL}(L, L_2 \ldots L_N)=\infty$ ($\exp(-\beta V_{NL})$ is continuous). V_{NL} is also symmetric with respect to any exchanges of its arguments. In the hard wall limit

$$V_{NL}(L_1 \ldots L_N) \to V_N(L_1 \ldots L_N) \qquad \text{if } 0<L_i<L\ \forall i$$
$$\to \infty \qquad \text{otherwise.}$$

Then

$$\frac{\partial}{\partial L} \ln \Xi\{V_{NL}\} = \frac{1}{\Xi} \sum_{N=0}^{\infty} z^N \int_0^L \mathrm{d}L_1 \ldots \int_0^L \mathrm{d}L_N \exp[-\beta V_{NL}(L_1 \ldots L_N)] - \beta \frac{\partial}{\partial L} V_{NL}|_{L_1 \ldots L_N}$$
$$= \beta \langle \text{force on wall} \rangle_{NL}.$$

Then in the hard wall limit

$$(\partial/\partial L) \ln \Xi = \beta P. \tag{2.7}$$

This is the exact expression for the pressure of the finite one-dimensional system in the grand canonical ensemble. The result usually quoted in the textbooks is the zero field case [5] in three dimensions or the asymptotic result $P \sim \ln \Xi/\beta V$ [6] in the limit $V \to \infty$ (assumed to be independent of the shape). In this work only pair potentials and an external field are involved, i.e.

$$V_N(L_1 \ldots L_N) = \sum_{i=1}^{N} V_{\mathrm{E}}(L_i) + \sum_{j=1}^{N} \sum_{i=1}^{j-1} \varphi(L_i - L_j) \tag{2.8}$$

where V_{E} is the external field and φ is the pair potential. Using the notation

$$u = \beta\varphi \qquad \text{and} \qquad z(x) = z \exp(-\beta V_{\mathrm{E}}(x)) \tag{2.9}$$

the grand partition function can be written as

$$\Xi = \sum_{N=0}^{\infty} \int_0^L \mathrm{d}L_1 \ldots \int_0^{L_{N-1}} \mathrm{d}L_N \prod_{k=1}^{N} z(L_K) \exp\left(-\sum_{1 \le i<j \le N} u(L_i - L_j)\right). \tag{2.10}$$

3. General relations for the grand partition function and the first-order approximation

To find the pressure at some intermediate point x_1 for $0<x_1<L$ the system should be replaced by one with the same values of β and $z(x)$ for $0<x<x_1$ and zero outside this range. The system is then confined to the interval $0<x<x_1$ and then the same calculation gives $P(x_1)$.

The pressure $P(x=L)$ is defined by these equations in terms of β and $z(x)$. In order to recover a sensible macroscopic limit $L \to \infty$, $z(x)$ should be scaled with L such that $z_L(x)=z^*(x/L)$ with $z^*(x)$ being kept fixed. This is expected to give $P(x)$ with the same scaling property, i.e. $P_L(x)=P^*(x/L)$ where $P_L(x)$ is the pressure $P(x)$ for the system of length L. Under these conditions local thermodynamics is expected to be valid [2]. In this work I shall not consider this point any further since my main interest here is to study the uniform case using the external field as a mathematical tool for deriving the necessary equations and then setting the field to zero afterwards.

For a uniform system $z_L(x)=z$, the fugacity. This can be inverted in principle to give $z(\beta, P)$ or $\mu(\beta, P)$; however, μ may not be unique in which case the smallest value must be chosen to represent the stable thermodynamic state; other values would correspond to metastable or unstable states. As explained by Callen [7] all other thermodynamic functions can be obtained from this relation.

From (2.10) it is straightforward to show that

$$\frac{\partial \Xi}{\partial L}\{L, z(x)\} = z(L)\Xi\{L, z(x)\exp[-u(L-x)]\} \tag{3.1}$$

or expressed in terms of $F = \ln \Xi$

$$\frac{\partial F\{L, z(x)\}}{\partial L} = z(L)\exp[F\{L, z(x)\exp[-u(L-x)]\} - F\{L, z(x)\}]. \tag{3.2}$$

This, together with the initial condition $F\{0, z(x)\} = 0$, completely determines $F\{L, z(x)\}$. Equations (3.1) and (3.2) are equivalent to the general relation given by Baxter [3] which was used in his treatment of the case when $u(x) = \alpha\exp(-\gamma x)$ with and without a hard core. For an argument to show that Baxter's equation, together with the initial condition, is necessary and sufficient to determine the grand partition function see [8, last section]. Applying the thermodynamic limit to (3.2) using (2.7) gives

$$P = \lim_{L\to\infty} \frac{1}{\beta} z(L)\exp[F\{L, z(x)\exp[-u(L-x)]\} - F\{L, z(x)\}]. \tag{3.3}$$

Writing the argument of the exponential as $\Delta F(L)$ suppose $\Delta F(L)$ is replaced by an approximation $G(L)$ such that

$$\lim_{L\to\infty} \Delta F(L) = \lim_{L\to\infty} G(L) \tag{3.4}$$

then (3.2) can be approximated by

$$\frac{\partial F\{L, z(x)\}}{\partial L} = z(L)\exp[G(L)] \tag{3.5}$$

but

$$P = \lim_{L\to\infty} \frac{1}{\beta} z(L)\exp[G(L)]$$

exactly. Hence it appears that a reasonable approach to calculating P is to find a suitable expression $G(L)$ such that (3.4) holds and (3.5) can be solved. Although I have not succeeded in doing this a reasonable first attempt is to replace $\Delta F(L)$ by the first-order term in its functional Taylor expansion about $F\{L, z(x)\}$ which is

$$\int_0^L \mathrm{d}s \frac{\delta F\{L, z(x)\}}{\delta z(s)} z(s) f(L-s)$$

where $f(x) = \exp[-u(x)] - 1$ is the Mayer function.

