# The 1-D Hard Rod Fluid Revisited Using NNPDFs

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The new scheme developed in an earlier paper for the determination of the free energy of classical systems is applied to the 1-D single component fluid of hard rods. Exact results for the nearest neighbor probability density functions (NNPDFs) are obtained with origin situated at one end of the 1-D medium of interest. The formulation for NNPDFs are then used to show that the new scheme converges and actually reproduces the well-known exact results for the free energy of the 1-D hard rod system at all densities.

In this paper, we employ the new scheme developed by one of the authors[1] for the exact determination of the free energy of arbitrary classical systems, to the one-dimensional fluid of identical hard rods. We begin by investigating structure in the fluid system using new methods (also developed by one of the authors)[2] which employ nearest neighbor probability density functions (NNPDFs). Although NNPDFs have long been known in the mathematics literature,[3] this method for describing structure in arbitrary systems has not been widely used for physical systems. Consequently, the development of NNPDFs in statistical mechanics has hitherto been relatively slow. The use of nearest neighbor distributions (especially the first nearest neighbor distribution) has, however, not been entirely avoided in the theory of fluids. Some of the notable works in this respect include those by Reiss,[4] who used the first nearest neighbor distribution functions to develop what was termed a "refined theory of Ion pairing". Later, Reiss and Casberg[5] used nearest neighbor distributions to develop an integral equation whose solution gave exact results for the hard rod fluid. (See also Reiss et al.,[5] where nearest neighbor functions were used to solve for distribution of cars in a single lane of a 1-D fluid of cars.) More recently, Bhattacharjee[6] provided a brief review (see also earlier works of refs 1 and 2) as well as expressed *n*th nearest neighbor distributions in terms of $(n − 1)$th nearest neighbor distributions and the pair correlation function. Torquato[6] also provided an excellent review, while Reiss et al.[6] provided Ornstein−Zernicke equations that rely heavily on nearest neighbor functions. In the current paper, we discuss NNPDFs providing a hierarchy of nearest neighbor functions as a means to thoroughly describe structure in the 1-D hard rod fluid system, where exact results are expected to be obtained readily.

In a recent paper,[2] exact expressions were obtained for NNPDFs for equilibrium systems with arbitrary interaction potentials at arbitrary densities and temperatures. The results (which were obtained chiefly for 3-D systems) may be adapted for 1-D systems by employing the following replacements (analogy):

$$\vec{r}_n \to \vec{l}_n; \qquad d\vec{r}_n (= d^3 r_n) \to d\vec{l}_n (= dl_n);$$
$$v_n \to 2l_n; \qquad V \to L$$

$V$ ($L$) is the volume (length) of the system containing $N$ identical particles in 3-D (1-D), and in the thermodynamic limit $N$, $V$, $L \to \infty$, and $(N/V) = (N/L) = \rho$. Also, $\vec{r}_n(\vec{l}_n)$ is the position of (say) the center of the *n*th nearest neighbor of some arbitrarily chosen "origin" in the middle of the 3-D (1-D) system ("microscopically far" from the boundary of $V$ ($L$)). Note that $\vec{r}_n(\vec{l}_n)$ may or may not be "generalized ordered".[1] $r_n$ ($l_n$) is the distance to the center of the *n*th nearest neighbor of the arbitrarily chosen "origin" in the 3-D (1-D) system, and $v_n$ ($2l_n$) is the volume (length) of the "sphere" containing the $n$ nearest neighbors (with the center of the *n*th nearest neighbor actually residing at the boundary of $v_n$ ($2l_n$), while the center of $v_n$ ($2l_n$) is at the origin). The analogous 3-D angles in the 1-D system are specified by indicating either "left" or "right" of the origin. Hence, we may specify the position vector ($\vec{l}_n$) for the *n*th nearest neighbor to the left of the origin as $l_n^{\mathrm{l}}$, while that to the right as $l_n^{\mathrm{r}}$. Note, for instance, that if the origin is situated at the left edge of "$L$", then the position vector to the *n*th nearest neighbor may only be written in the form $l_n^{\mathrm{r}}$, while the replacement for $v_n$ must necessarily be $l_n$ (instead of $2l_n$). In this case also, integration of the variable $l_n$ may go "microscopically" to infinity only along the direction to the right, instead of in both left and right directions (which obtains for the case when the origin is in the middle of L "microscopically far" from the edges).

