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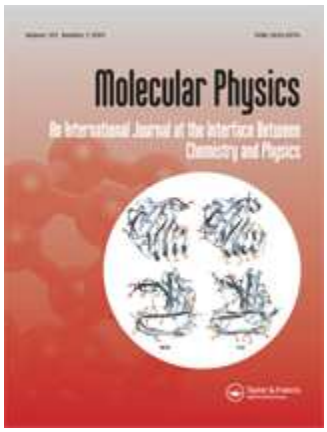

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Bridge diagrams and Fundamental Measure Theory: a test in Dimension One

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Abstract

A formal and general expression for the bridge function is obtained from the Fundamental Measure Theory. This expression involves solely the knowledge of an analytical form of the free-energy, the weight functions and the pair correlation function, and comes out in terms of combinations of convolution products of the two latter quantities, thus lifting the irreducibility of the concerned diagrams. It is applicable to mixtures and inhomogeneous fluids. The validity of this expression is then tested in the case of a one-dimensional hard rods fluid, for which

exact expression of the correlations are known, and the Fundamental Measure Theory is also exact. The formalism allows to sum the infinite series and produce a compact analytical expression for the exact bridge function. However, the numerical term by term evaluation of the series shows that severe convergence problems arise in the high density regime, questioning the pertinence of usual such attempts. The present approach opens interesting perspectives for the Theory of Liquids.

1 Introduction

In the Liquid State theory, the so-called bridge function represents an important unsolved many-body problem. This function comes as an infinite sum of highly connected sets of diagrams that are fundamentally irreducible[1, 2], which makes their calculation difficult at low order diagrammatic contributions[3] and impossible in the general case. Indeed, the diagrams involved in the virial series[4] already indicate that the task of calculating bridge diagrams beyond third order is very complex[5]. Yet, the knowledge of this function should allow to close exactly the Ornstein-Zernike equation, leading to the exact computation of the pair and direct correlation functions, therefore opening the route to an accurate calculation of the thermodynamical properties for any type of liquids. Any method which allows the computation such diagrams would be an invaluable contribution to the Liquid State theory. Many astute methods have been developed to palliate for our ignorance of the bridge function, mostly by making use of the available diagrammatically proper,

but approximate, known closure relations. The Verlet [6], Rogers-Young[7], or Zerah-Hansen HMSA[8] closures, are some example of such diagrammatically improper closures. The various degree of success and failures of these tentatives, have led for the search for alternative methods to obtain the correlation functions, one of the most successful being the Fundamental Measure Theory (FMT) of Rosenfeld[9, 10]. This theory is the most achieved of all density functional theories in the sense that it allows to obtain the Percus-Yevick (PY) expression for the direct correlation function (DCF) of the hard sphere fluid, solely from geometrical considerations on the overlap between two spheres, while all other DFT use the DCF as a conditional input. This theory involves a finite sets of *weight functions*, which are related to the geometrical properties of the *individual* particles. The pair DCF of the PY theory, in particular, as well as any higher order DCFs, can be expressed through this theory in terms of a sum of generalized convolution product of these weight functions. It turns out that, this property allows a neat factorisation of the irreducible bridge diagrams, which to my knowledge has not been previously reported, although Rosenfeld himself, and various authors after him, have investigated the possibility of accounting for the bridge function through the FMT, by invoking considerations on the thermodynamical self-consistency[11]. The expression for the bridge function derived here is compact and is free from any self-consistency requirements.

In order to test this new expression, I investigate the only case where an exact statistical mechanic solution of the liquid state is known, the one-

dimensional hard rod fluids. This solution is in fact the PY solution for this case[12, 13], and because of the structure of the FMT, it is also an exact solution of this latter theory.

2 General theory

In what follows, we consider a one component homogeneous molecular fluid, whose particles interact through a pairwise additive pair potential $v(1,2)$, where 1 and 2 represent the two particles and the shorthand notation $1 = (\vec{r_1}, \mathbf{\Omega_1})$ is understood (and similarly for 2), where $\vec{r}_1$ is the position of the particle 1 and $\mathbf{\Omega_1}$ its orientation, both in the lab fixed frame. The Mayer function is defined as usual through $f_M(1,2) = \exp(-\beta v(1,2)) - 1$, where $\beta = 1/k_B T$ is the Boltzmann factor where T is the temperature and k_B the Boltzmann constant.

The FMT, in its initial version, was formulated by Rosenfeld[9] under two assumptions. The first is the scaled particle expression (SPT)[14] for the excess Helmholtz free density $\beta F^{ex} = \int d1 \phi[\rho(1)]$, where the free energy density ϕ has been introduced as a functional of the inhomogeneous fluid with one-body density $\rho(1)$. This inhomogeneity need not necessarily arise from any external field. Indeed, using the Percus trick[18], a supplementary particle can be inserted into the homogeneous fluid in order to create the external field from the same interaction, thus transforming a N-component homogeneous fluid into a N+1 component inhomogeneous fluid. The second

assumption concerns the factorisation of the Mayer function into a sum of convolution product of weight functions. This second requirement is very restrictive. Indeed, the mathematical decomposition of $f_M(1,2)$ into products of weight functions can be rigorously obtained only for very few cases of interactions, all of them involving hard particles, such as for example, mixtures of hard sphere mixtures[9], hard hard cubes[15]. It does not work for hard convex particles in general[16, 17]. More importantly, it cannot be extended to more realistic interactions such as the Yukawa or Lennard-Jones interactions, without introducing further approximations. For hard spherical cores, it doesn't work in even dimensions[10]. So, this factorisation ansatz is certainly both the key point and the limitation of the FMT.

2.1 The bridge function within the FMT

Following Rosenfeld[9] and assuming this factorisation holds and that an appropriate excess free energy is available, the two following statements apply:

$$f_M(1,2) = \sum_{\alpha_1,\alpha_2} f_{\alpha_1\alpha_2} w_{\alpha_1}(1) \otimes w_{\alpha_2}(2) \tag{1}$$

$$\begin{aligned} c^{(n)}(1,2,..n) &= -\frac{\partial^n}{\partial \rho^n} \beta F_{ex}[\rho] \\ &= -\Pi_{\alpha_1 ... \alpha_n} \phi_{\alpha_1 ... \alpha_n} w_{\alpha_1}(1) \otimes ... \otimes w_{\alpha_n}(n) \end{aligned} \tag{2}$$

The first statement is the factorisation ansatz, which introduces the full

set of weight functions $w_\alpha(1)$: the notation $w_{\alpha_1}(1) \otimes w_{\alpha_2}(2)$ stands for a convolution of the spatial variable only $\int d\vec{x}\, w_{\alpha_1}(\vec{r}-\vec{x}, \mathbf{\Omega_1}) w_{\alpha_1}(\vec{x}, \mathbf{\Omega_2})$, and its generalization stands for a similar type of integral $\int d\vec{x} \Pi_k w_{\alpha_k}(\vec{r}_k - \vec{x}, \Omega_k)$. The constants $f_{\alpha\beta}$ serve to indicate that not all weight combinations might be allowed by construction - there value is zero or one accordingly. The second statement concerns the definition of the n-th order direct correlation function $c^{(n)}(1, 2, ..n)$, which is the n-order density derivative of the excess Helmholtz free-energy$F_{ex}[\rho]$, as expressed by the first equality. If the set of weighted density variables $\{\eta_\alpha\}$ is introduced, each of which defined by $\eta_\alpha = \rho \tilde{w}_\alpha(0)$ in terms of the $k = 0$ value of the Fourier transform of the corresponding weight function, then the second equality is just the result of applying the chain rule in terms of these new density variables, in the sense of functional derivative with weighted density function $\eta_\alpha(1) = \int d2\rho(2) w_\alpha(1, 2)$ (in this notation, an implicit spatial -and not angular- integration is assumed). The second equality follows then from restoring the homogeneity of the N-particle system. In the last equality we use the notation $\phi_{\alpha_1 ... \alpha_n} = \partial^n \phi / \partial \eta_{\alpha_1} ... \partial \eta_{\alpha_n}$. Since these steps have been numerously treated in the various literature concerning the FMT, I will not get into further details and just start from the two equations above. Note that these equations look perfectly general since no specific form for the free-energy has been required. However, the interrelation from the weighted densities and the free-energy is consistently required. It is noteworthy that the second order DCF should be identically equal to the Mayer function in the zero density limit, thus selecting the proper weight

combinations through the correct zero density limit of the excess free-energy.

The formal exact expression for the pair distribution function is:

$$g(1,2) = \exp(-\beta v(1,2) + h(1,2) - c(1,2) + B(1,2)) \tag{3}$$

where $h(1,2) = g(1,2) - 1$, $c(1,2)$ is the pair direct correlation function, and $B(1,2)$ the bridge function, which is formally defined as

$$B(1,2) = \sum_{n \geq 2} \rho^n B_n(1,2) \tag{4}$$

with

$$B_n(1,2) = \frac{1}{n!} \int ... \int d3..d(n+2)\, h(1,3)...h(1,n+2)\, c^{(n+1)}(2,..n+2) \tag{5}$$

Note that the sum in Eq.(4) starts at n=2, but in fact, it can be easily seen that the case $n = 1$ gives the second term in the exponential of Eq.3, $B_1(1,2) = h(1,2) - c(1,2)$, in virtue of Eq.(5) and the OZ equation:

$$h(1,2) - c(1,2) = \rho \int d3 h(1,2)c(2,3) \tag{6}$$

All three relations above are exact. The closure relation (3) holds under the pair-wise additivity assumption, but this is a minor restriction for the present purpose.