4. The general theory of non-linear first-order FDE

The resulting functional differential equation (FDE) is a member of a large class which have a simple solution. Since, to my knowledge, this material has not been published elsewhere I would like to develop in this section the basic technique for solving these equations and in the next section the solution which can be found in a class of equations of this type. The method is obtained by applying Volterra's method of analysis described as 'that of passing from the finite to the infinite' [4] to the theory of non-linear partial differential equations (PDE) with N independent variables [9]. Let F be a functional of $z(x)$ and a function of $L \in R^+$ where $z(x): R^+ \to R^+$ and R^+ is the set $\{x: 0<x<\infty\}$. Define the functional derivative

$$\frac{\delta F\{L, z(y)\}}{\delta z(x)} = \lim_{\varepsilon \to 0} \frac{\partial}{\partial \varepsilon} F\{L, z(y) + \varepsilon\delta(y-x)\}. \tag{4.1}$$

It will also be convenient to write

$$F\begin{Bmatrix} z(x) & x<L \\ 0 & x>L \end{Bmatrix} \qquad \text{as } F\{z(x)\theta(L-x)\}.$$

Then clearly

$$\frac{\delta}{\delta z(x)} \frac{\partial F\{L, z(x)\}}{\partial L} = \frac{\partial}{\partial L} \frac{\delta F\{L, z(x)\}}{\delta z(x)} \tag{4.2}$$

and

$$\frac{\mathrm{d}F\{L, z_L(x)\}}{\mathrm{d}L} = \frac{\partial F\{L, z_L(x)\}}{\partial L} + \int_0^\infty \mathrm{d}x \frac{\delta F\{L, z_L(x)\}}{\delta z(x)} \frac{\mathrm{d}}{\mathrm{d}L} z_L(x) \tag{4.3}$$

which is an application of the chain rule.

I shall consider here only first-order FDE. The general fo· is

$$\frac{\partial F\{L, z(x)\}}{\partial L} = G\left\{L, z(x), F, \frac{\delta F}{\delta z(x)}\right\} \tag{4.4}$$

where G is a functional of $z(x)$ and $\delta F/\delta z(x)$ and is an ordinary function of L and F.

In order to find the solution $F\{L, z(x)\}$ of (4.4) satisfying a suitable boundary condition the first step is to derive the equations for the characteristic strips which correspond to equation (2) on p 97 of [9]. These are equations (4.8), (4.9), (4.14) and (4.15) below. However the reader may assume the validity of these equations and follow the rest of the argument which shows how the required solution is constructed from the solutions of these equations and the initial conditions.

The characteristic strips of (4.4) are specified by giving $z(x)$, F, $\partial F/\partial L$ and $\delta F/\delta z(x)$ as functions of L and $z_0(x)$. $z_0(x)$ is constant for each strip and plays the role of $t_1 \ldots t_{n-1}$ of [9].

I shall use the following notation:

$$\begin{aligned}
A(L, x) &= z_L(x) = z(x)\{L, z_0(x)\} \qquad (z_0(x) = z_L(x)|_{L=0}) \\
B(L, x) &= \frac{\delta F\{L, z_L(x)\}}{\delta z(x)} = \frac{\delta F^*\{L, z_0(x)\}}{\delta z(x)} = t(x)\{L, z_L(x)\} \\
F(L) &= F\{L, z_L(x)\} = F^*\{L, z_0(x)\} \\
K(L) &= \frac{\partial F\{L, z_L(x)\}}{\partial L} = \frac{\partial F^*\{L, z_0(x)\}}{\partial L}.
\end{aligned} \tag{4.5}$$

It should be clear that this derivative is to be taken at constant $z(x)$ rather than at constant $z_0(x)$.

The condition needed to specify the characteristics is that the FDE involves no derivatives exterior to the characteristics when expressed in terms of L and $z_0(x)$.

Eliminating $\partial F\{L, z_L(x)\}/\partial L$ from (4.3) and (4.4) gives

$$\int_0^\infty dx \frac{\delta F\{L, z_L(x)\}}{\delta z(x)} \frac{d}{dL} z_L(x) - \frac{d}{dL} F\{L, z_L(x)\} + G\left\{L, z_L(x), F\{L, z_L(x)\}, \frac{\delta F\{L, z_L(x)\}}{\delta z(x)}\right\} = 0. \tag{4.6}$$

This equation is a relation involving L, $z_L(x)$, F, dF/dL, $(d/dL)z_L(x)$ and $\delta F/\delta z(x)$. The requirement that this equation involves only the first five terms is equivalent to requiring that the operator

$$\frac{\delta}{\delta(\delta F\{L, z_L(x)\}/\delta z(x))}$$

taken with these quantities constant, applied to (4.6) gives zero, i.e.

$$\frac{dz_L(x)}{dL} + \frac{\delta G\{L, z_L(x), F, t(x)\}}{\delta t(x)} = 0. \tag{4.7}$$

Equation (4.3) gives

$$\frac{dF(L)}{dL} = K(L) + \int_0^\infty dx\, B(L, x) \frac{dA(L, x)}{dL}. \tag{4.8}$$

Equation (4.7) can be written as

$$\frac{dA(L, x)}{dL} = -\frac{\delta G\{L, z_L(x), F, t(x)\}}{\delta t(x)}. \tag{4.9}$$