The joint PDF for *n*-nearest neighbors in 1-D is therefore written following eq 7 of ref 2 as:

$$g_{1,...,n}(\vec{l}_1, ..., \vec{l}_n)\prod_{i=1}^{n} d\vec{l}_i =$$
$$\frac{\exp(A/KT)}{(N - n - 1)!} \exp(-\beta U_{n+1})\prod_{j=1}^{n} d\vec{l}_j (\int_{\hat{L}}...\int_{\hat{L}} \exp[-\beta(U_{\mathrm{bdy}} + U_{N-n-1})]\prod_{k=n+1}^{N-1} d\vec{l}_k) \quad (1)$$

"A" is the configurational contribution to the free energy of ($N − 1$) particles in the space of length $L$ with an original particle located at the origin. $\hat{L}$ is the length ($L − 2l_n$), assuming the origin is microscopically far from the edges of $L$ (while $\hat{L} = L$

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$- l_n$ if the origin is situated at an edge of $L$). The coordinates $(\vec{l}_k)$ in the integral are not generalized ordered and are the coordinates of atmospheric particles, while the integral is termed the "atmospheric integral". $\beta = 1/KT$ where $K$ is the Boltzmann constant, $T$ is temperature. $U_{n+1}$ is the interaction energy of the set of particles involving only the original particle and its $n$-nearest neighbors (interaction of this set of particles with the set of atmospheric particles is assumed "turned off"). $U_{N-n-1}$ is the interaction energy of the set of atmospheric particles only, and $U_{bdy}$ is the additional energy resulting from "turning on" the interaction between the above two sets of particles. For the 1-D hard rod system of identical particles, the interaction energy is $\infty$ if any two or more particle hard cores overlap; otherwise it is zero. Also, the boundaries of the line $L$ are infinite barriers, and thus no particle center may come to within $(1/2)l_0$ of the line's boundaries. ($l_0$ is the length of the hard core of a particle.)

Equation 1 is valid for the "ordinary point process" where a particle center resides at the origin. For the $n$-nearest neighbor PDF for a "general point process" where the origin is an arbitrarily chosen point in $L$ (and thus the origin is not necessarily occupied by a particle center), "$A$" is reinterpreted as the configurational contribution to the free energy of $N$ particles, whereas $U_{n+1}$ and $U_{N-n-1}$ are respectively replaced by $U_n$ and $U_{N-n}$ in eq 1. (Also, the parameter $(N - 1)$ is generally replaced by $N$.) For the hard rod fluid, only the $n$th and $(n - 1)$th nearest neighbors may have their hard core protrude outside the length $2l_n$, which is centered at the origin for the case where the origin is situated microscopically far from the edge of $L$. Whereas for the case where the origin is situated at the left edge of $L$, only the $n$th nearest neighbor hard core may protrude outside the length $l_n$ whose left end coincides with the origin. Hence, $U_{bdy}$ (boundary effect)[2] may readily be exactly formulated as an appropriate equivalent reduction in the atmospheric length $\hat{L}$. Shape effect,[2] on the other hand, is accounted for by realizing that for the case where the origin is situated microscopically far from the edges of $L$, the atmospheric length $\hat{L}$ involves two disjoint regions of space. Such shape effect is absent for the case where the origin is situated at the edge of $L$. For this case also, the equivalent reduction in $\hat{L}$ due to boundary effect is $(1/2)l_0$. Hence, we may write $\hat{L} = L - l_n^r - 1/2 l_0$. We consider the joint PDF of eq 1 only for this case (and assume a general point process) because this is what is required in the statistical thermodynamic formalism developed in ref 1 for determining the partition function.

