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An investigation of critical and noncritical correlations in model colloidal fluids

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Abstract

We present a study of the correlation length ξ of a hard-core fluid with three different tail interactions, namely, the Asakura–Oosawa potential, an attractive Yukawa tail, and a double Yukawa tail which is attractive at short distance and repulsive at long distance. The correlation length is obtained along the critical isochore in the whole range of supercritical temperatures by determining the leading pole of the structure factor $S(k)$ in the complex plane, where $S(k)$ is obtained from the hierarchical reference theory. We focus on how ξ changes from its Ornstein–Zernike form in the critical region to its high-temperature limit, and find instances of both the Fisher–Widom and Kirkwood scenarios for the monotonic to oscillatory crossover of the decay of correlations at long distance.

1. Introduction

The main reason for the keen interest raised by colloidal dispersions, both experimentally and theoretically, consists in the ability to modify the effective interactions between the macroparticles by tuning the dispersion parameters such as the electrolyte ionic strength, the length and the concentration of adsorbed or nonadsorbed polymer, and so on. Unlike in atomic fluids, this implies that not only the strength, but also the shape of the interaction can be substantially changed, thereby leading to a much richer phase behaviour. Of course, asymptotically close to a critical point these features are bound to give way to the universality that rules critical phenomena, as a consequence of which the critical exponents belong to the same Ising class found in simple liquids. Nevertheless, some memory of the specific interaction remains in *how* the asymptotic power-law behaviour is reached. This was the topic of a recent study [1], where we considered the critical properties of several well-known model interactions for colloidal fluids, and showed that the crossover to the power-law regime is indeed strongly affected by features such as the range of the interaction or the degree of competition between attraction and repulsion, that cannot be modified or do not occur at all in simple fluids. In that study, we focused on

the isothermal compressibility χ_T and correlation length ξ , that are the quantities most directly accessible by experiments. In particular, the correlation length has been the subject of a recent experimental investigation of a colloidal dispersion subject to polymer-induced attractive depletion forces [2]. As observed in that work, the fact that the role of the (inverse) temperature of an atomic system is played by the polymer concentration allows one to map in a single experiment the correlation length from the critical regime, where ξ is much bigger than the particle size σ , to that of vanishingly small attraction, where ξ becomes comparable to σ . The latter regime was not explored in [1], and we have addressed it here for two of the effective interactions considered in that work, namely, the Asakura–Oosawa (AO) potential for depletion interactions [3], and a hard core plus two-Yukawa (HCTY) tail potential with competing short-range attraction and longer-ranged repulsion. While in the neighbourhood of the critical point the decay of the correlations is determined by the behaviour of the reciprocal of the structure factor $1/S(k)$ at small wavevector k , thereby leading to the Ornstein–Zernike correlation length ξ_{OZ} , this is no longer true away from the critical point, where ξ_{OZ} becomes meaningless, and one needs to turn to the *true* correlation length, as determined by the leading pole of the full $S(k)$ in the complex plane. The

nature of the singularities also dictates whether the asymptotic decay of the correlations is monotonic or oscillatory, whether a change from one type of decay to the other takes place as the thermodynamic state is changed, and according to which mechanism this may come along. We have looked upon all of these issues, and found that the two model interactions studied here give quite a complete picture of the different possible scenarios. This is one more instance, in which the behaviour of colloidal systems turns out to be richer than that of their atomic counterparts. In section 2, we briefly summarize the theoretical framework of the present investigation; in sections 3 and 4 we present our results for the AO and the HCTY case respectively; in section 5 we draw our conclusions.

2. Theory

As in [1], the AO and HCTY fluids have been described by the hierarchical reference theory (HRT). A detailed account of this method has been given elsewhere [4]. Here we just recall that its purpose is to implement the main ideas of renormalization group within liquid-state theory. As is customary in perturbation theories, one starts from a ‘reference’ system whose constituents interact only via short-ranged, possibly singular repulsive forces, and whose properties are assumed to be known. For the potentials considered here, the hard-sphere gas is the obvious choice. The perturbation, namely, the remaining part of the interaction, is then fed into the system by gradually switching on its Fourier components of longer and longer wavelengths, so that the long-wavelength fluctuations driving criticality and phase separation are allowed to develop only at the end of the process. The corresponding evolution of the Helmholtz free energy is described by an exact equation that involves the direct correlation function in momentum space $\hat{C}_Q(k)$, where the subscript Q represents the smallest wavevector for which the Fourier components of the interaction have been taken into account at a certain stage of the evolution. The physical system is recovered in the limit $Q \rightarrow 0$. A closed theory is obtained by supplementing this equation with an approximate expression for \hat{C}_Q which, as in the previous applications of HRT, is assumed to be given by