Apply the identity (4.3) to $\partial F\{L, z_L(x)\}/\partial L$ gives

$$\frac{d}{dL}\left(\frac{\partial F\{L, z_L(x)\}}{\partial L}\right) = \frac{\partial^2 F\{L, z_L(x)\}}{\partial L^2} + \int_0^\infty dx \frac{\partial}{\partial L}\left(\frac{\delta F\{L, z_L(x)\}}{\delta z(x)}\right) \frac{d}{dL} z_L(x) \tag{4.10}$$

and apply (4.3) to $\delta F\{L, z_L(x)\}/\delta z(x)$ gives

$$\frac{d}{dL}\left(\frac{\delta F\{L, z_L(x)\}}{\delta z(x)}\right) = \frac{\partial}{\partial L}\left(\frac{\delta F\{L, z_L(x)\}}{\delta z(x)}\right) + \int_0^\infty dx_1 \frac{\delta^2 F\{L, z_L(x)\}}{\delta z(x) \delta z(x_1)} \frac{dz_L(x_1)}{dL}. \tag{4.11}$$

Equation (4.4) may now be regarded as an identity once the correct form for F has been found. Applying $\partial/\partial L$ gives

$$\frac{\partial^2 F\{L, z(x)\}}{\partial L^2} = \frac{\partial G}{\partial L} + \frac{\partial G}{\partial F} \frac{\partial F}{\partial L} + \int_0^\infty dx \frac{\delta G}{\delta t(x)} \frac{\partial}{\partial L}\left(\frac{\delta F\{L, z(x)\}}{\delta z(x)}\right) \tag{4.12}$$

and applying $\delta/\delta z(x)$ gives

$$\frac{\delta}{\delta z(x)} \frac{\partial F\{L, z(x)\}}{\partial L} = \frac{\delta G}{\delta z(x)} + \frac{\partial G}{\partial F} \frac{\delta F\{L, z(x)\}}{\delta z(x)} + \int_0^\infty ds \frac{\delta G}{\delta t(s)}\left(\frac{\delta^2 F\{L, z(x)\}}{\delta z(x)\, \delta z(s)}\right). \tag{4.13}$$

Eliminating $\partial^2 F/\partial L^2$ between (4.10) and (4.12), with $z(x)$ replaced by $z_L(x)$, gives, with (4.5),

$$\frac{dK(L)}{dL} = \left.\frac{\partial G}{\partial L}\right|_{z=z_L} + \left.\frac{\partial G}{\partial F}\right|_{z=z_L} K(L) + \int_0^\infty dx \left.\frac{\delta G}{\delta t(x)}\right|_{z=z_L} \frac{\partial}{\partial L}\left(\frac{\delta F\{L, z_L(x)\}}{\delta z(x)}\right) + \int_0^\infty dx \frac{\delta}{\delta z(x)}\left(\frac{\partial F\{L, z_L(x)\}}{\partial L}\right) \frac{d}{dL} z_L(x).$$

Because of (4.7) this simplifies to

$$\frac{\mathrm{d}K(L)}{\mathrm{d}L}=\frac{\partial G}{\partial L}\bigg|_{z=z_L}+\frac{\partial G}{\partial F}\bigg|_{z=z_L}K(L). \tag{4.14}$$

Eliminating

$$\frac{\partial}{\partial L}\left(\frac{\delta F\{L, z(x)\}}{\delta z(x)}\right)$$

from (4.11) and (4.13) evaluated at $z=z_L$ gives, using (4.5),

$$\frac{\mathrm{d}B(L,x)}{\mathrm{d}L}=\frac{\delta G}{\delta z(x)}\bigg|_{z=z_L}+\frac{\partial G}{\partial F}\bigg|_{z=z_L}B(L,x)$$
$$+\int_0^\infty \mathrm{d}s\frac{\delta G}{\delta t(s)}\frac{\delta^2 F\{L, z_L(x)\}}{\delta z(x)\,\delta z(s)}+\int_0^\infty \mathrm{d}s\frac{\delta^2 F\{L, z_L(x)\}}{\delta z(x)\,\delta z(s)}\frac{\mathrm{d}}{\mathrm{d}L}z_L(s).$$

Again, because of (4.7) this becomes

$$\frac{\mathrm{d}B(L,x)}{\mathrm{d}L}=\frac{\delta G}{\delta z(x)}\bigg|_{z=z_L}+\frac{\partial G}{\partial F}\bigg|_{z=z_L}B(L,x). \tag{4.15}$$

The required equations for the four functions in (4.5) are (4.8), (4.9), (4.14) and (4.15). Suppose the initial conditions for F are given on an initial manifold $\{L, z(x)\}$ as follows:

$$F=R\{z(x)\} \qquad L=0 \qquad z(x)=z_0(x). \tag{4.16}$$

Then from (3.5)

$$\frac{\partial F\{0, z_0(x)\}}{\partial L}=G\left\{0, z_0(x), R\{z_0(x)\}, \frac{\delta R\{z_0(x)\}}{\delta z_0(x)}\right\}. \tag{4.17}$$

To verify the strip equations it is only necessary to show that $(\mathrm{d}/\mathrm{d}L)(\partial F/\partial L-G)=0$ for every strip. This calculation is a straightforward application of the chain rule provided one remembers that $z(x)$, $\delta F/\delta z(x)$, F, $\partial F/\partial L$ are to be regarded as independent variables, each of which is a function of L. Since the initial conditions for every strip at $L=0$ are chosen to satisfy (4.4) it follows that (4.4) is satisfied identically by the solutions of the strip equation. To obtain $F\{L, z(x)\}$ as required it is only necessary to eliminate $z_0(x)$ in favour of $z(x)$ in the expression for $F\{L, z(x)\}$. Before proceeding to the special case I want to consider I shall need two lemmas which are quite straightforward to prove; the first is well known [4].

