Pramāṇa, Vol. 18, No. 1, January 1982, pp. 89–98. © Printed in India.

Solution of Ornstein-Zernike equation for one-dimensional fluids

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MS received 19 September 1981

Abstract. The application of Wiener-Hopf factorisation procedure as adopted by Baxter has been used to solve the one-dimensional Ornstein and Zernike (OZ) equation for a fluid of interacting hard rods. Exact solution is obtained for the Kac potential in the van der Waals limit. We also obtain perturbative results which agree exactly with the lowest order calculations of Kac, Uhlenbeck and Hemmer.

Keywords: Ornstein-Zernike equation; one-dimensional fluid; hard rod; Baxter method; direct correlation function; total correlation function; radial distribution function; exponential tail; van der Waals limit; phase transition.

1. Introduction

The study of statistical mechanics of fluids in one dimension has been a subject of considerable interest. A soluble one-dimensional exponentially interacting gas model was first proposed by Kac (1959). Soon afterwards rigorous solutions of the model were obtained by Kac *et al* (1963). They gave an exact derivation of the partition function in the thermodynamic limit and found that for a finite range of the attractive force, the system does not show a phase transition in conformity with the results of Gursey (1950) and van Hove (1950). However, for a weak but very long range attractive force a phase transition appears which is described by the van der Waals equation. They also deduced the distribution functions, specially the pair distribution function for the interacting gas. Percus (1976) has also studied the equilibrium state of a classical fluid of hard rods in an external field. All direct correlation functions are shown to be of finite range in all pairs of variables.

Unlike the Kac model, the many body problems which are of physical interest are difficult to solve exactly. One integral equation due to Ornstein and Zernike (1926) which can be deduced by summing up majorised graphs of cluster expansion methods (Rice and Gray 1965), appears to describe the physical situations in a simpler prospective. Even this approximate integral equation requires further approximations for the direct correlation function, the convolution hypernetted chain (CHNC) and the Percus-Yevic (PY) approximations. Recently Baxter (1968) has suggested a very powerful method of solving OZ equation in PY approximation using the Wiener-Hopf technique (Morse and Feshback 1953). This has been applied successfully to study the problems in three dimensions.

It is not at all clear whether this method, when applied to the one-dimensional Kac model will reproduce the results of Kac *et al* (1963) in the van der Waals limit. Since the phenomenon of phase transition in one dimension is a highly controversial subject, it is worth-while to deduce it by other independent methods. Furthermore, the highly successful exponential approximation of Andersen and Chandler (1972) seems to disagree with the machine calculation of structure function for small wave numbers (Stell and Weis 1980). There is a need to have diverse methods of solution which can follow the manner of obtaining solution from one-dimensional models. The present note is an attempt in these directions.

We find that the Kac problem can be solved elegantly by the Baxter (1968) method. §2 describes Baxter's technique and its application to solve the problem of hard rods. A general method of solution for the interacting rods which can be extended to three dimensions is given in §3. Kac model is also solved in this section to the lowest order of perturbation in both the long and the short range limits.

2. Solution by the Wiener-Hopf and Baxter technique

2.1 *General formulation*

In one dimension, the OZ equation is

$$h(x) = C(x) + \frac{1}{l} \int_{-\infty}^{+\infty} \mathrm{d}x' \, C(x') \, h(x-x'), \tag{1}$$

where $1/l = N/L$ is the density of hard rods and its Fourier transformed equation

$$\tilde{h}(k) = \tilde{C}(k) + \frac{1}{l} \tilde{h}(k) \, \tilde{C}(k), \tag{2}$$

can be rewritten in the form

$$(1 + \tilde{h}(k)/l)\,(1 - \tilde{C}(k)/l) = 1. \tag{3}$$

We define a new function $\tilde{A}(k)$ by the relation

$$\tilde{A}(k) = 1 - 1/l \, \tilde{C}(k) = (1 + 1/l \, \tilde{h}(k))^{-1}. \tag{4}$$

For a disordered fluid, $\tilde{h}(k)$ is finite. Consequently $\tilde{A}(k)$ has no zeroes for real values of k and it can always be factorized (Baxter 1968) as

$$\tilde{A}(k) = \tilde{\Gamma}_1(k) \, \tilde{\Gamma}_2(k). \tag{5}$$

$\tilde{\Gamma}_1(k)$ is analytic in the upper half of the complex k plane and has zeroes only in the lower half of the plane, whereas $1/\tilde{\Gamma}_2(k)$ is analytic in the lower half of the plane and has zeroes only in the upper half of the plane. From the defining equations and assumed analyticity it follows that (Baxter 1968)

$$\tilde{\Gamma}_{1,2}(k) \sim 1 + O\left(\frac{1}{|\mathrm{Re}\, k|}\right) \tag{6}$$