Now, if one inserts Eq.(2) into Eq.(5), one obtains an explicit expression

for each terms of the bridge function, which is more clearly expressed in Fourier space:

$$\tilde{B}_n(1,2) = -\frac{1}{n!} \sum_{\alpha_1 \ldots \alpha_{n+1}} \phi_{\alpha_1 \ldots \alpha_{n+1}} \tilde{w}_{\alpha_1}(2) \tilde{K}^{(n)}_{\alpha_2 \ldots \alpha_{n+1}}(1,2) \tag{7}$$

where the $K^{(L)}_{\alpha_1 \ldots \alpha_L}(1)$ are generally defined at order L as a product over the T_α functions as:

$$K^{(L)}_{\alpha_1 \ldots \alpha_L}(1,2) = \Pi_{k=1..L} T_{\alpha_k}(1,2) \tag{8}$$

and the T_α functions are convolution product over the spatial variable, better expressed in Fourier space as:

$$\tilde{T}_\alpha(1,2) = \tilde{h}(1,2) \tilde{w}_\alpha(1) \tag{9}$$

Eqs(7,8,9) represent the main result of this paper. As can be seen, each of the bridge term is expressed as a convolutions or simple products, either in r-space or k-space. As an illustration, we write down explicit forms of the first two bridge terms of the density expansion Eq.(5), for a *spherically symmetric* interaction, where the angular dependence is removed.

$$\tilde{B}_2(k) = -\frac{1}{2} \sum_{\alpha,\beta,\gamma} \phi_{\alpha\beta\gamma} \tilde{w}_\alpha(k) \tilde{K}_{\beta\gamma}(k) \tag{10}$$

$$\tilde{B}_3(k) = -\frac{1}{6} \sum_{\alpha,\beta,\gamma,\delta} \phi_{\alpha\beta\gamma\delta} \tilde{w}_\alpha(k) \tilde{K}_{\beta\gamma\delta}(k) \tag{11}$$

where $K_{\alpha\beta}(r) = T_\alpha(r) T_\beta(r)$ and $K_{\alpha\beta\gamma}(r) = T_\alpha(r) T_\beta(r) T_\gamma(r)$, with $\tilde{T}_\alpha(k) =$

$\tilde{h}(k)\tilde{w}_\alpha(k)$.

These expressions are very compact and easily computable, if the following quantities are available: the weights functions $w_\alpha(r)$, an analytical expression for the free-energy density $\phi[\eta_\alpha]$, and the pair correlation function $h(r)$. This is the case of the SPT based FMT formalism, for the first two ingredients are provided. Therefore, one should be able to come up with explicit term by term expressions for the infinite sum of bridge diagrams, within any approximate closure that will produce the pair correlation. From here on, we coin the acronym BFMT to this approximation of the bridge function.

We note that the expression derived above is very explicit in terms of the various contributions. Rosenfeld has formulated a self-consistent functional form based on the FMT[11], which involves the calculation of the bridge function, but only indirectly so. His calculation rests on the self-consistent evaluation of the excess chemical potential, as obtained by the SPT-FMT expression of the free-energy, and using the radial distribution function in place of the one-body density[11]. The existence of the explicit FMT based expression seems to have been unnoticed by him. Other authors that have followed this route do not seem to have realized these underlying details either.

2.2 Differences between the PY and FMT bridge functions

It is important to note that, if the PY solution for hard spheres (and hard rods in 1D) is compatible with the FMT formulation of the pair DCF, it does not mean that the PY closure approximation itself is compatible with the BFMT expression derived above. In other words, higher order DCFs may not be consistent with higher order expansion of the PY closure. We demonstrate below that this is indeed not the case.

The PY closure approximation consists on neglecting the $B(1,2)$ term in the exact expression Eq.(3) and subsequently linearizing the part of the remaining exponential that contains $\eta(1,2) = h(1,2) - c(1,2)$. It is then written as:

$$g(1,2) = \exp(-\beta v(1,2)[1 + \eta(1,2)] \tag{12}$$

This expression can be, in turn, cast into that similar to Eq.(3), giving the following effective PY-Bridge:

$$B_{PY}(1,2) = \ln[1 + \eta(1,2)] - \eta(1,2) \tag{13}$$

Expanding the exponential, and using the OZ equation Eq.(6), it is seen that this approximation leads to the following expression for each of the $B_n(1,2)$

$$B_n^{(PY)}(1,2) = (-1)^n(n-1)! \int .. \int d3..d(n+12)h(1,3)c(3,2)...h(1,n+2)c(2,n+2) \tag{14}$$

which, in turn, implies that the PY approximation for the n-order DCF is a product over pair DCFs:

$$c_{PY}^{(n)}(1,2,...,n) = (-1)^n(n-2)!c(1,2)c(1,3)...c(2,n) \tag{15}$$

While this expression gives back the correct $c_{PY}(1,2)$ for the case $n=2$, it will not give the FMT expression of the higher order DCF Eq.(2) when the pair expression for c_{PY} is inserted into the above equation. This is an important remark, because it indicates that the bridge term computed through the weights and an independent expression for the $h(1,2)$, is truly a new approximation for the bridge function, unrelated to any previous expressions. In particular, it would be very interesting to see what is the outcome of such an expression in the case of the hypernetted chain equation. We investigate this issue in a particular case below. Indeed, the only case when the above approximation in Eq.(15) is exact is for the case of hard rods in one dimension.

3 The one-dimensional hard-rod fluid

Now that an expression for the bridge diagram is formulated, it should be tested under the best possible conditions. Since the exact solution for the Helmholtz free-energy and the pair direct correlation function are known in the one-dimensional case of hard-rods, it is an ideal system to test the BFMT.

3.1 Theoretical details

The hard rods interactions in one dimension is defined as $v(r) = \infty$ if $r < \sigma$ and $v(r) = 0$ if $r \geq \sigma$, where σ is the hard rod length. The excess free energy is exactly known for this system[12, 13], and can be expressed in terms of the FMT variables as[10]

$$\beta F^{ex}/V = \phi^{(1D)} = -\eta_0 \ln(1 - \eta_1) \tag{16}$$

where $\eta_0 = \rho$ and $\eta_1 = \rho\sigma$. The exact expression for the pair direct correlation function is also known[12, 13]:

$$c(r) = -\frac{1 - \rho r}{(1 - \rho)^2} \quad (r < \sigma) \tag{17}$$

and zero for $r \geq \sigma$. This is in contrast with the two and three dimensional cases, for which the exact DCF has a tail beyond the core part. This DCF is also exactly recovered from the FMT in this case. The Mayer function, $f_M(r) = -H(\sigma - r)$, where $H(r)$ is the Heaviside function, is exactly written

as $f_M(r) = -w_0 \otimes w_1$ in terms of the following weight functions[10]

$$w_0(r) = H(r - R) \tag{18}$$

$$w_1(r) = \frac{1}{2}(\delta(r - R) + \delta(r + R)) \tag{19}$$

where $R = \sigma/2$ is the "radii" of the hard rod. The one dimensional Fourier transform of these weights are therefore

$$\tilde{w}_0(k) = \sigma \frac{\sin(kR)}{kR}$$

$$\tilde{w}_1(k) = \cos(kR)$$

With the help of these functions and the FMT expression for the DCF Eq(2) it is easily seen that

$$c(r) = -\frac{\partial^2 \phi_{1D}}{\partial \eta_1^2}[w_1 \otimes w_1](r) - 2\frac{\partial^2 \phi_{1D}}{\partial \eta_0 \partial \eta_1}[w_0 \otimes w_1](r) \tag{20}$$

Similarly, general expressions for any higher order DCFs can be obtained, which are identical to their expression published three decades ago by Percus[13].

We now focus on the expression for the bridge function. Noting that the n-order derivative of the free energy Eq.(16) falls into one the two following categories, the first of which has $(n-1)$ permutations

$$\phi^{(1D)}_{01..1} = \frac{(n-2)!}{(1-\eta_1)^{(n-1)}} \tag{21}$$

$$\phi_{1..1}^{(1D)} = \frac{(n-1)!\,\eta_0}{(1-\eta_1)^n} \tag{22}$$

we obtain the following expression for the BFMT bridge function, suitably better expressed in the Fourier space as:

$$\tilde{B}(k) = \sum_{n\geq 2} \tilde{B}_n(k) \tag{23}$$

$$\tilde{B}_n(k) = -\left(\frac{\rho}{1-\eta_1}\right)^n \tilde{b}_n(k) \tag{24}$$

with

$$\tilde{b}_n(k) = \frac{1}{n}\tilde{w}_0(k)\tilde{T}_n(k) + \tilde{w}_1(k)\tilde{T}_{0(n-1)}(k) + \frac{\eta_0}{1-\eta_1}\tilde{w}_1(k)\tilde{T}_n(k) \tag{25}$$

where the functions $T_n(r)$ and $T_{0n}(r)$ are defined as

$$T_n(r) = (T_1(r))^n \tag{26}$$

$$T_{0n}(r) = T_0(r)(T_1(r))^n \tag{27}$$

with the T_n (n=0,1) functions defined in Fourier space as $\tilde{T}_n(k) = \tilde{w}_n(k)\tilde{h(k)}$. Note that in Eqs.(2324) we have used a slightly different notation that in the general formalism, in order to merge the density factor in a unique factor in Eq.(24).