Let $f^{(N)}(x_1\ldots x_N)$ be a symmetric function of its N arguments, i.e.

$$f^{(N)}(x_1\ldots x_N)=f^{(N)}(x_{p(1)}\ldots x_{p(N)})$$

where p is any permutation of the indices $1,\ldots,N$. Then by using the definition (4.1) and exploiting the symmetry it is easy to show that

$$\frac{\delta}{\delta w(x)}\int_0^\infty \mathrm{d}x_1\int_0^{x_1}\mathrm{d}x_2\ldots\int_0^{x_{N-1}}\mathrm{d}x_N\prod_{i=1}^{N} w(x_i)f^{(N)}(x_1\ldots x_N)$$
$$=\int_0^\infty \mathrm{d}x_1\int_0^{x_1}\mathrm{d}x_2\ldots\int_0^{x_{N-2}}\mathrm{d}x_{N-1}\prod_{i=1}^{N-1} w(x_i)f^{(N)}(x_1\ldots x_{N-1}, x). \tag{4.18}$$

The general form of a functional Maclaurin expansion of a functional is

$$H\{w(x)\}=\sum_{N=0}^{\infty}\int_0^\infty \mathrm{d}x_1\int_0^{x_1}\mathrm{d}x_2\ldots\int_0^{x_{N-1}}\mathrm{d}x_N\prod_{i=1}^{N} w(x_i)f_H^{(N)}(x_1\ldots x_N). \tag{4.19}$$

By using the above result it follows that

$$\frac{\delta H\{w(x)\}}{\delta w(t)}=\sum_{N=1}^{\infty}\int_0^{\infty}\mathrm{d}x_1\int_0^{x_1}\mathrm{d}x_2\ldots\int_0^{x_{N-2}}\mathrm{d}x_{N-1}\prod_{i=1}^{N-1}w(x_i)f_H^{(N)}(x_1\ldots x_{N-1},t). \tag{4.20}$$

Hence

$$\begin{aligned}\int_0^L \mathrm{d}t\, w(t)&\frac{\delta H\{w(x)\theta(t-x)\}}{\delta w(t)}\\ &=\sum_{N=1}^{\infty}\int_0^L \mathrm{d}t\, w(t)\int_0^t \mathrm{d}x_1\int_0^{x_1}\mathrm{d}x_2\ldots\int_0^{x_{N-2}}\mathrm{d}x_{N-1}\\ &\quad\times\prod_{i=1}^{N-1}w(x_i)f_H^{(N)}(x_1\ldots x_{N-1},t)\\ &=\sum_{N=1}^{\infty}\int_0^L \mathrm{d}L_1\int_0^{L_1}\mathrm{d}L_2\ldots\int_0^{L_{N-1}}\mathrm{d}L_N\prod_{i=1}^{N}w(L_i)f_H^{(N)}(L_1\ldots L_N)\\ &=H\{w(x)\theta(L-x)\}-f^{(0)}.\end{aligned} \tag{4.21}$$

By replacing $H\{w(y)\}$ by $\delta M\{w(y)\}/\delta w(x)$ (4.21) can be written as

$$\int_0^L \mathrm{d}t\, w(t)\frac{\delta^2 M\{w(x)\theta(t-x)\}}{\delta w(t)\,\delta w(x)}=\frac{\delta M\{w(x)\theta(L-x)\}}{\delta w(x)}-f_H^{(0)}. \tag{4.22}$$

A term in M of the form

$$\int_0^{\infty}\mathrm{d}x_1 w(x_1)f_M^{(1)}(x_1)$$

gives a term $f_M^{(1)}(x)$ in H which is identified with $f_H^{(0)}$. Hence if M is a functional of the form

$$M\{w(x)\}=\sum_{N=2}^{\infty}\int_0^{\infty}\mathrm{d}x_1\int_0^{x_1}\mathrm{d}x_2\ldots\int_0^{x_{N-1}}\mathrm{d}x_N\prod_{i=1}^{N}w(x_i)f_M^{(N)}(x_1\ldots x_N).$$

Then $f_H^{(0)}=0$ in (4.22).

5. A more explicit solution of a class of FDE

Returning to the main argument I now consider the case when

$$G=z(L)\exp\left\{\frac{\delta H\{w(x)\}}{\delta w(L)}\right\}$$

where $w(x)=z(x)t(x)$. First one has to write down the derivatives of G with respect to L, F, $z(x)$ and $t(x)$:

$$\frac{\partial G}{\partial F}=0$$

$$\frac{\partial G}{\partial L}=\left.\frac{\mathrm{d}z(x)}{\mathrm{d}x}\right|_{x=L}\exp\left\{\frac{\delta H\{w(x)\}}{\delta w(L)}\right\}+z(L)\exp\left\{\frac{\delta H\{w(x)\}}{\delta w(L)}\right\}\frac{\partial}{\partial L}\left(\frac{\delta H\{w(x)\}}{\delta w(L)}\right)$$

$$\frac{\partial G}{\delta t(x)}=z(L)\exp\left\{\frac{\delta H\{w(x)\}}{\delta w(L)}\right\}z(x)\frac{\delta^2 H\{w(x)\}}{\delta w(L)\,\delta w(x)}$$

$$\frac{\delta G}{\delta z(x)}=\delta(L-x)\exp\left\{\frac{\delta H\{w(x)\}}{\delta w(L)}\right\}+z(L)\exp\left\{\frac{\delta H\{w(x)\}}{\delta w(L)}\right\}\frac{\delta^2 H\{w(x)\}}{\delta w(x)\,\delta w(L)}t(x).$$

Equations (4.9), (4.14) and (4.15) can be written as follows using (4.5):

$$\frac{\mathrm{d}A(L,x)}{\mathrm{d}L} = -A(L,L)E(L)X(L,x)A(L,x) \tag{5.1}$$

$$\frac{\mathrm{d}K(L)}{\mathrm{d}L} = \frac{\mathrm{d}A(L,x)}{\mathrm{d}x}\bigg|_{x=L} E(L) + A(L,L)E(L)\frac{\partial}{\partial L}\left(\frac{\delta H\{w(x)\}}{\delta w(L)}\right)\bigg|_{z=z_L} \tag{5.2}$$

$$\frac{\mathrm{d}B(L,x)}{\mathrm{d}L} = \delta(L-x)E(L) + A(L,L)E(L)B(L,x)X(L,x) \tag{5.3}$$

where

$$E(L) = \exp\left\{\frac{\delta H\{w(x)\}}{\delta w(L)}\right\}\bigg|_{z=z_L} \tag{5.4}$$

and

$$X(L,x) = \frac{\delta^2 H\{w(x)\}}{\delta w(x)\,\delta w(L)}\bigg|_{z=z_L} \tag{5.5}$$

This set of equations together with (4.8) will now be solved with the initial conditions $F\{0, z(x)\} = 0$.