The atmospheric integral may therefore be written (after successive integration) as:

$$(N - n)! \int_{l_n^r + (N-n)l_0}^{(L+(1/2)l_0) - l_0} \cdots \int_{l_n^r + 2l_0}^{l_{n+3}^r - l_0} \int_{l_n^r + l_0}^{l_{n+2}^r - l_0} \prod_{k=n+1}^{N} dl_k^r =$$
$$\left(L - l_n^r - \frac{1}{2}l_0 - (N - n)l_0\right)^{N-n} \quad (2)$$

Observe that the boundary effect ($U_{bdy}$) has required the lower limits of the integrals in eq 2 to be written as $(l_n^r + il_0)$ instead of $(l_n^r + 1/2 l_0 + (i - 1)l_0)$ had it been that $U_{bdy} = 0$. (Hence, the result of eq 2 is equivalent to employing $\hat{L} = L - l_n^r - 1/2 l_0$ instead of $\hat{L} = L - l_n^r$ as earlier discussed.)

Hence, eq 1 for a general point process of hard rods becomes:

$$g_{1,\ldots,n}(l_1^r, \ldots, l_n^r) = \frac{N!}{(N - n)!} \frac{1}{(L - Nl_0)^N} \left(L - l_n^r - \frac{1}{2}l_0 - (N - n)l_0\right)^{N-n} F(l_1^r, \ldots, l_n^r) \quad (3)$$

where $F(l_1^r, \ldots, l_n^r)$ is an indicator function which is zero if any

two of the $n$-nearest neighbors of the origin overlap; otherwise, it is 1. (Also, the indicator function is zero if $l_1^r < 1/2 l_0$.) The following well-known[7] result for the free energy of identical hard rods has been used to obtain eq 3.

$$A = KT \ln(N!) - NKT \ln(L - Nl_0) \quad (4)$$

In the thermodynamic limit and using Stirling's approximation ($k! \approx \sqrt{2\pi} k^{k+1/2} \exp(-k)$ for $k \gg 1$)[8], we obtain:

$$g_{1,\ldots,n}(l_1^r, \ldots, l_n^r) =$$
$$\rho^n (1 - \eta)^{-n} \exp\left(-\rho\left(l_n^r + \frac{1}{2}l_0 - nl_0\right)(1 - \eta)^{-1}\right) F(l_1^r, \ldots, l_n^r) \quad (5)$$

($\eta$ is the packing fraction $\rho l_0$). By successive integration, this function is readily shown to normalize:[8]

$$\int_{(n-1/2)l_0}^{\infty} \cdots \int_{(3/2)l_0}^{l_3^r - l_0} \int_{(1/2)l_0}^{l_2^r - l_0} g_{1,\ldots,n}(l_1^r, \ldots, l_n^r) \prod_{i=1}^{n} dl_i^r$$
$$= \int_{(n-1/2)l_0}^{\infty} \frac{\rho^n \left(l_n^r + \frac{1}{2}l_0 - nl_0\right)^{n-1}}{(1 - \eta)^n (n - 1)!} \times$$
$$\exp\left(-\rho\left(l_n^r + \frac{1}{2}l_0 - nl_0\right)(1 - \eta)^{-1}\right) dl_n^r$$
$$= \frac{\rho^n \exp\left(\frac{+\rho}{1 - \eta}\left(nl_0 - \frac{1}{2}l_0\right)\right)}{(1 - \eta)^n (n - 1)!} \int_{nl_0 - (1/2)l_0}^{\infty} \left(l_n^r - \left(nl_0 - \frac{1}{2}l_0\right)\right)^{n-1} \times$$
$$\exp\left(\frac{-\rho}{1 - \eta} l_n^r\right) dl_n^r = 1$$

With the above exact result, other interesting results are also found exactly. For instance, we may easily write the following exact conditional PDF:

$$g_n(l_n^r | l_1^r, \ldots, l_{n-1}^r) =$$
$$\begin{cases} \rho(1 - \eta)^{-1} \exp(-\rho(l_n^r - l_{n-1}^r - l_0)(1 - \eta)^{-1}) & (l_n^r \geq l_{n-1}^r + l_0) \\ 0 & (l_n^r < l_{n-1}^r + l_0) \end{cases} \quad (6)$$

This function is also seen to normalize adequately; i.e., $\int_{l_{n-1}^r + l_0}^{\infty} g_n(l_n^r | l_1^r, \ldots, l_{n-1}^r) dl_n^r = 1$.