The expression above is an infinite sum, and one would only hope that it converges. However, the presence of the term $(\rho/(1-\rho))^n$ (we set $\sigma = 1$,for

which value $\eta_1 = \rho$) casts serious doubts about it, since this term diverges at large n when $\rho > 0.5$. Fortunately, the series can be exactly summed in the r-space by expressing it in terms of products of the variable $T(r) = \rho/(1-\rho)T_1(r)$. The exact result for the summation is then, in Fourier space:

$$\tilde{B}(k) = \tilde{w}_0(k)\tilde{Q}_0(k) - \frac{\rho}{1-\rho}\tilde{w}_1(k)\tilde{Q}_1(k) \tag{28}$$

where the functions $Q_i(r)$ (i=0,1) are compactly expressed in the r-space as:

$$Q_0(r) = \ln(1 - T(r)) \tag{29}$$

$$Q_1(r) = T(r)\frac{T_0(r) + T(r)}{1 - T(r)} \tag{30}$$

The above expression Eq(28) is the *exact* expression for the 1D bridge function for the hard rod fluid. It is important to note that the above compact expression was obtained by summing unconditionally a series expansion for values that might not be necessarily within the correct radius of convergence. In fact, the summation should be mathematically incorrect as soon as $\rho > 0.5$. Nevertheless, the expression given above turns out to be the correct one even in this case, by making use of the analytic continuation techniques.

Alternatively, the bridge function can be exactly calculated from the exact DCF Eq.(17), through the PY expression Eq.(3)

$$B_{1D}(r) = \ln(g(r)) - \eta(r) \tag{31}$$

where the radial distribution function (RDF) $g(r)$, and consequently $h(r)$, needs to be computed from the OZ equation with the exact DCF. Note the above relation gives the bridge function only for distances greater than σ, since $g(r) = 0$ inside the core gives indeterminate contribution in the expression above. The BFMT expression, on the contrary, gives the bridge function for all distances.

The exact thermodynamics of the hard rod fluid allows one to compute exactly the value of $B_{1D}(r = 0)$. Indeed, for hard core objects one has an exact relation between the value at $r = 0$ of the cavity function $y(r) = exp(\beta v(r))g(r)$ and the excess chemical potential: $y(r = 0) = exp(\beta\mu_{ex})$. Therefore, from Eq(3) one has exactly

$$B(r = 0) = \beta\mu_{ex} + 1 + c(r = 0) \tag{32}$$

The excess chemical potential can be computed exactly from Eq(16) as $\beta\mu_{ex} = -ln(1 - \rho) + \rho/(1 - \rho)$. Using this result and Eq(17) one arrives at the *exact* result:

$$B_{1D}(r = 0) = -ln(1 - \rho) - \frac{\rho}{(1 - \rho)^2} \tag{33}$$

A comparison of this equation to that given by Eqs(23,24) (albeit in r-space) shows that the former is a limit of an infinite sum on density. It can be shown that, at r=0, all the r-functions are rigorously equal to unity, and therefore Eqs.(23,24) become

$$B_{1D}(r=0) = -\sum_{n\geq 2}(-)^n(\frac{\rho}{1-\rho})^n(\frac{1}{n}+1+\frac{\rho}{1-\rho}) \qquad (34)$$

This expression reveals the serious convergence problems mentioned above one has if one is to evaluate such sum directly. Indeed, while it is a simple task to show the expression sums exactly to the result given above in Eq(33), the direct evaluation of the series shows that it is convergent for $\rho < 0.5$, but oscillatory for $\rho = 0.5$ and divergent for $\rho > 0.5$. The same considerations apply equally to the full r-dependence function, and direct evaluation of Eq(23) is possible only for $\rho < 0.5$. The numerical analysis of the series above shows that, for $\rho > 0.5$ it diverges by oscillating around the correct value given in Eq(33). It is easily verified that the expression is the correct one for any densities by making use of analytic continuation techniques on Eq.(34).

A final remark concerns the behaviour of the bride function for distances within the core $0 < r < \sigma$. I find numerically (see below) that $B(r)$ is strictly linear. Therefore, if $B(0)$ is known, one can complement Eq(31) by a linear interpolation between $B(0)$ and $B(\sigma)$.

3.2 Results

The numerical implementation of the various functions needs a very accurate Fourier transform. Since fast Fourier transform techniques are used, the functions are discretised on a grid with a number of points of 2^{13} , and with

a r-space grid-width of $\Delta r = 0.005\sigma$, where σ is the hard rod diameter. The reduced density is defined as $\rho^* = \rho\sigma$ and the reduced distance as $r^* = r/\sigma$.

First of all, in order to get an idea of the importance of the bridge diagram, we display the radial distribution function in Fig.1 and direct correlation function in Fig.2, both for the exact results and those obtained from the hypernetted-chain (HNC) approximation (dashed lines). This latter approximate closure consists in setting $B(1,2) = 0$ in Eq.(3), therefore neglecting the bridge function. These results are displayed for three different densities ($\rho^* = 0.2, 0.6, 0.78$) in both figures. The importance of the bridge function become clearly important at higher density, as witnessed by the increasing differences between the exact and HNC results. We note in Fig.2 that the HNC approximation predicts that the DCF is non-zero outside the hard core part for $r^* > 1$, while the exact result is strictly zero. The HNC approximation could not be solved numerically for densities larger than $\rho^* = 0.78$ because the solution become unstable beyond. We equally solved numerically the PY approximation, in order to test the accuracy of our calculations. The results are indistinguishable from the exact ones. However, the numerical solution of the PY approximation becomes very sluggish for densities higher than $\rho^* = 0.884$, requiring very small density increments to reach the next solution. We have not tried here to improve the numerical solution methods, since the main goal is to test the accuracy of the FMT bridge function.

Fig.3 shows the $T_i(r)$ functions (i=0,1), for three different densities. These functions, generally defined in Eq.(9), are the building blocks of the FMT

bridge, as can be seen from Eqs.(24-27). There as many such functions as the number of weights functions (here 2), and they all depend on the density through the pair correlation function. For hard spheres, $T_0(r)$ is discontinuous at $r^* = 1$ while $T_1(r)$ has a discontinuous derivative at the same point.

Fig.4 shows the bridge function for different densities, as calculated by Eqs(28-30) and Eq(31), the latter which has been interpolated linearly to the exact value at r=0. The two curves are indistinguishably superimposed. Fig.5 shows the small scale structure at large distances and reveals that the bridge function has considerable structure at higher densities.

Fig.6 shows how the series converge for two densities, $\rho = 0.3$ and $\rho = 0.8$. It is obvious that the convergence is attained quickly in the first case while it will never be obtained in the second case. The first term in the series expansion is equally shown (dotted lines), and in the latter case one sees that it is very far from the correct result. For the high density regime, the analysis indicates that it is useless to incorporate the first few terms of the bridge, as it is often done in the literature, through various techniques such as virial expansions and such.

4 Conclusion

The present investigation has led to a formal expression of the bridge function within the FMT formalism, that appears very promising since it allows, for

the first time, to break into the irreducibility of the Mayer cluster diagrams. Moreover, it is formulated in the general case including orientational dependence of the interaction between particles. By construction of the FMT, it is easily extended to mixtures as well, and to the inhomogeneous cases, as shown in the appendixes below. While the FMT is initially formulated for spherical particles, the extension to anisotropic hard core objects, such as ellipsoids for example, can be implemented by following the lines of Ref.[17, 19]. The important feature of the BFMT, which allows the irreducibility of the exact diagrammatic formulation to be broken into convolution products, relies ultimately in the underlying *geometrical* formulation of the FMT. This feature is certainly important and deserves future analysis.

The fact that an analytical approach to B(r) exists in 1D, opens now many interesting perspectives. In particular, this approximation deserved to be tested in both two and three dimensional cases, and away from the sole hard sphere case. Indeed, as indicated here, the bridge term can be computed for any sorts of interactions, provided the pair correlation function $h(r)$ is given. It is not required to have a decomposition of the full Mayer function in terms of weights, since those corresponding to the hard core could serve this purpose as a reference term. The other parts of the interactions would enter through the $h(r)$. This amounts to treat the hard core part of the bridge within the FMT approximation for it. Accordingly, the BFMT formulation can be used for interactions are different as charged systems, dipolar fluids, and realistic interactions such as water, for which a reference

hard sphere FMT is directly applicable, since it is a single hardcore site. Some of these research directions are currently being investigated. To conclude, the BFMT bridge formulation presented here seem a promising new direction in extending and improving liquid state theory.