The functions $1 - \tilde{\Gamma}_{1,2}(k)$ are therefore Fourier integrable along the real axis and the two functions defined by

$$\Gamma_{1,2}(x) = l \int_{-\infty}^{\infty} \mathrm{d}k/2\pi \, (1 - \tilde{\Gamma}_{1,2}(k) \exp(-ikx), \tag{7}$$

are such that $\Gamma_1(x)$ vanishes for $x < 0$ and $\Gamma_2(x)$ vanishes for $x > 0$. Equation (4) with the help of (5) can be written in the form

$$\frac{1}{l}\tilde{C}(k) = 1 - \tilde{\Gamma}_1(k) + 1 - \tilde{\Gamma}_2(k) - (1 - \tilde{\Gamma}_1(k))\,(1 - \tilde{\Gamma}_2(k)). \tag{8}$$

From (8), one easily gets $C(x)$ in terms of $\Gamma_{1,2}(x)$ as

$$C(x) = \Gamma_1(x) + \Gamma_2(x) - 1/l \int_{x}^{\infty} \Gamma_1(t)\, \Gamma_2(x-t)\, \mathrm{d}t. \tag{9}$$

Multiplying $\exp(-ikx)$ to both sides of the equation

$$\tilde{\Gamma}_1(k)\ [1 + 1/l\, \tilde{h}(k)] = 1/\tilde{\Gamma}_2(k), \tag{10}$$

and integrating with respect to k from $-\infty$ to ∞ and noting that

$\int_{-\infty}^{+\infty} 1/\tilde{\Gamma}_2(k) \exp(-ikx)\, \mathrm{d}k = 0$ for $x > 0$, we get

$$h(x) = \Gamma_1(x) + 1/l \int_{0}^{\infty} \mathrm{d}t\, \Gamma_1(t)\, h(x-t), \tag{11}$$

for $x > o$. Thus besides the direct correlation function $C(x)$ and the total correlation function $h(x)$, (9) and (11) show that a third analytic function $\Gamma(x)$ can be introduced which is related to $C(x)$ and $h(x)$ in a convenient manner.

2.2 *Hard rods*

Following Baxter's notation let us replace Γ by Q in the hard rod problem. For a rod of length δ

$$h(x) = -1 \qquad \text{for } 0 < |x| < \delta,$$

and

$$C(x) = 0 \qquad \text{for } |x| > \delta.$$

It follows that, for $x > \delta$

$$Q(x) = \Gamma_1(x) = 0. \tag{12}$$

Substituting these values in (11), we get, for $0 < x < \delta$

$$-1 = Q(x) + 1/l \int_0^\delta Q(t)\, h(x-t)\, dt, \tag{13}$$

when both x and t are in the range 0 to δ, then $h(x-t) = -1$ in (13). So $Q(x)$ can be easily found and then from (9), $C(x)$ can be obtained.

$$Q(x) = -l/(l-\delta), \tag{14}$$

and

$$C(x) = -l(l-x)/(l-\delta)^2, \tag{15}$$

which is the correct result (Wertheim 1964). Equation (11) for $x > \delta$ for non-interacting hard rods become

$$g(x) = 1 - 1/l \int_0^\delta Q(t)\, dt + 1/l \int_0^\delta Q(t)\, g(x-t)\, dt. \tag{16}$$

The Laplace transform of $g(x)$ is obtained as

$$G(s) = \int_0^\infty \exp(-Sx)\, g(x)\, dx = \frac{l}{[1 + s(1-\delta)] \exp(s\delta) - 1}. \tag{17}$$

The inverse Laplace transform is easily calculated to find the radial distribution function

$$g(x) = l \sum_{n=1}^{\infty} \theta(x - n\delta) \exp[-(x - n\delta)/(l-\delta)] \frac{(x - n\delta)^{n-1}}{(l-\delta)^n (n-1)!}, \tag{18}$$

where $\theta(x - n\delta)$ is the Heaviside step function, agreeing with the results of Kac *et al* (1963) and Zernike and Prins (1927). Thus we are assured that the one-dimensional version of Baxter's formalism together with the PY approximation solves the problem of hard rod exactly.