Equation (5.1) gives $(\mathrm{d}/\mathrm{d}L)\ln A(L,x) = -A(L,L)E(L)X(L,x)$. Hence

$$A(L,x) = A(0,x)\exp\left(-\int_0^L \mathrm{d}s\, A(s,s)E(s)X(s,x)\right). \tag{5.6}$$

Similarly (5.3) with $B(0,x)=0$ gives $B(L,x)=0$ for $L<x$ and $B(x^+,x)-B(x^-,x)=E(x)$ so $B(x^+,x)=E(x)$ and for $L>x$

$$\frac{\mathrm{d}\ln B(L,x)}{\mathrm{d}L} = A(L,L)E(L)X(L,x).$$

Hence

$$B(L,x) = E(x)\exp\left(\int_x^L \mathrm{d}s\, A(s,s)E(s)X(s,x)\right) \tag{5.7}$$

$$A(L,x)B(L,x) = E(x)A(0,x)\exp\left(-\int_0^x \mathrm{d}s\, A(s,s)E(s)X(s,x)\right)$$

if $x<L$ and zero otherwise. Set $x = L-\varepsilon$ and define $g(L) = A(L,L)$ then

$$g(L) = A(0,L)\exp\left(-\int_0^L \mathrm{d}s\, g(s)E(s)X(s,L)\right). \tag{5.8}$$

A and X are here assumed to be continuous functions of both their arguments. Hence

$$\begin{aligned} A(L,x)B(L,x) &= E(x)g(x) && \text{if } x<L \\ &= 0 && \text{otherwise} \end{aligned}$$

and it follows that

$$E(L) = \exp\left\{\frac{\delta H\{E(x)g(x)\theta(L-x)\}}{\delta w(L)}\right\}$$

and

$$X(L,x)=\frac{\delta^2 H\{E(x)g(x)\theta(L-x)\}}{\delta w(s)\,\delta w(L)}.$$

Using the identity (4.22) gives

$$\int_0^L \mathrm{d}s\, E(s)g(s)X(s,L)=\ln E(L).$$

Combining this with (5.8) gives $A(0,L)=g(L)E(L)$; hence

$$\begin{aligned} A(L,x)B(L,x) &= A(0,x) && \text{if } x<L \\ &=0 && \text{otherwise.} \end{aligned} \tag{5.9}$$

Using (4.22) again gives

$$\int_0^L \mathrm{d}s\, E(s)g(s)\frac{\delta^2 H\{E(x)g(x)\theta(s-x)\}}{\delta w(s)\,\delta w(x)}=\frac{\delta H\{E(x)g(x)\theta(L-x)\}}{\delta w(x)}.$$

The LHS of this is

$$\int_0^L \mathrm{d}s\, E(s)g(s)X(s,x).$$

Hence (5.6) can be written as

$$A(L,x)=A(0,x)\exp\left\{\frac{-\delta H\{A(0,x)\theta(L-x)\}}{\delta w(x)}\right\}. \tag{5.10}$$

Combining (5.9) with (5.10) gives

$$\begin{aligned} B(L,x) &= \exp\left\{\frac{\delta H\{A(0,x)\theta(L-x)\}}{\delta w(x)}\right\} && \text{if } x<L \\ &=0 && \text{otherwise} \end{aligned} \tag{5.11}$$

and from above

$$E(L)=\exp\left\{\frac{\delta H\{A(0,x)\theta(L-x)\}}{\delta w(L)}\right\}. \tag{5.12}$$

The next steps are to use (5.10), (5.11) and (5.12) to evaluate (5.2) to obtain $K(L)$ and finally to use (4.8) to evaluate $F(L)$. From (4.16) it is easy to show that $\mathrm{d}K(L)/\mathrm{d}L = \mathrm{d}A(0,L)/\mathrm{d}L$. The initial condition is

$$K(0)=z_L(L)\exp\left\{\frac{\delta H\{A(0,x)\theta(L-x)\}}{\delta w(L)}\right\}\Bigg|_{L=0}=A(0,0). \tag{5.13}$$

Hence $K(L)=A(0,L)$ (5.13) and from (4.8) since $F(0)=0$

$$F(L)=\int_0^L \mathrm{d}s\, A(0,s)\left(1-\int_0^s \mathrm{d}x\, A(0,x)\frac{\delta^2 H\{A(0,x)\theta(s-x)\}}{\delta w(x)\,\delta w(s)}\right). \tag{5.14}$$

Combining (5.10) with (5.14) gives the required solution, i.e. the solution of

$$\frac{\partial F\{L,z(x)\}}{\partial L}=z(L)\exp\left(\frac{\delta H\{w(x)\}}{\delta w(L)}\right) \tag{5.15}$$

with

$$w(x)=\frac{\delta F\{L, z(x)\}}{\delta z(x)}z(x) \tag{5.16}$$

and the initial condition $F\{0, z(x)\}=0$ can be written as

$$F\{L, z(x)\}=\int_0^L \mathrm{d}t\, h(t)\left(1-\int_0^t \mathrm{d}s\, h(s)\frac{\delta^2 H\{h(x)\theta(t-x)\}}{\delta h(t)\,\delta h(s)}\right) \tag{5.17}$$

where $h(x)$ is given by

$$z(x)=h(x)\exp\left(\frac{-\delta H\{h(x)\theta(L-x)\}}{\delta h(x)}\right) \qquad \text{for } 0<x<L. \tag{5.18}$$