Appendix A: mixtures

The BFMT is readily formulated for the case of mixtures, since the underlying SPT has been formulated in such case[14]. Consider a mixture of n species, each consisting of N_i particles, for a total of N particles. For each species, we introduce the appropriate set of weight functions from the factorisation of the pair Mayer functions $f_{M;ij}(1,2) = \exp(-\beta v_{ij}(1,2)) - 1$, where $v_{ij}(1,2)$ is the pair interaction energy between particle 1 belonging to species i and particle 2 for species j:

$$f_{M;ij}(1,2) = \sum_{\alpha_1,\alpha_2} w_{i\alpha_1}(1) \otimes w_{j\alpha_2}(2) \tag{A.1}$$

where the weights of each species are additionally labeled by the species index i or j. The weighted densities, initially introduced for the inhomogeneous case as above, are summed over all species contributions for each weight:

$$\eta_\alpha(1) = \sum_i \int dx\, w_{i\alpha}(1x)\rho(1) \tag{A.2}$$

From there, one builds the homogeneous n-DCF following Eq(2) and using

again the chain rule. The bridge functions for mixtures come in species pair, like the pair correlations and the interactions, but is expressed over all possible species combinations, much like for the case of OZ for mixtures

$$B_{ij}(1,2) = \sum_{n=2}^{\infty} \rho^n B_{ij;n}(1,2) \tag{A.3}$$

with

$$\begin{aligned} B_{ij;n}(1,2) &= \frac{1}{n!} \sum_{k_3..k_{n+2}} x_3...x_{n+2} \int ... \int d3..d(n+2)\, h_{ik_3}(1,3)...h_{ik_{n+2}}(1,n+2) \\ &\times c^{(n+1)}_{jk_3...k_{n+2}}(2,3,...,n+2) \end{aligned} \tag{A.4}$$

where $x_i = N_i/N$ is the mole fraction of species i, and the expression above is valid from $n \geq 2$. Inserting the FMT expression of the DCF into the above equation gives directly an expression similar to Eq.(7), expressed in Fourier space as

$$\tilde{B}_{ij;n}(1,2) = -\frac{1}{n!} \sum_{\alpha_1...\alpha_{n+1}} \phi_{\alpha_1...\alpha_{n+1}} \sum_{k_3..k_{n+2}} x_3...x_{n+2} \tilde{w}_{j\alpha_1}(1) \tilde{K}^{ik_3...k_{n+2}}_{\alpha_2...\alpha_{n+1}}(1,2) \tag{A.5}$$

where the $K^{ik_1...k_L}_{\alpha_{11}...\alpha_L}(1,2)$ are the generalization to multicomponent system of those defined in Eq.(8)

$$K^{ik_1...k_L}_{\alpha_1...\alpha_L}(1,2) = \Pi_{l=1..L} T_{ik_l\alpha_l}(1,2) \tag{A.6}$$

and the new T functions (see Eq.(9)) are defined as:

$$\tilde{T}_{ij\alpha}(1,2) = \tilde{h}_{ij}(1,2)\tilde{w}_{j\alpha}(1) \tag{A.7}$$

Eqs.(A.3A.5,A.6,A.7) represent the generalization to mixtures of the BFMT bridge function.

Appendix B: The inhomogeneous case

Inhomogeneity is built into the formulation of the FMT[9, 10]. The principal difference with the treatment given in the formulation in Section 2 is the expression of the n-DCF for an inhomogeneous system. The inhomogeneity comes solely from the one-body function$\rho(1)$, and consequently from the weighted densities, as formulated in Section 2. The inhomogeneous DCF becomes

$$\begin{aligned} c^{(n)}(1,2,..n) &= -\frac{\partial^n}{\Pi_k \partial\rho(k)}\beta F_{ex}[\rho] \\ &= -\Pi_{P(\alpha_1...\alpha_n)} \int dx \phi_{\alpha_1...\alpha_n}(x) w_{\alpha_1}(1,x) \otimes ... \otimes w_{\alpha_n}(n,x) \end{aligned} \tag{B.1}$$

where the integral is over the spatial variable, which could also have an angular contribution if the inhomogeneity has an angle dependence (such as for a nematic fluid, for example), and the free-energy density derivatives now depend of this variable also because of the explicit dependence through $\rho(x)$.

The definition of the weights needs to be adjusted to handle the inhomogeneity through the individual geometrical properties they previously contained. If the inhomogeneity is purely spatial, such for a hard sphere fluid next to a wall, then the previous spherical weight are conserved[9].

The bridge function can be defined for the inhomogeneous case very generally as

$$B(1,2) = \sum_{n=2}^{\infty} \frac{1}{n!} \int ... \int d3..d(n+2)\; H(1,3)...H(1,n+2)\; c^{(n+1)}(2,..n+2) \tag{B.2}$$

by introducing the generalized correlation functions

$$H(1,2) = \rho(2)h(1,2) \tag{B.3}$$

The formal expression for the inhomogeneous bridge function follows directly by following the same steps as in Section 2, and replacing $h(1,2)$ by $H(1,2)$ defined above. This amounts to change only the definition of the T functions in Eq.(9) as

$$\tilde{T}_\alpha(1,2) = \tilde{H}(1,2)\tilde{w}_\alpha(1) \tag{B.4}$$

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Figure captions

Fig.1 The RDFs for the hard rod fluid in 1D, for three different value of the density ρ^*. Exact results in full lines, HNC in dashed lines. The inset in the lower panel shows the details at the contact distance.

Fig.2 The DCFs for the hard rod fluid in 1D, for the same densities as in Fig.1, with the same line conventions. The inset shows details of the tail part of the DCF of the HNC approximation (full line for $\rho^* = 0.78$, dotted for $\rho^* = 0.6$ and dashed for $\rho^* = 0.2$).

Fig.3 The functions $T_i(r)$ (see Eq.(9)) for the hard rod fluid in 1D, for three different value of the density ρ^*. Full lines for $T_0(r)$ and dotted lines for$T_1(r)$.

Fig.4 The bridge functions $B(r)$ for the hard rod fluid in 1D, for three different densities: $\rho^* = 0.2, 0.6, 0.8$. The solid line is the BFMT result, and the dashed line the result from Eq.(31)

Fig.5 Same as Fig.4, but a close up of the behaviour of B(r) for small distances.

Fig.6 The convergence of the series expansion for two densities $\rho^* = 0.3$(top panel) and 0.8(bottom panel). Solid line for $B(r)$, dotted line for $B_2(r)$, and dashed lines for successive summations to B(r)

(only $n = 2, 3, 4$ are shown).