3. *General method of solution*

3.1 *Interacting hard rods*

To discuss the problem of interacting hard rods (Smith 1979) it is convenient to consider $C(x)$ on $x > \delta$ separately from its behaviour on $o < x < \delta$.

$$C(x) = C_0(x)\, \theta(\delta - |x|) + C_1(x)\, \theta(|x| - \delta). \tag{19}$$

It is important to note that $C_0(x)$ is not identical with the hard core value, even though the latter may be a good approximation to it in most of the problems of physical interest. The Fourier transform of $C(x)$, $\tilde{C}(k)$ may also be written in the form

$$\tilde{C}(k) = \tilde{C}_0(k) + \tilde{C}_s(k). \tag{20}$$

$C_s(k)$ can be taken as the Fourier transform of $C_1(x)$ which contains the unknown function $g(x)$. Thus one has to resort to further approximation depending upon the physical problem under consideration. PY proposed to approximate $C_1(x)$ by

$$C_1(x) \simeq g(x)\,[(1 - \exp(\beta v)(x))], \tag{21}$$

where $\beta = 1/KT$ Similarly for the two regions we decompose $\Gamma(x)$ as

$$\Gamma_1(x) = \Gamma_0(x)\,\theta(\delta - x) + \Gamma_\infty(x)\,\theta(x - \delta). \tag{22}$$

Now we assert that

$$\Gamma_\infty(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{\tilde{C}_s(k)}{\tilde{\Gamma}_2(k)} \exp(-ikx). \tag{23}$$

To demonstrate the correctness of this assertion, use (9) for $x > \delta$ to get

$$C_1(x) = \Gamma_\infty(x) - \frac{1}{l}\int_x^{\infty} \Gamma_\infty(x)\,\Gamma(t - x)\,dt, \tag{24}$$

and then substitute (23) for $\Gamma_\infty(x)$. Then

$$C_1(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \exp(-ikx) \frac{\tilde{C}_s(k)}{\tilde{\Gamma}_2(k)} \left[1 - \frac{1}{l}\int_0^{\infty} \Gamma(t) \exp(-ikt)\,dt\right]. \tag{25}$$

Since by definition,

$$\tilde{\Gamma}_2(k) = 1 - 1/l \int_0^{\infty} \Gamma(t) \exp(-ikt)\,dt, \tag{26}$$

(25) follows.

Once $\Gamma_\infty(x)$ is known, (11) can be used within the range $0 < x < \delta$ to get

$$\Gamma_0(x) = -\tilde{\Gamma}(0) - 1/l \int_\delta^{\infty} \Gamma_\infty(t)\, g(x - t)\,dt, \tag{27}$$

where $\tilde{\Gamma}(0)$ is given by

$$\tilde{\Gamma}(0)=\frac{1}{l-\delta}-\frac{1}{l-\delta}\int_{\delta}^{\infty}\Gamma_{\infty}(t)\,\mathrm{d}t+\frac{1}{l(l-\delta)}\int_{0}^{\delta}\mathrm{d}x\int_{\delta}^{\infty}\mathrm{d}t\,\Gamma_{\infty}(t)\,g(x-t). \quad (28)$$

Thus $\Gamma(x)=\Gamma_0(x)+\Gamma_\infty(x)$, is known. Using this $\Gamma(x)$ in (9) and (11), the functions $C(x)$ and $g(x)$ can be found out. This is illustrated below.

3.2 *Kac model*

As an example consider the Kac model (Kac 1959) of hard rods interacting *via* an exponential attraction. The weak long-ranged potential is

$$v_1(x)=-\,\alpha\exp(-\gamma\,|x|)\,\theta(|x|-\delta). \quad (29)$$

In the limit $\gamma\to 0$, the range of the potential tends to infinity and as $\alpha\to 0$, the potential becomes only weakly attractive. The limit where both the α and γ tend to zero but with $\alpha/\gamma=\alpha_0$ finite, is called the van der Waals limit. This limiting procedure actually provides the escape from the Gursey-Van Hove results.