If boundary effects were ignored, as may be accurately done for large enough (finite) $n$ in all dimensions in general (see ref 2), we would employ for $\hat{L}$ in the configurational integral the value $L - l_n^r$ (instead of $L - l_n^r - 1/2 l_0$). Hence, the atmospheric integral would yield $(L - l_n^r - (N - n)l_0)^{N-n}$, and by introducing a normalization constant $h_n$, eq 5 would have been rewritten as:

$$g_{1,\ldots,n}(l_1^r, \ldots, l_n^r) =$$
$$h_n \rho^n (1 - \eta)^{-n} \exp(-\rho(l_n^r - nl_0)(1 - \eta)^{-1}) F(l_1^r, \ldots, l_n^r)$$

The normalization condition would then require $h_n = \exp(-1/2(\eta(1-\eta)^{-1}))$, which is a simple constant in consonance with the theory of ref 2.

In the Poisson limit of noninteracting particles, $l_0 \to 0$, and eq 5 reduces to the well-known result:[3]

$$g_{1,\ldots,n}(l_1^r, \ldots, l_n^r) = \rho^n \exp(-\rho l_n^r) \quad (7)$$

Next, we show that the NNPDF of eq 5 is consistent with known exact results for the free energy of the hard rod system employing the statistical thermodynamic formalism of ref 1. In the formalism of ref 1, the general point process NNPDF with origin situated at the boundary of the system's volume ($V$) was required to determine the function $P(\vec{X}'_1, v_1)$ (which is the moment generating function of the energy $E_2$). $E_2$ is the energy contribution to the system (for a given configuration of particles) when the energy of interaction between two sets of particles is "turned on". (The first set constituting only one particle said to be situated at the origin, and the second set being the rest particles in the system). $\vec{X}'_1$ is the origin assumed to be situated at the boundary of $v_1$, which is a volume that expands "microscopically smoothly" to $V$. ($v_1$ and $V$ are macroscopic in size with boundaries assumed "microscopically smooth".) Hence, within a microscopic locality of the boundary, the system "looks like" a "half space" (see Figure 1 of ref 1). Equation 5 of ref 1 provides the expression for $P(\vec{X}'_1, v_1)$, and for the 1-D system of hard rods, only the NNPDF for the $n = 1$ case is sufficient to provide exact results for $P(\vec{X}'_1, v_1)$ (which is rewritten as $P(0, l)$ for the 1-D system). $v_1$ is replaced by $l$, which may expand to $L - l_0$, and the origin is written as $\vec{0}$, which may be taken as the left end of length $l$. Note that $l$ expands only as far as to $L - l_0$ (instead of $L$) because particles may not come to within $1/2 l_0$ of both ends of $L$. In which case, we have been able to account exactly for boundary effects of $L$. Hence, we may write:

$$P(\vec{0}, L - l_0) = \int_{(1/2)l_0}^{\infty} g_1(l^r_1) \exp(-\beta E_2) \, dl^r_1 \tag{8}$$

where $E_2 = \infty$ if the hard core of the nearest neighbor at distance $l^r_1$ overlaps that of the particle whose center is said to be placed at the origin which is situated at the left edge of $l$ (whose length is now $L - l_0$); otherwise it is zero. (Note that $l^r_1$ is measured relative to the left edge of $L$). Observe also in eq 8 that $l^r_1$ is required to vary from $1/2 l_0$ (because the left edge of $l$ is distance $1/2 l_0$ from the left edge of $L$). Also, $l^r_1$ may vary as far as $L - 1/2 l_0$ (in principle), which in the thermodynamic limit, is taken microscopically as $\infty$; hence, the upper limit of the integral in eq 8 is in order. The nature of $E_2$ allows us to increase the lower limit of the integral in eq 8 from $1/2 l_0$ to $3/2 l_0$ Hence, eq 8 becomes:

$$P(\vec{0}, L - l_0) = \int_{(3/2)l_0}^{\infty} \rho(1 - \eta)^{-1} \exp\left(-\rho\left(l^r_1 - \frac{1}{2}l_0\right) \times \right.$$
$$\left. (1 - \eta)^{-1}\right) dl^r_1$$
$$= \exp(-\eta(1-\eta)^{-1}) \tag{9}$$