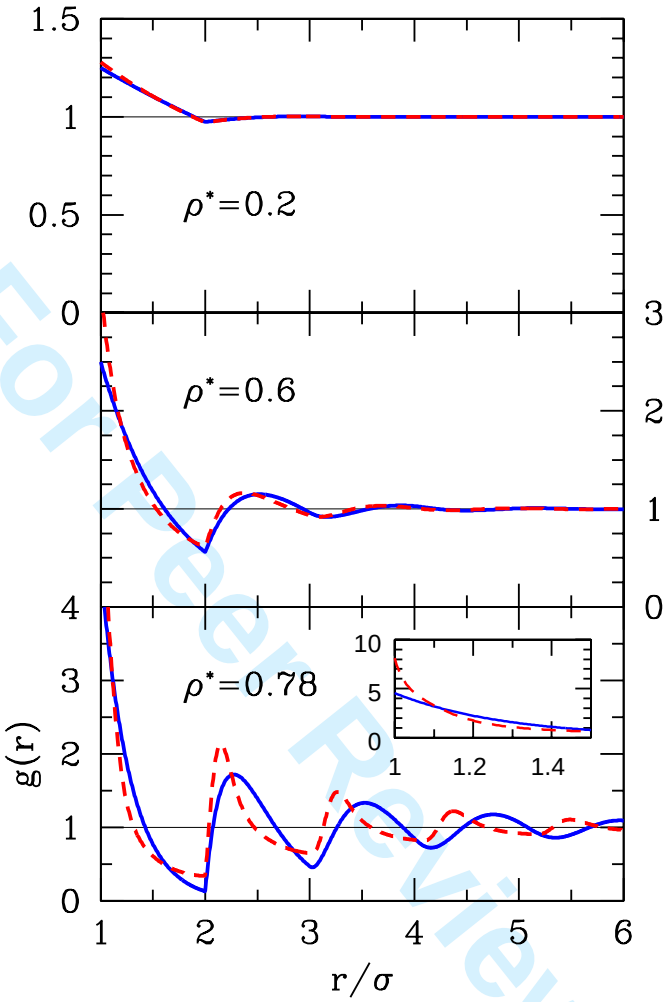

Fig.1 Perera

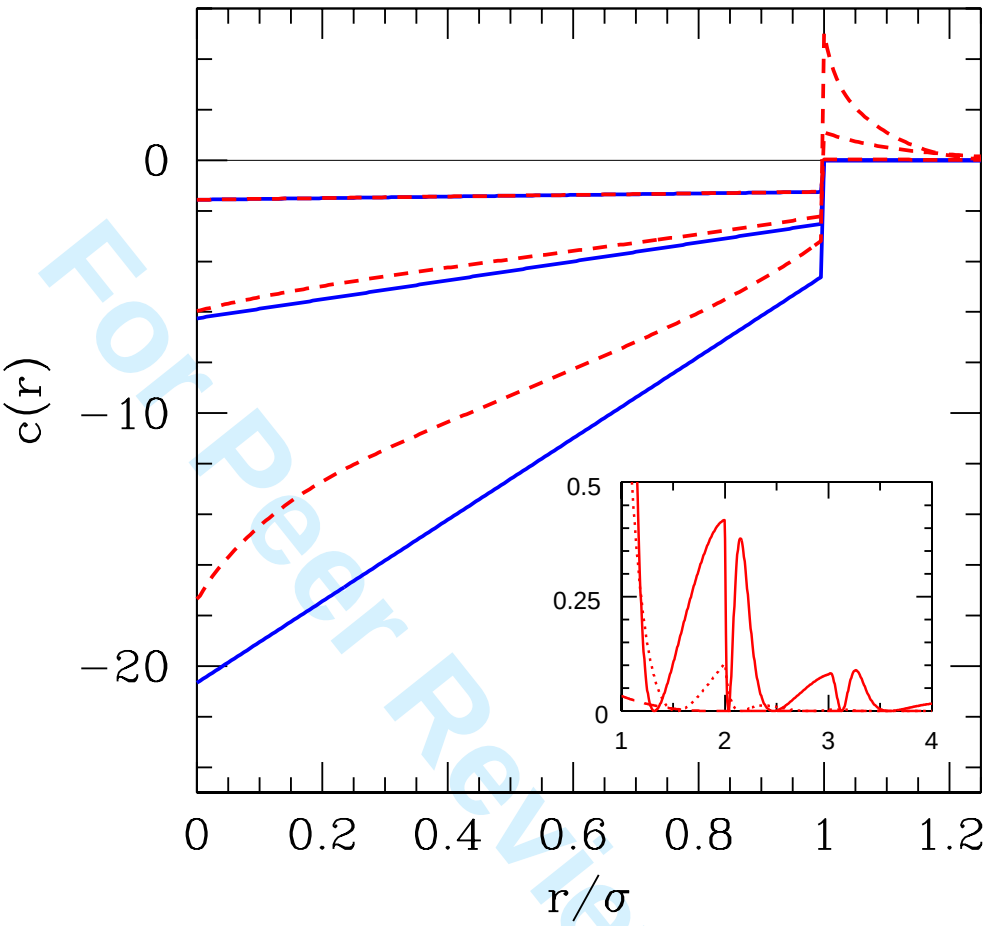

Fig.2 Perera

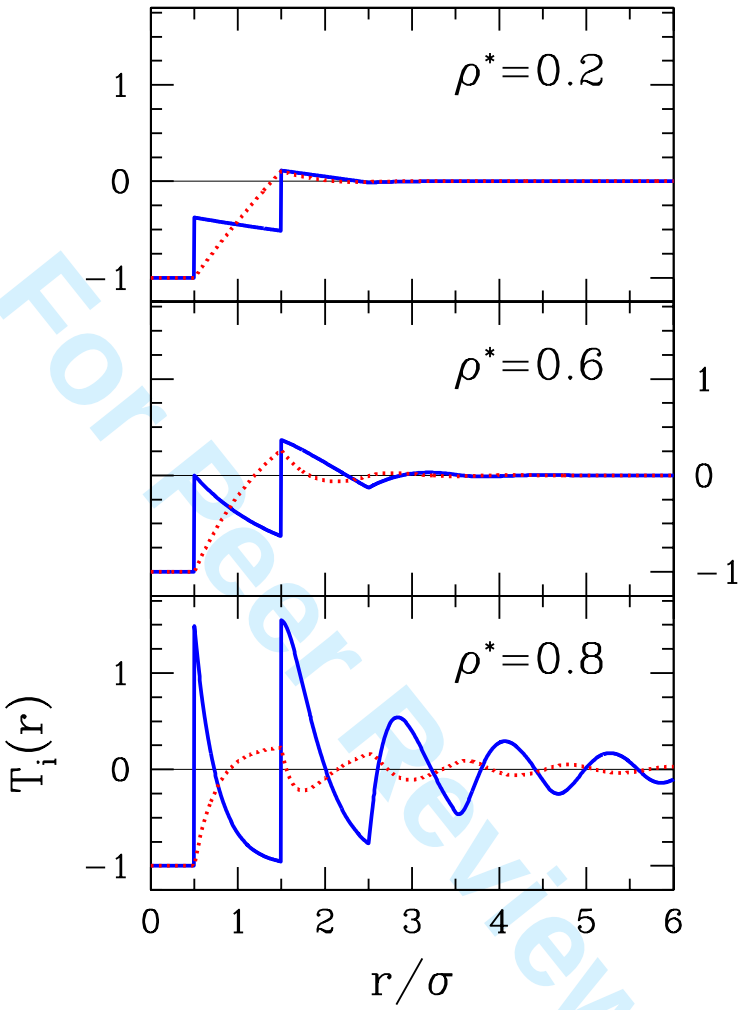

Fig.3 Perera

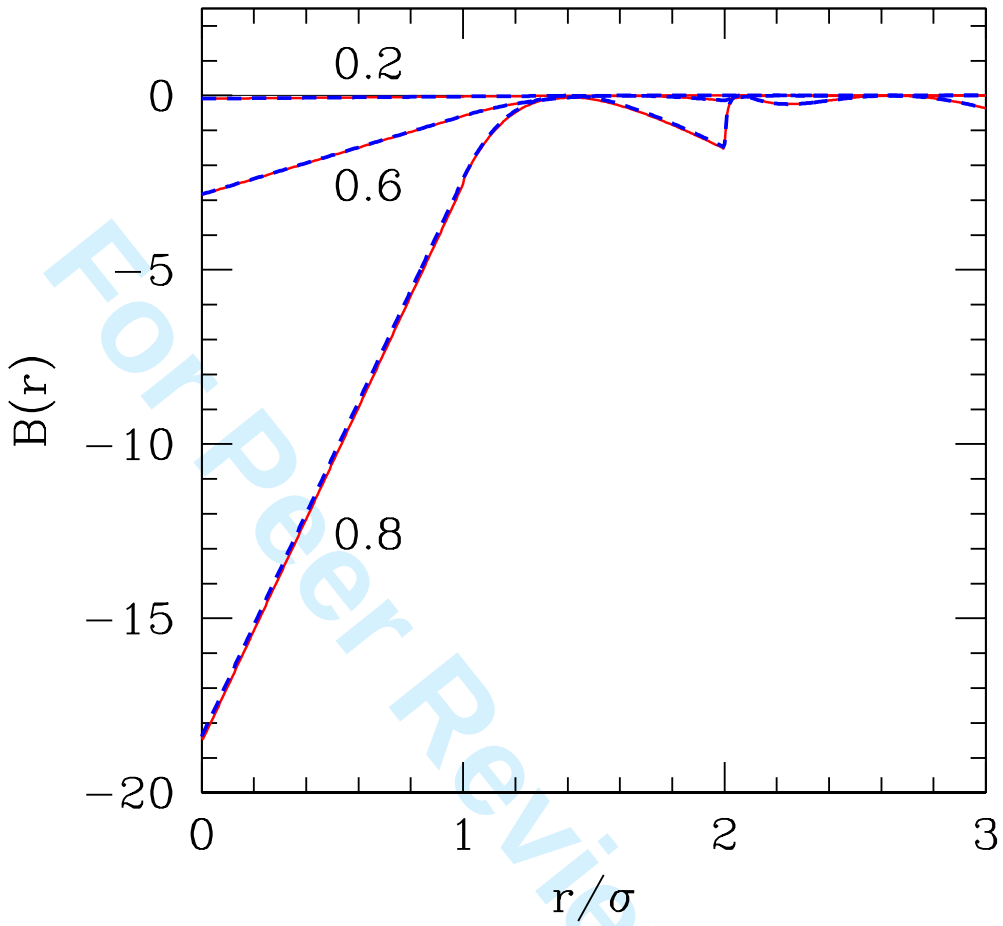

Fig.4 Perera

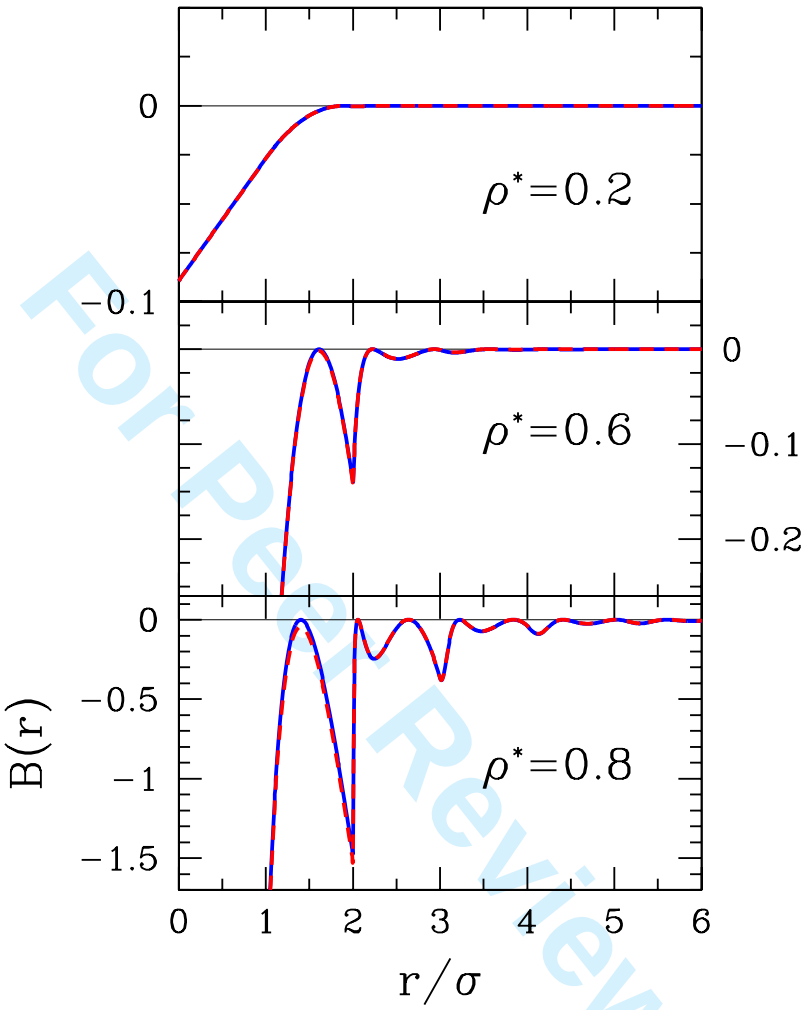

Fig.5 Perera

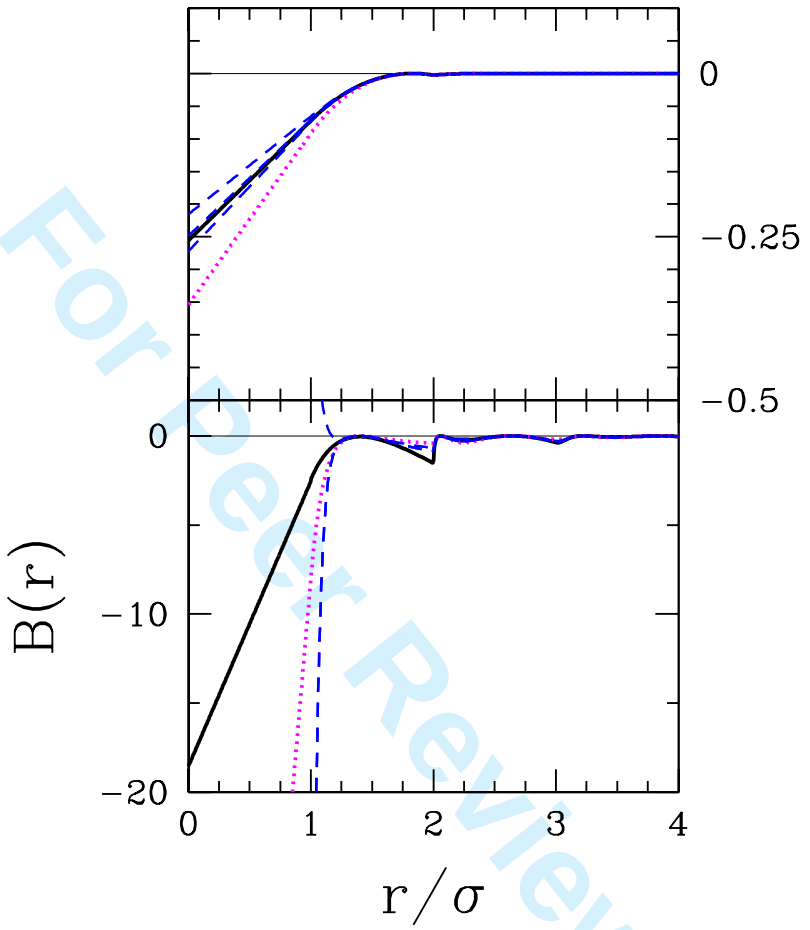

Fig.6 Perera

Answer to the Referee's comments.

I fully agree with the Reviewer that since the FMT is exact in 1D, it should give back the exact bridge diagram. It took me some time to investigate this point numerically in detail, and it turned out to be not such a trivial task at the end because of the divergence associated in the series expansion at high densities.
The present version -hopefully free of previous misprints- contains a compact expression of the bridge function (Eqs(28-30) which is the first exact expression for this function, if I am not mistaken.

The manuscript is now totally revised in what concerns the part of the application to 1D hard rod fluid. The abstract had to be rewritten as well.

I am more satisfied with the current version, and the work done for this system has also allowed to better interpret numerical problems I was having in 3D with the same approach.

So I can only than this Reviewer for his very insightful comment.