6. Equations for the correlation functions n_1 and n_2 in general and the translation invariant case

If $H\{z(x)\}$ is chosen to be

$$\int_0^\infty \mathrm{d}t \int_0^t \mathrm{d}s\, z(t)z(s)f(t-s)$$

then the above result reduces to the following. The solution of

$$\frac{\partial F\{L, z(x)\}}{\partial L}=z(L)\exp\left(\int_0^\infty \mathrm{d}x\, z(x)\frac{\delta F\{L, z(x)\}}{\delta z(x)}f(L-x)\right) \tag{6.1}$$

with $F\{0, z(x)\}=0$ is

$$F\{L, z(x)\}=\int_0^L \mathrm{d}t\, h(t)\left(1-\int_0^t \mathrm{d}s\, h(s)f(t-s)\right) \tag{6.2}$$

where $h(x)$ is given by

$$z(x)=h(x)\exp\left(-\int_0^L \mathrm{d}t\, h(t)f(x-t)\right). \tag{6.3}$$

Hence equations (6.2) and (6.3) provide an approximate expression for $F\{L, z(x)\}$ as defined in equation (3.2). It is possible to obtain from this not only the thermodynamic functions, as described above, but also all the correlation functions for the system in equilibrium as was pointed out by Percus [10] among others. Probably the easiest way to do this is to define the k-particle distribution functions excluding coincidences by

$$n_k(x_1\ldots x_k)=\left\langle \sum_{i_1=1}^{N}\cdots\sum_{i_k=1}^{N}\prod_{j=1}^{k}\delta(L_{i_j}-x_j)\right\rangle \qquad \text{indices unequal.} \tag{6.4}$$

Then by repeated functional differentiation of (2.10) one obtains

$$\frac{\delta\Xi\{L, z(x)\}}{\delta z(x_1)}=\sum_{N=0}^{\infty}\int_0^L \mathrm{d}L_1\int_0^{L_1}\mathrm{d}L_2\ldots\int_0^{L_{N-1}}\mathrm{d}L_N\exp\left(-\sum_{1\le i<j\le N}u(L_i-L_j)\right)$$
$$\times\sum_{i_1=1}^{N}\prod_{\substack{j=1\\ j\neq i_1}}^{N}z(L_j)\,\delta(L_{i_1}-x_1)$$

$$\frac{\delta^2\Xi\{L, z(x)\}}{\delta z(x_1)\,\delta z(x_2)} = \sum_{N=0}^{\infty}\int_0^L \mathrm{d}L_1 \ldots \int_0^{L_{N-1}} \mathrm{d}L_N \exp\left(-\sum_{1\le i<j\le N} u(L_i - L_j)\right) \times \sum_{i_1=1}^{N} \delta(L_{i_1} - x_1) \sum_{\substack{i_2=1\\ i_2\ne i_1}}^{N} \prod_{\substack{j=1\\ j\ne i_1 \text{ or } i_2}}^{N} z(L_j)\,\delta(L_{i_2} - x_2)$$

etc, and in general

$$\frac{\delta^k\Xi\{L, z(x)\}}{\prod_{i=1}^{k}\delta z(x_i)} = \frac{\Xi\{L, z(x)\}}{\prod_{i=1}^{k} z(x_i)}\, n_k(x_1 \ldots x_k). \tag{6.5}$$

To test the accuracy of the approximation (6.2) and (6.3) I shall use it to calculate n_1 and n_2 for arbitrary L and $z(x)$ and the pressure for fixed L and constant z. For the latter I have also obtained a power series in z which can be checked against the well known result for the thermodynamic pressure.

βP for arbitrary values of L and $z(x)$ is obtained by first solving for $h(x)$ (which should more precisely be written as $h\{x; L, z(x)\}$) in equation (6.3) and substituting the result in (2.7) using (6.2). For the uniform case $z(x) = z$; using the expansion

$$h(x; L, z) = \sum_{N=0}^{\infty} z^N h(x; L, N)$$

gives

$$\sum_{N=0}^{\infty} z^N h(x; L, N) = z \exp\left(\int_0^L \mathrm{d}t\, h(t; L, 0) f(x-t)\right) \times \left[\sum_{j=0}^{\infty} \frac{z^j}{j!}\left(\int_0^L \mathrm{d}t\, h(t; L, 1) f(x-t)\right)^j\right] \times \left[\sum_{k=0}^{\infty} \frac{z^{2k}}{k!}\left(\int_0^L \mathrm{d}t\, h(t; L, 2) f(x-t)\right)^k\right] \times \ldots.$$

Equating coefficients of powers of z gives $h(x; L, 0) = 0$, $h(x; L, 1) = 1$ and

$$h(x; L, 2) = \int_0^L \mathrm{d}t\, f(x-t)$$

$$h(x; L, 3) = \int_0^L \mathrm{d}t\, f(x-t) \int_0^L \mathrm{d}s\, f(t-s) + \frac{1}{2}\left(\int_0^L \mathrm{d}t\, f(x-t)\right)^2.$$

Hence for the uniform system

$$\beta P(L) = \sum_{i=1}^{\infty} b_i^* z^i$$

where

$$b_1^* = 1 \qquad b_2^* = \int_0^L \mathrm{d}t\, f(t-L)$$

and

$$b_3^* = \frac{1}{2}\left(\int_0^L \mathrm{d}s\, f(L-s)\right)^2 + \int_0^L \mathrm{d}t \int_0^L \mathrm{d}s\, f(t-s) f(t-L) \tag{6.6}$$

from which it follows that $b_1^* = b_1$, $b_2^* = 2$ but $b_3^* \neq b_3$, etc, where b_i are the exact values which occur in the series

$$\beta P = \sum_{i=1}^{\infty} b_i z^i.$$

Considering next the correlation functions it is straightforward to obtain from (6.2), (6.3) and (6.5) closed equations for the correlation functions for any number of particles.