From (21), for $\alpha\,\beta=\nu$ tending to zero,

$$C_1(x)\simeq\nu\exp(-\gamma\,|x|)\,g(x)+0(\nu^2)+\dots . \quad (30)$$

Omitting ν^2 and the higher order terms, the Fourier transform of (30) is

$$\tilde{C}_s(k)=\nu\,[G(\gamma-ik)+G(\gamma+ik)], \quad (31)$$

where

$$G(\gamma\mp ik)=\int_0^\infty \mathrm{d}x\,g(x)\exp[-x(\gamma\mp ik)]. \quad (32)$$

Substituting (31) in (23) and integrating we get

$$\Gamma_\infty(x)=\frac{\nu\exp(-\gamma x)}{\tilde{\Gamma}_2(-i\gamma)}. \quad (33)$$

Using (33) in (27), we get

$$\Gamma_0(x)=-\,\tilde{\Gamma}(0)-\frac{\nu}{l}G(\gamma)\exp(-\gamma x)\frac{1}{\tilde{\tilde{\Gamma}}_2(-i\gamma)}, \quad (34)$$

where

$$G(\gamma)=\int_0^\infty \exp(-\gamma t)\,g(t)\,\mathrm{d}t. \quad (35)$$

$\tilde{\Gamma}(k)$, the Fourier transform of $\Gamma(x)$ is

$$\tilde{\Gamma}(k)=1+\frac{1}{l}\tilde{\Gamma}(0)\frac{\exp(ik\delta)-1}{ik}+\frac{\nu}{l^2}\frac{G(\gamma)}{}\frac{\{1-\exp[-\delta(\gamma-ik)]\}}{\tilde{\Gamma}_2(-i\gamma)(\gamma-ik)}$$
$$-\frac{\nu}{l}\frac{\exp[-\delta(\gamma-ik)]}{\tilde{\Gamma}_2(-i\gamma)(\gamma-ik)}. \tag{36}$$

Approximating $G(\gamma)$ by its hard core value $1/\gamma$ (in the limit $\gamma - 0$), defining $-\nu_0=\nu/\gamma$ and putting $k=0$,

$$\tilde{\Gamma}(0)\simeq\frac{l}{l-\delta}-\frac{\nu_0}{l\,\tilde{\Gamma}_2(-i\gamma)}. \tag{37}$$

For $k=i\gamma$, using (37) and (26), (36) becomes

$$\tilde{\Gamma}(i\gamma)\simeq\frac{l}{l-\delta}-\frac{\nu_0}{2l\,\tilde{\Gamma}(i\gamma)}. \tag{38}$$

Solving for (38)

$$\tilde{\Gamma}(i\gamma)=1/2\left[\frac{l}{l-\delta}\pm\left\{\left(\frac{l}{l-\delta}\right)^2-2\nu_0/l\right\}^{1/2}\right] \tag{39}$$

Substituting (38) and (39) in (37)

$$\tilde{\Gamma}(0)=[(l/l-\delta)^2-2\nu_0/l]^{1/2}. \tag{40}$$

It is to be noted that (40) can be very simply obtained if one assumes $\tilde{C}_0(k)$ to be given by the hard core value. Then

$$\tilde{\Gamma}(0)^2=1-\frac{1}{l}[\tilde{C}_0(0)+\tilde{C}_s(0)]$$
$$=\left(\frac{l}{l-\delta}\right)^2-\frac{2\nu_0}{l}.$$

The inverse compressibility equation of state (Baxter 1968) is

$$\beta\left.\frac{\partial p}{\partial\rho}\right|_T=\tilde{\Gamma}(o)^2=(l/l-\delta)^2-2\nu_0/l, \tag{41}$$

and leads as usual to the van der Waals equation of state.

$$p=\frac{1}{\beta(l-\delta)}-a_0/l^2, \tag{42}$$

where $a_0 = a/\gamma$. Thus in the van der Waals limit there is phase transition in the Baxter method of solution in one dimension.

It is not obvious, whether the highly involved expressions for the radial distribution function obtained by Kac *et al* (1963) can also be obtained by this simple and elegant method. To examine this point, let us denote the hard core values as

$$1 - \frac{1}{l}\tilde{C}_0(k) = \tilde{Q}(k)\,\tilde{Q}(-k). \tag{43}$$

So,

$$\tilde{\Gamma}_1(k)\,\tilde{\Gamma}_2(k) = 1 - \frac{1}{l}[\tilde{C}_0(k) + \tilde{C}_s(k)]$$

$$= \frac{\tilde{Q}(k)\,\tilde{Q}(-k)}{\gamma^2 + k^2}[k^2 + \gamma^2 B^2(k)], \tag{44}$$

where,

$$B^2(k) = 1 - \frac{v}{l\gamma^2}\left[\frac{G(\gamma - ik) + G(\gamma + ik)}{\tilde{Q}(k)\;\tilde{Q}(-k)}\right][\gamma^2 + k^2]. \tag{45}$$