$$\hat{C}_Q(k) = \hat{c}_{\text{HS}}(k) + \lambda_Q \hat{w}(k) + \hat{G}_Q(k) \quad (1)$$

where $\hat{c}_{\text{HS}}(k)$ is the direct correlation function of the hard-sphere gas and $\hat{w}(k)$ is the perturbation, both taken in Fourier space. For $\hat{c}_{\text{HS}}(k)$ the Verlet–Weis parametrization [5] has been used. The function $\hat{G}_Q(k)$ is found so as to satisfy, albeit approximately, the requirement that the radial distribution function $g_Q(r)$ should be vanishing inside the hard core. In practice, its inverse Fourier transform $\mathcal{G}_Q(r)$ has been taken as a fourth-degree polynomial with adjustable coefficients for $0 < r < \sigma$, and is identically vanishing for $r > \sigma$, σ being the hard-core diameter. The parameter λ_Q is instead determined by requiring that the Helmholtz free energy given by the HRT evolution satisfies the compressibility rule $\hat{C}_Q(k = 0) = \partial^2 \mathcal{A}_Q^{\text{ex}} / \partial \rho^2$, where $\mathcal{A}_Q^{\text{ex}}$ is the excess Helmholtz free energy per unit volume divided by $-k_B T$. Enforcing these conditions gives a partial differential equation for $\mathcal{A}_Q^{\text{ex}}$ that is solved numerically from $Q = \infty$ down to $Q = 0$.

In this work we will be concerned with the asymptotic decay of the pair correlation function $h(r) = g(r) - 1$, that is related to the direct correlation function in Fourier space by the Ornstein–Zernike equation

$$h(r) = \int \frac{d^3 \mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\hat{c}(k)}{1 - \rho \hat{c}(k)} \quad (2)$$

where ρ is the number density of particles and we have omitted the subscript Q in referring to the fully interacting system. For potentials that have a finite support or decay exponentially such as those considered here, $h(r)$ at large r is exponentially damped, and the decay rate is determined by the leading pole of the integrand in (2), i.e., by the complex solution of the equation

$$1 - \rho \hat{c}(\alpha) = 0 \quad (3)$$

which has the smallest imaginary part in absolute value [6]. This gives the correlation length ξ via the relation $\xi = 1/\text{Im}(\alpha)$. The decay of $h(r)$ is monotonic or oscillatory depending on whether α is purely imaginary, or it has also a real part. We note that, within the closure (1) and for the potentials investigated here, $\hat{c}(q)$ is known analytically in the whole complex plane once the amplitude of the perturbation λ_Q and the coefficients of $\hat{G}_Q(k)$ have been determined. This analytical expression was substituted into (3), and the resulting equation was solved numerically.

For thermodynamic states near the critical point, the leading singularity is close to the origin and therefore is determined by the behaviour of $1 - \rho \hat{c}(k)$ at small k . In this limit (1) yields

$$1 - \rho \hat{c}(k) \sim \frac{1}{\chi_T} + b k^2 \quad (4)$$

where χ_T is the reduced isothermal compressibility and b is proportional to the second moment of $c(r)$ in real space. This gives the expression of the Ornstein–Zernike correlation length ξ_{OZ} as

$$\xi_{\text{OZ}} = \sqrt{\rho b \chi_T}. \quad (5)$$

As one approaches the critical point, ξ and ξ_{OZ} become identical. The coefficient b is state-dependent and, according to the approximate closure (1) used here, at the critical point it remains finite and strictly positive. Equation (5) then gives the relation $\nu = \gamma/2$ between the critical exponents of the correlation length and isothermal compressibility on the critical isochore, thereby setting the critical exponent η to 0. This shortcoming is not very severe in three dimensions, owing to the small value of η .

3. Asakura–Oosawa potential

For the AO potential, the interaction $w_{\text{AO}}(r)$ outside the hard core is given by [3]

$$\beta w_{\text{AO}}(r) = \begin{cases} -\eta_p^r \frac{(1+q)^3}{q^3} \left[1 - \frac{3r}{2(1+q)} \right. \\ \quad \left. + \frac{r^3}{2(1+q)^3} \right] & 1 < r < 1+q \\ 0 & r > 1+q \end{cases} \quad (6)$$