Functional Taylor expansions of these WRT $z(x)$ would show how these results compare with other approximations and the formally exact theory given by Stell [11]:

$$n_1(x_1) = z(x_1)\frac{\delta F\{L, z(x)\}}{\delta z(x_1)} = z(x_1)\int_0^L \mathrm{d}t\left(1 - \int_0^L \mathrm{d}s\, h(s) f(t-s)\right) m_1(t, x_1) \tag{6.7}$$

where

$$m_1(t, x_1) = \frac{\delta h\{t; L, z(x)\}}{\delta z(x_1)}$$

can be obtained from an integral equation found by differentiating (6.3)

$$\delta(x - x_1) = m_1(x, x_1)\frac{z(x)}{h(x)} - z(x)\int_0^L \mathrm{d}s f(x-s) m_1(s, x_1). \tag{6.8}$$

From (6.5) using $F = \ln \Xi$ I obtain

$$n_2(x_1, x_2) = z(x_1)z(x_2)\frac{\delta^2 F\{L, z(x)\}}{\delta z(x_1)\,\delta z(x_2)} + n_1(x_1)n_1(x_2) \tag{6.9}$$

$$\frac{\delta^2 F\{L, z(x)\}}{\delta z(x_1)\,\delta z(x_2)} = \int_0^L \mathrm{d}t[m_2(t, x_1, x_2) - \int_0^L \mathrm{d}s f(t-s)$$
$$\times\{m_1(s, x_2)m_1(t, x_1) + h(s)m_2(t, x_1, x_2)\}] \tag{6.10}$$

where $m_2(t, x_1, x_2)$ satisfies the following equation obtained by differentiating (6.8):

$$0 = m_2(x, x_1, x_2)\frac{z(x)}{h(x)} + \frac{m_1(x, x_1)}{h(x)}\delta(x - x_2) - \frac{m_1(x, x_1)}{h^2(x)} z(x) m_1(x, x_2)$$
$$- \delta(x - x_2)\int_0^L \mathrm{d}s f(x-s) m_1(s, x_1) - z(x)\int_0^L \mathrm{d}s f(x-s) m_2(s, x_1, x_2). \tag{6.11}$$

The density $n_1(x_1)$ is defined by equations (6.7) and (6.8) and $n_2(x_1, x_2)$ is defined by (6.9), (6.10) and (6.11). Suppose that the system is uniform, i.e. $z(x) = z$ and z is independent of L, then for small systems with nearly hard core potentials packing will force $n_1(x)$, and presumably the other functions defined above, to be oscillating with period of the order of the range of the pair potential at high densities. However, provided L is large compared with the range of the pair potential it is reasonable to assume that $h(x_1)$, $n_1(x_1)$, $n_2(x_1, x_2)$, $m_1(t, x_1)$, $m_2(t, x_1, x_2)$ are all translation invariant (provided $0 \ll x_1, x_2, t \ll L$). Leff and Coopersmith [12] have shown that this holds rigorously for n_j, $1 \leq j \leq N$ for the canonical ensemble with finite N and L provided that the pair potential is zero beyond some range R, $L > 2(N-j)R$ and $(N-j)R < x_i < L-(N-j)R$; hence the above functions can be written as

$$h,\ n_1,\ n_2(x_1 - x_2),\ m_1(t - x_1),\ m_2(t - x_1, t - x_2) \tag{6.12}$$

respectively. From their definitions m_2 and n_2 are symmetric with respect to exchange of x_1 and x_2 . Also $f(x)=f(-x)$ and I shall assume that under these conditions m_1 is symmetric and m_1 and m_2 decay quickly enough for their Fourier transforms to exist. Under these assumptions an asymptotic analysis of βP and the correlation functions is possible whict gives simple results.

Replacing $h\{x;\, L, z(x)\}$ in (6.3) by $h(L, z)$ gives

$$z=h(L, z)\exp(-Jh(L, z))$$

where

$$J=\int_0^L \mathrm{d}s f(x-s) \tag{6.13}$$

and J is almost independent of x when $0\ll x\ll L$. Hence it follows that $h=h(z)$ only; and since $z>0$, assuming that $J<0$, the solution of

$$h(z)=z\exp[Jh(z)] \tag{6.14}$$

is unique and positive. Under these conditions equation (6.2) gives $F(L, z)=h(z)L(1-Jh(z)/2)$ and hence

$$\beta P=h(1-Jh/2). \tag{6.15}$$

The series expansion derived from this is

$$\beta P=z+\tfrac{1}{2}z^2J+\tfrac{1}{2}z^2J^3+\tfrac{3}{2}z^4J^3+\ldots$$

the first two terms of which are the exact values and they agree with results for finite systems found earlier.

Under the above assumptions the correlation functions can be obtained from equations (6.7)-(6.11) which can then be greatly simplified. Equation (6.8) gives the following:

$$\delta(x-x_1)=m_1(x-x_1)\frac{z}{h}-z\int_0^L \mathrm{d}s f(x-s)m_1(s-x_1).$$

The singular part of m_1 can be separated out by writing

$$m_1(x-x_1)=m_1^*(x-x_1)+A\delta(x-x_1) \tag{6.16}$$

where m_1^* is continuous. Substituting this and choosing $h=Az$ to cancel the singular terms gives the following:

$$0=\frac{z}{h}m_1^*(x-x_1)-z\int_0^L \mathrm{d}s f(x-s)m_1^*(s-x_1).$$

Fourier transforming this gives

$$\tilde{m}_1(k)=\frac{h\tilde{f}(k)}{z(1/h-\tilde{f}(k))}$$

and hence

$$\tilde{m}_1(0)=\frac{hJ}{z(1/h-J)} \tag{6.17}$$

where $\tilde{f}(0)=J$ and the Fourier transform is defined by

$$\tilde{f}(k)=\int_{-\infty}^{\infty}\mathrm{d}x\exp(\mathrm{i}kx)f(x).$$

Using these results (6.7) gives the simple result $n_1 = h$; hence the equation of state is given by