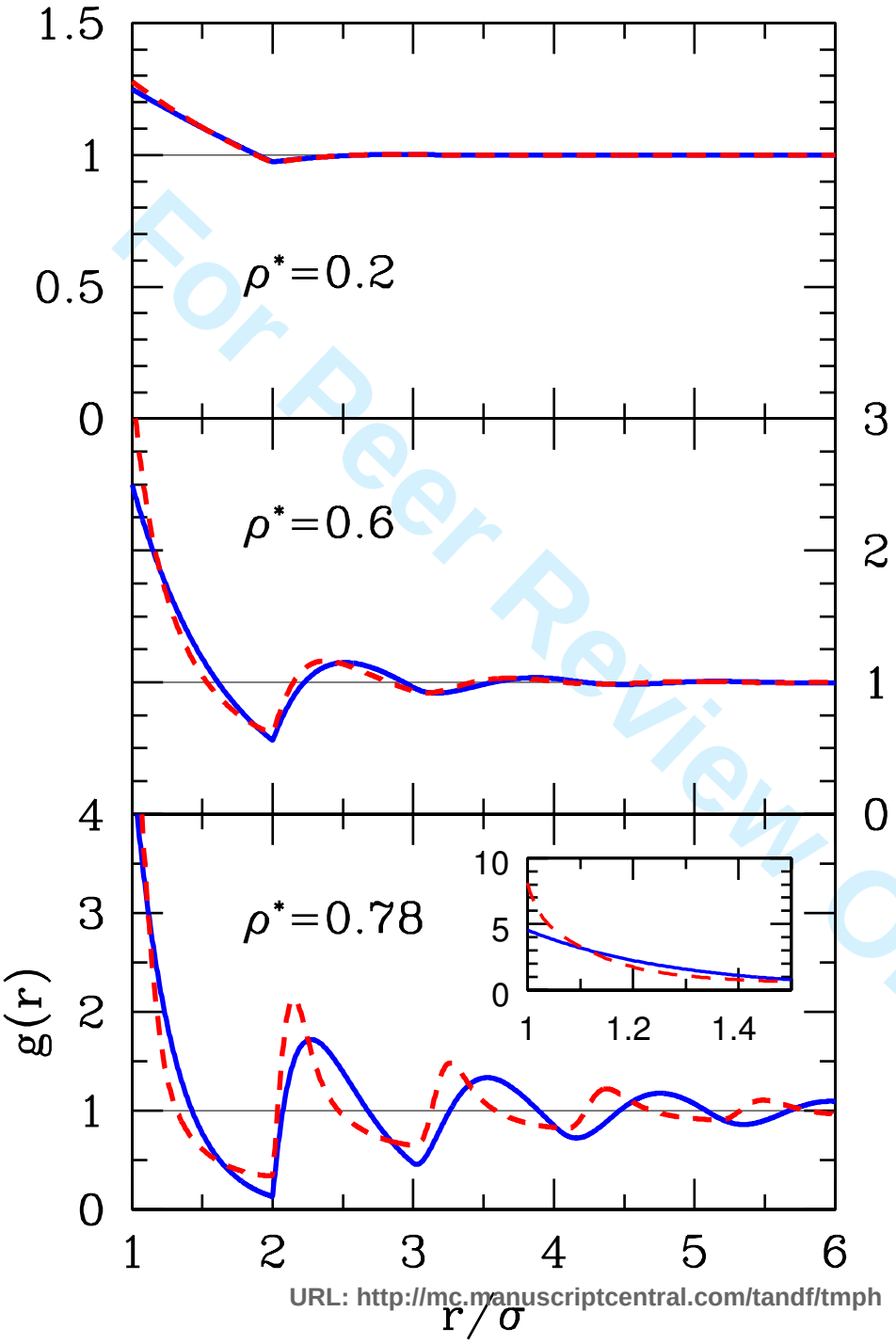

Fig.1 Perera

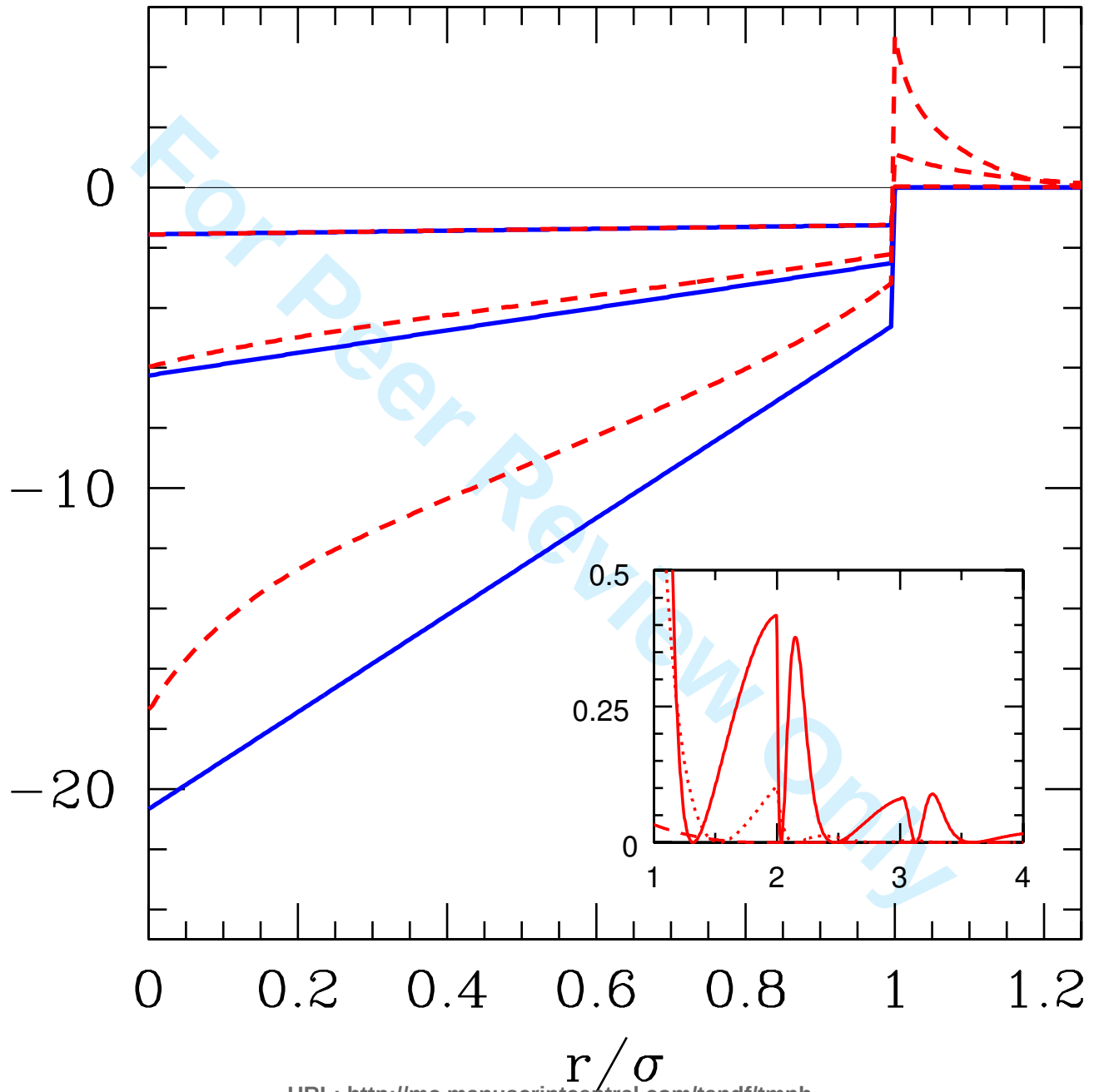

Fig.2 Perera

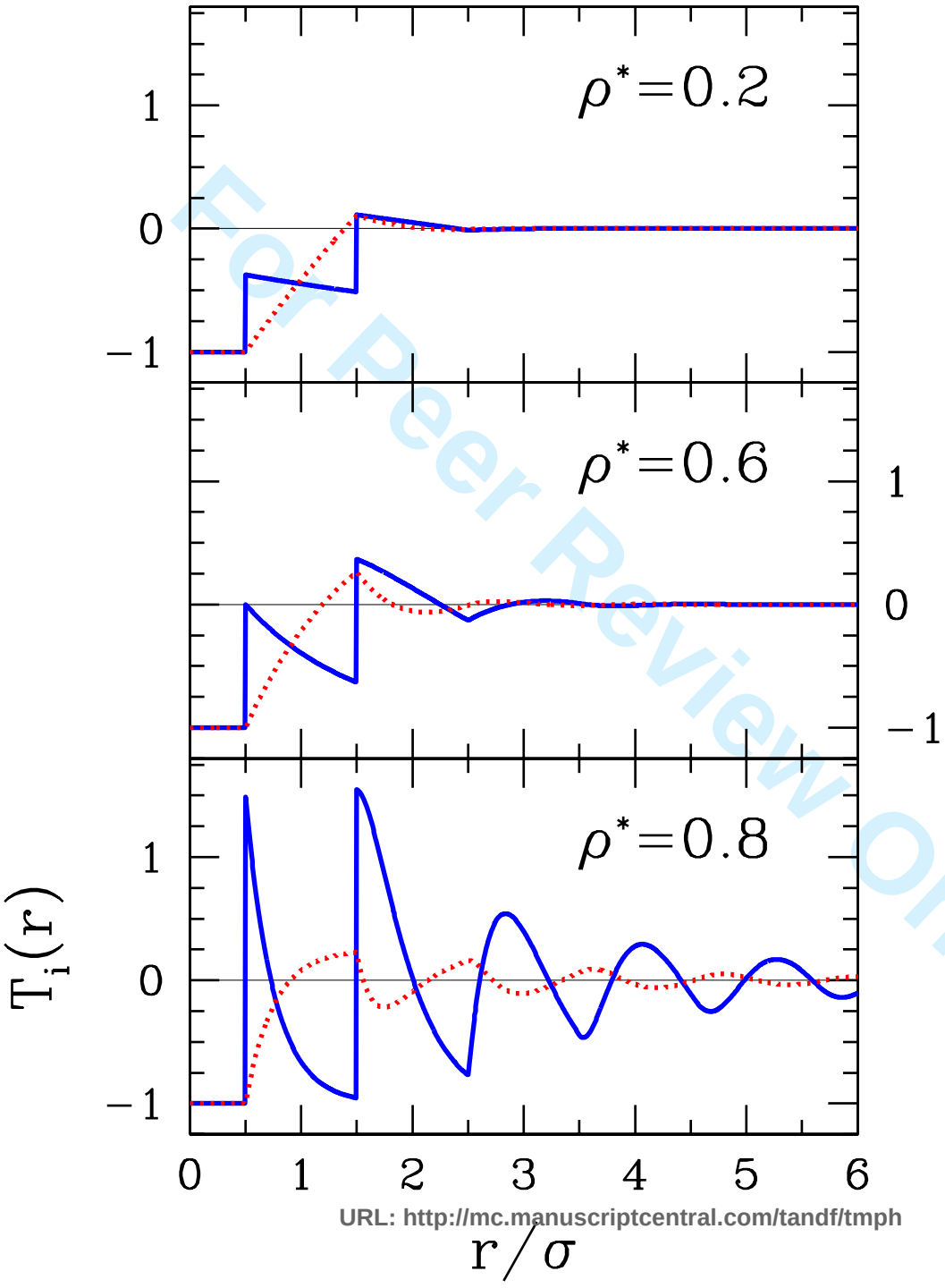

Fig.3 Perera