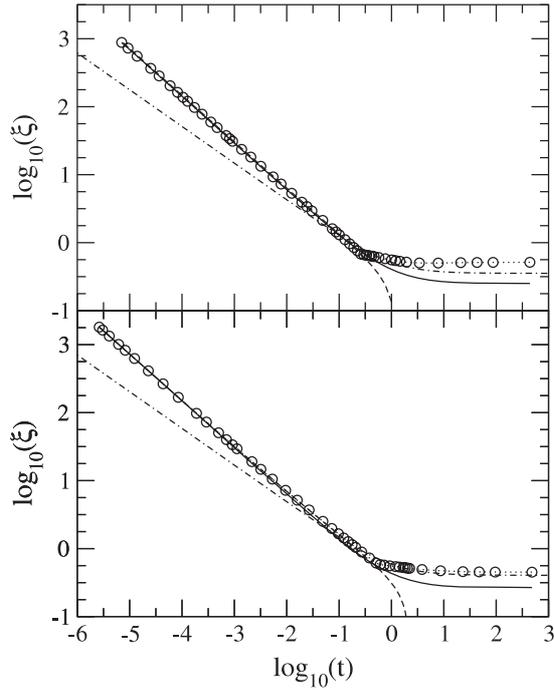


Figure 1. Correlation length on the critical isochore of the AO fluid with polymer-to-colloid size ratio $q = 0.4$ (upper panel) and $q = 0.8$ (lower panel) as a function of the reduced temperature $t = (\eta_{p,c}^r - \eta_p^r)/\eta_p^r$. Open circles: true correlation length ξ . Dotted lines are a guide to the eye. Solid line: power-law fit of ξ in the critical region according to $\xi = \xi_0[t/(t + 1)]^{-\nu}$. Dash-dotted line: same as above, but with ν set at 0.54 and $\xi_0, \eta_{p,c}^r$ determined by fitting to data in the interval $-1.5 \lesssim \log(t) \lesssim -0.5$ (see the text). Dashed line: Ornstein–Zernike correlation length ξ_{OZ} .

where $\beta = 1/(k_B T)$, the colloid diameter σ has been set equal to unity, q is the ratio between the polymer and colloid diameters, and η_p^r is the packing fraction of the pure polymer in osmotic equilibrium with the polymer in the mixture. This ‘reservoir’ packing fraction plays the same role as the inverse temperature β in a thermal system. Therefore, the control parameter, usually identified with $(T - T_c)/T_c$, now becomes $t = (\eta_{p,c}^r - \eta_p^r)/\eta_p^r$, where T_c and $\eta_{p,c}^r$ are the critical values of T and η_p^r .

In figure 1 we have displayed the true correlation length ξ at the critical colloid density $\rho = \rho_c$ as a function of t on a log–log plot for two AO potentials with $q = 0.4$ and $q = 0.8$. HRT gives $\eta_{p,c}^r = 0.4404$, $\rho_c = 0.431$ and $\eta_{p,c}^r = 0.4825$, $\rho_c = 0.362$ for $q = 0.4$ and $q = 0.8$ respectively. As the critical point is approached, the log–log plot becomes a straight line, corresponding to the power-law behaviour $\xi \sim \xi_0 t^{-\nu}$ with $\nu = 0.689$ according to HRT. The figure shows also the Ornstein–Zernike correlation length ξ_{OZ} given by (5). From inspecting the results reported in the figure, a number of observations can be made. First, the log–log plot of ξ versus t shows a ‘knee’ located at a reduced temperature t_{FW} which lies in the interval $-1 < \log t < 0$. t_{FW} is the temperature at which the critical isochore $\rho = \rho_c$ intersects the Fisher–Widom (FW) line [6]: for $t < t_{FW}$, the leading pole given by (3) is purely imaginary, $\alpha_1 = i\kappa_1$, and $h(r)$ decays monotonically at large r . As t increases, κ_1 moves up, and

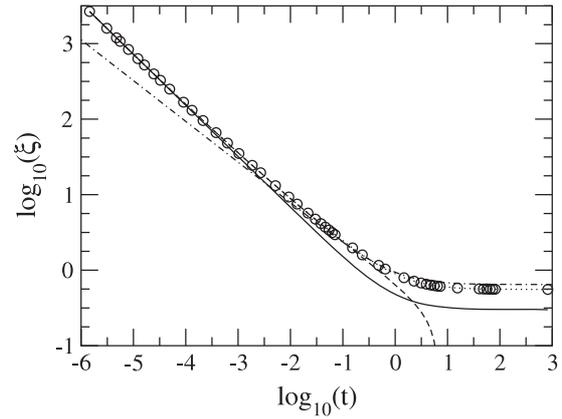


Figure 2. The same as figure 1 for the HCY potential with $z = 1.8$. The reduced temperature is $t = (T - T_c)/T_c$.

for $t > t_{FW}$ it gets above the imaginary part of another pole $\alpha_2 = \lambda + i\kappa_2$ with $\lambda \neq 0$, which then becomes the leading singularity and gives oscillatory decay for $h(r)$. In other words, at $t = t_{FW}$ the correlation length ξ ‘jumps’ from a purely imaginary branch of solution of (3) to a nonpurely imaginary one.