$$\beta P = n_1 - \tfrac{1}{2} J n_1^2. \tag{6.18}$$

For the pair correlation function n_2 equation (6.11) gives, using assumptions (6.12),

$$\begin{aligned} 0 = m_2(y_1, y_2)\frac{z}{h} - m_1^*(y_1) m_1^*(y_2)\frac{z}{h^2} - m_1^*(y_2)\,\delta(y_1)\frac{1}{h} \\ - \delta(y_2)\int_0^L \mathrm{d}s\, f(x-s) m_1^*(s-x+y_1) - \delta(y_2) f(y_1)\frac{h}{z} \\ - z\int_0^L \mathrm{d}s\, f(x-s) m_2^*(s+y_1-x, s+y_2-x) \end{aligned}$$

where $y_1 = x - x_1$ and $y_2 = x - x_2$.

By introducing $m(y_1, y_3) = m_2(y_1, y_2)$ with $y_3 = y_2 - y_1$ this can be simplified to

$$\begin{aligned} m(y_1, y_3) = \frac{1}{h} m_1^*(y_1) m_1^*(y_1+y_3) + \frac{1}{z} m_1^*(y_1+y_3)\,\delta(y_1) \\ + \frac{1}{z} m_1^*(y_1)\,\delta(y_1+y_3) + h\int_{-x}^{L-x} \mathrm{d}s\, f(-s) m(s+y_1, y_3). \end{aligned}$$

By Fourier transforming this equation WRT y_1 and solving for m this yields

$$\begin{aligned} \tilde{m}(k, y_3) = \frac{1}{(1-h\tilde{f}(k))}\bigg(\frac{1}{h}\int_{-\infty}^{\infty} \mathrm{d}y_1 \exp(\mathrm{i}ky_1) m_1^*(y_1) m_1^*(y_1+y_3) \\ + \frac{1}{z}(m_1^*(y_3) + \exp(-\mathrm{i}ky_3) m_1^*(y_3))\bigg). \end{aligned}$$

In this work I shall only need the result for $k = 0$ which is

$$\tilde{m}(0, y_3) = \frac{(1/h) m_1^* * m_1^*(y_3) + (2/z) m_1^*(y_3)}{1 - hJ} \tag{6.19}$$

where * is the convolution operation. Equations (6.9) and (6.10) with assumptions (6.12) yield

$$\begin{aligned} n_2(y) = h^2 + z^2\bigg(\tilde{m}(0, y) - \int_0^L \mathrm{d}t\int_0^L \mathrm{d}s\, f(t-s) m_1^*(s-x_2) m_1^*(t-x_1) \\ - \frac{h}{z}\int_0^L \mathrm{d}t\, f(t-x_2) m_1^*(t-x_1) - \frac{h}{z}\int_0^L \mathrm{d}s\, f(x_1-s) m_1^*(s-x_2) \\ - \frac{h^2}{z^2} f(x_1-x_2) - h\int_0^L \mathrm{d}t\int_0^L \mathrm{d}s\, f(t-s) m(t-x_1, y)\bigg). \end{aligned}$$

Introducing the radial distribution function $g(x)$ by $n_2(y) = n_1^2 g(y)$ gives

$$g(y) = \frac{z^2}{h^2}\bigg(\frac{1}{h} m_1^* * m_1^*(y) + \frac{2}{z} m_1^*(y) - m_1^* * m_1^* * f(y) - \frac{2h}{z} m_1^* * f(y) - \frac{h^2}{z^2} f(y)\bigg) + 1.$$

Taking the Fourier transform of this equation and using (6.17) yields the surprisingly simple result

$$c(x)=f(x) \tag{6.20}$$

where $c(x)$ is the direct correlation function which is defined by the Ornstein-Zernike relation

$$g(x)-1=c(x)+n_1(g-1)*c(x). \tag{6.21}$$

7. Summary and conclusions

This work shows clearly that from $F\{L, z(x)\}$ it is possible, in principle, to derive all the thermodynamic functions and the correlation functions for any number of particles. The only approximation that has been made for the finite system is the first-order expansion of the term in the exponential of equation (3.2). It is hoped that it will be possible to systematically improve on this approximation by taking higher terms into account by expressing (3.2) as a system of constant coefficient linear functional differential equations. Simple results were obtained for the thermodynamics and the correlation functions for the system in the thermodynamic limit. In order to calculate $g(x)$ from any proposed model pair potential (which may be given numerically) it is only necessary to use (6.20) and the Fourier transform of (6.21). To calculate the pressure only requires the integral J to be found. Then βP is given in terms of h from (6.15) which satisfies a transcendental equation (6.14). This is to be compared with the existing approximation schemes which often require numerical iteration of integral equations. I believe that this fact, together with series expansion results stated here, will make this approximation (and its generalisations) useful in many applications of statistical mechanics despite the act that it is probably less accurate than some existing approximations at high densities. I also think that a systematic evaluation of the usefulness of the method can only be made after much subsequent work has been published.

The assumptions concerning large uniform systems need careful consideration. A thorough account would attempt to justify them with rigorous mathematical argument rather than introduce them as additional assumptions. I am not able to do this yet and I think it only makes sense to do so within the thermodynamic limit of an exact mathematical treatment.

On the purely mathematical side I have given the general method of solution of a non-linear first-order functional differential equation and I have applied the method to a subset of these equations for which the solution can be given explicitly in terms of the solution of a non-linear integral equation. This solution is a generalisation of the solution needed for this work and it may be useful in other fields.

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