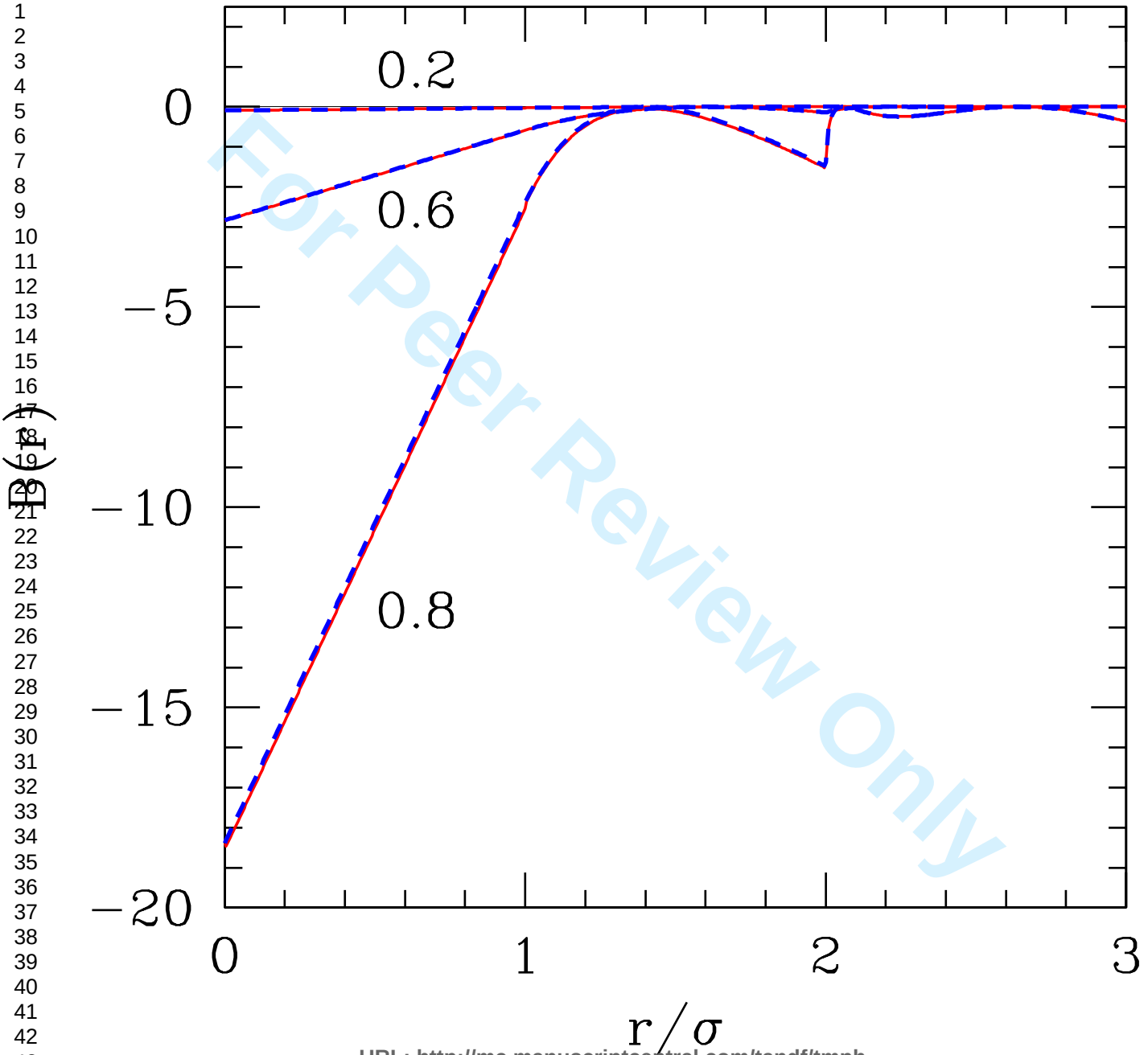

Fig.4 Perera

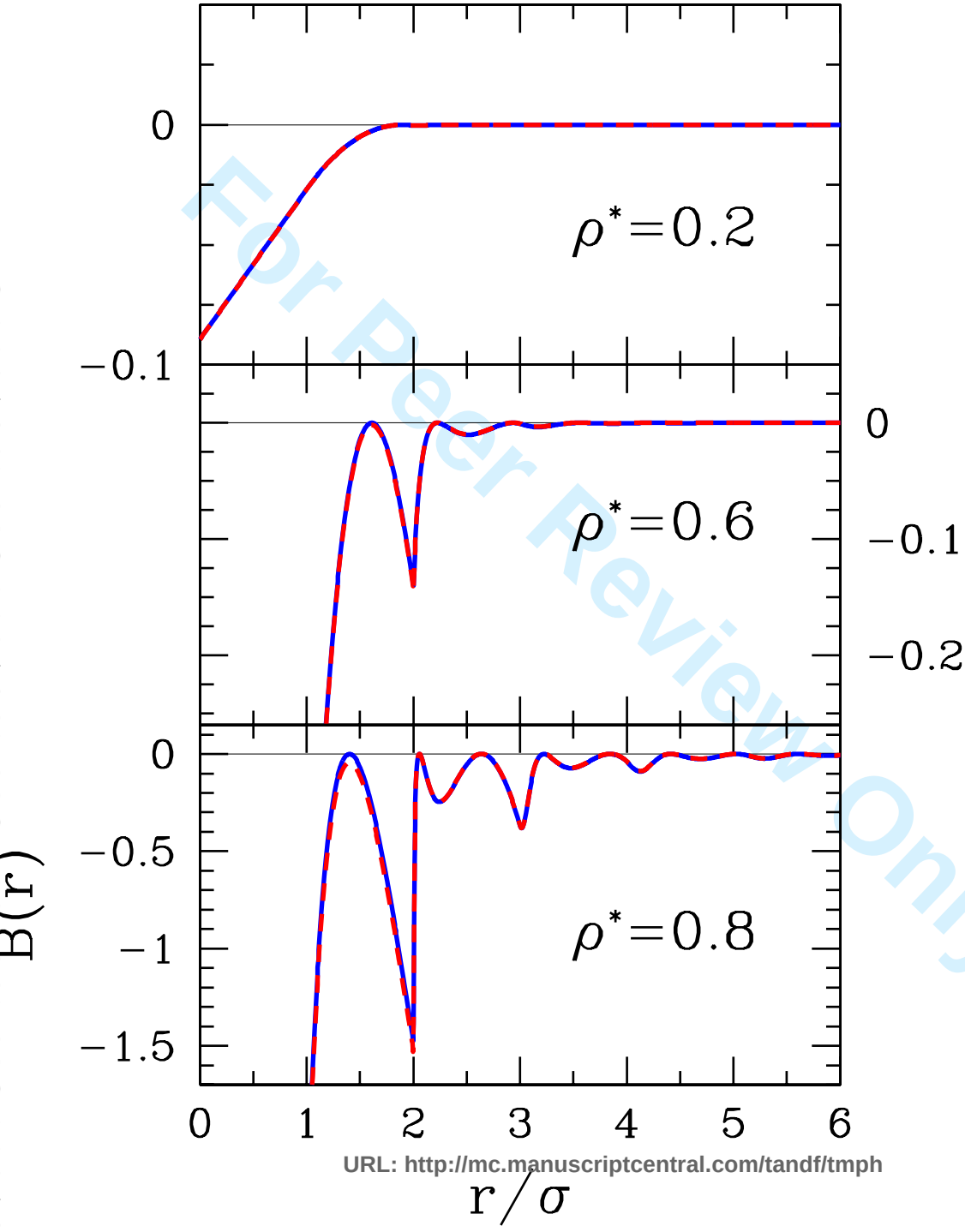

Fig.5 Perera

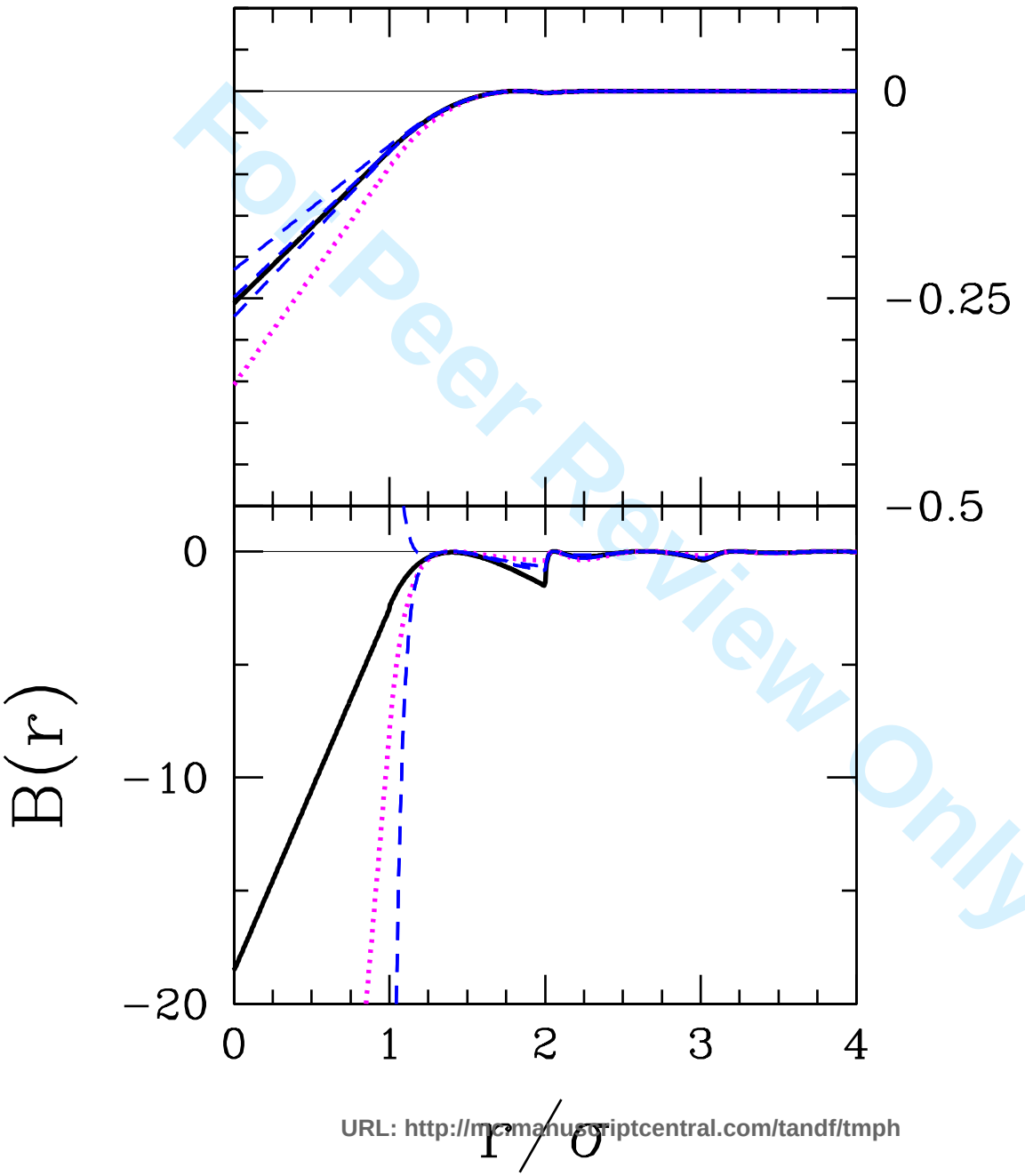

Fig.6 Perera