Equation 10 of ref 1 (which is to be solved next) is restated below:

$$\epsilon\left(1 - \frac{\rho}{\epsilon}\frac{\partial\epsilon}{\partial\rho}\right) = \langle P\rangle \exp\left(-\frac{\rho}{\epsilon}\frac{\partial\epsilon}{\partial\rho}\right) \tag{10}$$

where the average $\langle P\rangle$ may actually be replaced by $P$ (i.e., $P(\vec{0}, l)$), since the edge of $l$ is a single point. Also, we assume the partition function of the system may be written as[1]

$$Z(N,L) = \frac{(\epsilon L)^N}{N!} \tag{11}$$

Using the exact free energy result of eq 4, we then have that:

$$\epsilon = 1 - \eta \tag{12}$$

where, as before, $\eta = Nl_0/L$. Substituting eq 9 in eq 10 yields:

$$\epsilon\left(1 - \frac{\eta}{\epsilon}\frac{\partial\epsilon}{\partial\eta}\right) = \exp(-\eta(1 - \eta)^{-1}) \exp\left(-\frac{\eta}{\epsilon}\frac{\partial\epsilon}{\partial\eta}\right) \tag{13}$$

This highly nonlinear differential equation is satisfied by the expression for $\epsilon$ in eq 12. Hence the NNPDF of eq 5 is consistent with known exact results for the free energy of the hard rod system, employing the formalism of ref 1.

Finally, we investigate the convergence nature of the iteration scheme outlined in ref 1 for the hard rod system. We begin by employing an $\epsilon$ value equal to $\epsilon_c + \epsilon'$ (where $\epsilon_c$ is the correct value of $1 - \eta$, and $\epsilon'$ is the initial error made in a given iteration). Observe that if results for the noninteracting "Poisson point process on the line" were employed, we would have that the error $\epsilon' = \eta$ (since $\epsilon = 1$ for the Poisson case).

The partition function will then be written as:

$$Z(N,L) = \frac{L^N}{N!}(1 - \eta + \epsilon')^N \tag{14}$$

The iteration process of the formalism then requires that this partition function be used to construct an approximate general point process NNPDF with origin at an edge of $L$. The atmospheric integral in eq 1 may be said to result in a value which is clearly larger than the partition function of atmospheric particles (restricted in $\hat{L}$) by a factor of $(N - n - 1)!$. For the general point process, we have $(N - n)$ atmospheric particles within length $(L - l^r_n)$ approximately, and thus the $\epsilon$ value used in this case is written as:

$$\epsilon(N - n, L - l^r_n) \approx \epsilon(N,L) - n\frac{\partial\epsilon(N,L)}{\partial N} - l^r_n\frac{\partial\epsilon(N,L)}{\partial L}$$

$$= 1 - \eta + \epsilon' - n\frac{\partial(1 - \eta + \epsilon')}{\partial N} - l^r_n\frac{\partial(1 - \eta + \epsilon')}{\partial L}$$

$$= (1 - \eta + \epsilon') + \frac{nl_0}{L} - \eta\frac{l^r_n}{L} - n\frac{l_0}{L}\frac{\partial\epsilon'}{\partial\eta} + \eta\frac{l^r_n}{L}\frac{\partial\epsilon'}{\partial\eta}$$

Hence, the value for the atmospheric integral we may use (similar to eq 2) is:

$$((L - l^r_n)\epsilon(N - n, L - l^r_n))^{N-n} =$$
$$\left((L - l^r_n)\left(1 - \eta + \epsilon' + \frac{nl_0}{L} - \frac{\eta l^r_n}{L} - \frac{nl_0}{L}\frac{\partial\epsilon'}{\partial\eta} + \frac{\eta l^r_n}{L}\frac{\partial\epsilon'}{\partial\eta}\right)\right)^{N-n} \tag{15}$$

Also, the free energy of the system in the present approximation is:

$$A = KT\ln(N!) - NKT\ln(\epsilon L) \tag{16}$$

After a lengthy algebra, we obtain the approximate general point process NNPDF (ignoring higher order terms) with origin at left edge of $L$ as:

$$g_{1,...,n}(l^r_1, ..., l^r_n) \approx \frac{h_n N!}{(N - n)!} \times$$
$$\frac{\left(L - Nl_0 - l^r_n + L\epsilon' - l^r_n\epsilon' + nl_0 - nl_0\frac{\partial\epsilon'}{\partial\eta} + \eta l^r_n\frac{\partial\epsilon'}{\partial\eta}\right)^{N-n}}{(L - Nl_0 + \epsilon'L)^N} \times$$
$$F(l^r_1, ..., l^r_n)$$