Moreover, in the region of monotonic decay $t < t_{FW}$ the two lengths ξ and ξ_{OZ} are extremely close, and both of them deviate very little from linearity for $q = 0.8$ and even less so for $q = 0.4$. As t increases above t_{FW} , the deviations between ξ and ξ_{OZ} become immediately very large, with $\log(\xi)$ saturating at a finite value $\log(\xi_{HS})$ determined by the correlation length ξ_{HS} of the hard-sphere gas at $\rho = \rho_c$, and $\log(\xi_{OZ})$ getting more and more negative. The latter feature is due to the fact that, as η_p^r decreases, the perturbation $\hat{w}(k)$ in (1) becomes less and less important with respect to $\hat{c}_{HS}(k)$, and the coefficient b in (4) is more and more dominated by its negative hard-sphere contribution. Therefore, b will vanish at some value of η_p^r and, according to (5), so will ξ_{OZ} . Obviously, in this regime ξ_{OZ} becomes meaningless, since it has no bearing any more with the decay of $h(r)$.

It is interesting to compare the behaviour of ξ just illustrated for the AO potential to that found when the interaction is given by a hard core plus attractive Yukawa (HCY) tail

$$w_{HCY}(r) = -\frac{e^{-z(r-1)}}{r} \quad r > 1 \quad (7)$$

where the strength of the interaction has been taken equal to unity and the inverse range z has been set at the value $z = 1.8$ appropriate to model the phase diagram of a Lennard–Jones (LJ) fluid. The HRT critical temperature and density are $T_c = 1.2137$, $\rho_c = 0.314$. The results for ξ are shown in figure 2. It appears that, in order to observe the asymptotic power law for ξ , it is necessary to get much closer to the critical point than in the AO case. In fact, deviations from linearity in the log–log plot show up already for $\log(t) > -3$. As observed in [1], this is due to the fact that for $z = 1.8$ the range of w_{HCY} is longer than that of w_{AO} , even for relatively large values of the polymer-to-colloid size ratio q such as $q = 0.8$.

This pushes the onset of the Ising regime for w_{HCTY} to smaller reduced temperatures, in agreement with the renormalization group predictions [7]. Another notable difference with respect to the AO potential is that there is no change from monotonic to oscillatory decay of $h(r)$ as t increases. Instead, the decay at large r is monotonic throughout the critical isochore, and ξ crosses over smoothly to its high-temperature limit. That this should be the case is easily understood by considering (3) for a purely imaginary solution $\alpha_1 = i\kappa_1$. On the one hand, the compressibility rule $1 - \rho\hat{c}(k=0) = 1/\chi_T$ implies that for $\kappa_1 = 0$ the lhs of (3) is positive. On the other hand, according to (1) an attractive Yukawa tail will contribute to $\hat{c}(i\kappa_1)$ a term $1/(z^2 - \kappa_1^2)$ with a positive amplitude, so that the lhs of (3) will diverge to $-\infty$ for $\kappa_1 \rightarrow z^-$. Therefore, (3) will have a purely imaginary solution with $0 < \kappa_1 < z$ provided the amplitude λ_Q in (1) is not vanishing, i.e., provided $\beta \neq 0$. For $z = 1.8$ and $\rho = \rho_c$, κ_1 is always smaller than the imaginary part κ_2 of the leading nonpurely imaginary solution α_2 . As a consequence, ξ is always given by $1/\kappa_1$. For $\beta \rightarrow 0$, one has $\lambda_Q \rightarrow 0$, so that κ_1 must get closer and closer to z to satisfy (3). Unlike in the AO case, the critical isochore never crosses the FW line, and the high-temperature limit of ξ is not determined by the hard-sphere correlation length, but rather by the range of the potential.