The crucial and novel point in this analysis is to be able to correctly guess the values of $\tilde{\Gamma}_1(k)$ and $\tilde{\Gamma}_2(k)$ so that these latter functions satisfy the required analytic properties. After some intuitive thought and following the discussion by Morse and Feshback (1953) we found that they are as follows

$$\tilde{\Gamma}_1(k) = \frac{k^2 + \gamma^2 B^2(k)}{(k + i\gamma)\,C}\tilde{Q}(k),$$

and

$$\tilde{\Gamma}_2(k) = \frac{C}{k - i\gamma}\tilde{Q}(-k), \tag{46}$$

where C is an unknown constant factor. $1/\tilde{\Gamma}_2(k)$ cannot have zeroes on the lower half of the complex k plane. So it has zeroes at $k = +i\gamma$. The conjugate pole occurs in $\tilde{\Gamma}_1(k)$.

We emphasize here, that the approach of other authors in this regard can be entirely erroneous specially in the case of three dimensions (Hoye and Blum 1977; Blum and Hoye 1978). In perturbative analysis, much notice is not taken of the analyticity requirements of the exact solution which can be quite different from the unperturbed case.

From equations (4), (5) and (44) we have,

$$\tilde{Q}(k)\left(1 + \frac{1}{l}\tilde{h}(k)\right) = \frac{k^2 + \gamma^2}{k^2 + \gamma^2 B^2(k)}\,\frac{1}{\tilde{Q}(-k)}. \tag{47}$$

On rearranging the above equation, multiplying both the sides with exp $(-ikx)$ and integrating with respect to k from $-\infty$ to ∞ we get

$$h(x) = Q(x) + \frac{1}{l}\int_0^\infty \mathrm{d}t\, Q(t)\, h(x-t) + v\int_{-\infty}^{\infty}\frac{\mathrm{d}k}{2\pi}\,\frac{\exp(-ikx)}{\tilde{Q}(-k)}$$

$$\times\frac{k^2 + \gamma^2}{k^2 + \gamma^2 B^2(k)}\left[\frac{G(\gamma - ik) + G(\gamma + ik)}{\tilde{Q}(k)\,\tilde{Q}(-k)}\right]. \tag{48}$$

The Laplace transform is

$$G(s) = G_0(s) + v/B(0)\frac{(l-\delta)^4}{l^2}s^2 \exp(2s\delta)\frac{(s+\gamma)\,G(\gamma+s)}{\lambda^2(s)\,(s+\gamma B)}, \tag{49}$$

where $\lambda(s) = [1 + s(l-\delta)]\exp(s\delta) - 1$ and

$$G_0(s) = l/\lambda(s), \tag{50}$$

is the hard core value. Equation (49) can be written as

$$G(s) = G_0(s) + \Delta G(s), \tag{51}$$

where

$$\Delta G(s) = \frac{v}{B(0)}\,\frac{(l-\delta)^4}{l^2}\,\frac{s^2\exp(2s\delta)}{\lambda^2(s)}\,\frac{s+\gamma}{(s+\gamma B)}\,G(\gamma+s). \tag{52}$$

Incorporating van der Waals limit the first order perturbation effect for short ranges is

$$\Delta G(s) = \frac{v}{B(0)}\,\frac{(l-\delta)^4}{l}\,\frac{s^2\exp(2s\delta)}{\lambda^3(s)}. \tag{53}$$

In the long range, S is replaced by $S\gamma$ and then the limit $\gamma \to 0$ is taken with the result

$$\Delta G(s) = v_0(l-\delta)^4/[B(0)\,l^4(S+B)]. \tag{54}$$

The equations (53) and (54) agree exactly with the results of Kac *et al* (1963) and Lebowitz and Percus (1963) both in the long range and the short range limits.

4. Conclusion

The application of Wiener-Hopf method of factorisation has greatly facilitated the study of OZ equation in PY approximation. In a one-dimensional system there is a phase transition in van der Waals limit and for weakly attracting hard rods the results are in total agreement with the results of Kac *et al* (1963) at least to the first order of perturbation. Baxter's method can be used with confidence in perturbative study of the statistical mechanics of fluids in three dimensions as well.

Acknowledgement

The authors BPD and ACN are grateful to the UGC, India for the award of teacher fellowships.

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