($h_n$ has been introduced for normalization because of the

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approximate process of derivation). In the thermodynamic limit, and for $n = 1$, we get:

$$g_1(l_1^r) = \frac{h_1 \rho}{(1 - \eta + \epsilon')} \times$$
$$\exp\left(-\rho\left(l_1^r + l_1^r \epsilon' - l_0 + l_0\frac{\partial \epsilon'}{\partial \eta} - \eta l_1^r \frac{\partial \epsilon'}{\partial \eta}\right)(1 - \eta + \epsilon')^{-1}\right)F(l_1^r)$$
(17)

where $\int_{(1/2)l_0}^{\infty} g_1(l_1^r)\, dl_1^r = 1$, and hence

$$h_1 = \left(1 - \eta\frac{\partial \epsilon'}{\partial \eta} + \epsilon'\right)\exp\left(\frac{\frac{1}{2}\eta\left(1 - \eta\frac{\partial \epsilon'}{\partial \eta} + \epsilon'\right) - \eta + \eta\frac{\partial \epsilon'}{\partial \eta}}{1 - \eta + \epsilon'}\right)$$

Hence:

$$P(\vec{0}, L - l_0) = \int_{(3/2)l_0}^{\infty} \rho\frac{\left(1 + \epsilon' - \eta\frac{\partial \epsilon'}{\partial \eta}\right)}{(1 - \eta + \epsilon')} \times$$
$$\exp\left(\frac{\left(1 + \epsilon' - \eta\frac{\partial \epsilon'}{\partial \eta}\right)\left(\frac{1}{2}\eta - \rho l_1^r\right)}{(1 - \eta + \epsilon')}\right)dl_1^r$$
$$= \exp\left(-\eta\left(\frac{1 + \epsilon' - \eta\frac{\partial \epsilon'}{\partial \eta}}{1 - \eta + \epsilon'}\right)\right)$$
(18)

Substituting eq 18 in eq 10 yields:

$$\epsilon\left(1 - \frac{\eta}{\epsilon}\frac{\partial \epsilon}{\partial \eta}\right) = \exp\left(-\eta\left(\frac{1 + \epsilon' - \eta\frac{\partial \epsilon'}{\partial \eta}}{1 - \eta + \epsilon'}\right)\right)\exp\left(-\frac{\eta}{\epsilon}\frac{\partial \epsilon}{\partial \eta}\right)$$
(19)

A solution to this highly nonlinear differential equation can be sought by observing that the lhs of the equation is equal to unity if $\eta(\partial \epsilon/\partial \eta) = \epsilon - 1$.

We then use this condition on the rhs of the equation and require that the arguments of the exponentials add to zero; i.e., $1 - \epsilon = \epsilon\eta(1 + \epsilon' - \eta(\partial \epsilon'/\partial \eta))(1 - \eta + \epsilon')^{-1}$.

Hence, the solution for $\epsilon$ becomes:

$$\epsilon = (\epsilon_c + \epsilon')\left(1 + \epsilon' + \epsilon'\eta - \eta^2\frac{\partial \epsilon'}{\partial \eta}\right)^{-1}$$
(20)

If the initial error $\epsilon'$ is small and thus may usually not vary too fast, we can approximate the new estimate for $\epsilon$ as $\epsilon \approx \epsilon_c + \epsilon' - (\epsilon_c + \epsilon')(\epsilon' + \epsilon'\eta - \eta^2(\partial \epsilon'/\partial \eta))$.

Hence, for small initial error in the choice for $\epsilon$ in general, we easily see that the iteration scheme in question readily converges, and for large initial errors, this may not be the case. For instance, if the Poisson case value for $\epsilon$ were used initially, the initial error $\epsilon'$ would be $\eta$, and after one iteration, the error becomes $\eta^2/(1 + \eta)$, which amounts to a reduction in error.

The above developments therefore validate the authenticity and usefulness of the statistical thermodynamic formalism presented in ref 1 at least for the case of the 1-D hard rod fluid. Also, to the best of our knowledge, the NNPDFs provided in this paper are new results and should find use in various applications.

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