Finally, we recall that in [2], experimental and simulation data for the correlation length over a wide range of t were found to be well represented by the relation $\xi \sim \xi_0[t/(1+t)]^{-\nu}$. In the critical region this is indistinguishable from $\xi \sim \xi_0 t^{-\nu}$, but at high ‘temperature’, i.e., low η_p^r , it saturates at ξ_0 instead of going to 0. This ‘extended’ power law has also been shown in figures 1 and 2, where in each case ξ_0 , ν , and $\eta_{p,c}^r$ or T_c have been determined by a least-square fit to the HRT results in the critical region $\log(t) \lesssim -4$. It appears that in the high-temperature region the extended power law performs quite poorly, the deviations between the actual results for ξ and its predictions being much more substantial than it was found in [2], see figure 2 of that paper. However, one should take into account that the region of t probed there was farther from the critical point, $\log(t)$ being always greater than -3 , and that power-law fits are quite delicate since in the critical region very small changes in $\eta_{p,c}^r$ (or T_c) and ν correspond to large changes in the critical amplitude ξ_0 . With this in mind, we tried to fit our results to the extended power law by fixing the critical exponent to the same value $\nu = 0.54$ used in [2] and restricting to values of $\log(t)$ above -2 , which correspond to the range investigated in [2] for the AO and the LJ potentials. The results, again reported in figures 1 and 2, show a much better agreement with the actual data in the range of t considered. We then conclude that the extended power-law scaling $\xi \sim \xi_0[t/(1+t)]^{-\nu}$ cannot be reliably extrapolated to high temperatures, if ν and ξ_0 are determined on the basis of the behaviour of ξ in the very neighbourhood of the critical point, but on the other hand its accuracy at high temperature considerably improves, if one focuses on the region $\log(t) \gtrsim -2$, as was done in [2], and as is the case with most experimental investigations. Of course, in this case ξ_0 and ν will not coincide with their asymptotic values for $t \rightarrow 0$, so the deviations can be quite large in this limit, as shown in figures 1 and 2.

4. Competing interactions

For the HCTY fluid, the tail potential is given by

$$w_{\text{HCTY}}(r) = -\frac{e^{-z_1(r-1)}}{r} + A\frac{e^{-z_2(r-1)}}{r} \quad r > 1 \quad (8)$$

where, for the case we are interested in, one has $z_1 > z_2$, $A > 0$ so that $w_{\text{HCTY}}(r)$ is attractive at short distance and repulsive at long distance. This kind of competing interaction potential has recently been given much attention because, when the relative strength A of the repulsion is high enough, the fluid–fluid phase transition driven by the attractive contribution is replaced by equilibrium cluster formation [8]. Such a mechanism for the formation of large particle aggregates is expected to be relevant for several colloidal systems, including protein solutions [9], since competition between attraction and repulsion may stem from a number of different scenarios. In some previous papers [10] we focused on the effect of competition on the bulk fluid–fluid transition as A approaches the value beyond which cluster formation takes over, and showed that the main effects of competition are the strong enhancement of large density fluctuations, and the appearance in the large-fluctuation region of two characteristic lengths in $h(r)$. The mechanism at the origin of the latter feature is in fact quite general and it has already been pointed out a number of times in different contexts [11]. As A is increased, the second moment of $w_{\text{HCTY}}(r)$ gets smaller, and so does the coefficient b in (4). For A large enough, b actually becomes negative, thereby giving a ‘pre-peak’ in $S(k)$ at low, but nonvanishing k that signals the tendency towards microphase formation. Here we focus on lower values of A , where b is still positive, but because of its small value, the expansion (4) needs to be taken to the order k^4 in order to extract a reliable value of the correlation length, even assuming that χ_T is large:

$$1 - \rho\hat{c}(k) \sim \frac{1}{\chi_T} + b k^2 + c k^4. \quad (9)$$

Substitution of (9) into (3) yields two different lengths ξ , μ , both of which are much bigger than the particle size in the regime in which χ_T is large and competition is important. In [1], we reported the behaviour of these characteristic lengths in the critical region based on the truncated expansion (9) for $z_1 = 1$, $z_2 = 0.5$, and repulsion strength $A = 0.0973$, that is very close to the limit beyond which the fluid–fluid transition disappears. Here we would like to see how the results reported there compare with those obtained from (3) using the full expression of $\hat{c}(k)$. The comparison is shown in figure 3 for $\rho = \rho_c$. HRT gives $T_c = 1.6794$, $\rho_c = 0.25$. For $\xi \gtrsim 10$, the two sets of values are completely superimposed. This shows that (9) can be reliably used to determine ξ and μ in the whole region where they are large compared to the particle size. In the critical region, ξ follows the expected power-law behaviour, and $h(r)$ decays monotonically, as in the systems discussed in the previous section. The decay becomes oscillatory above a temperature t_{K1} located in the interval $-2 < \log(t_{K1}) < -1$, at which ξ displays a kink. However, the mechanism that governs the change from monotonic decay to oscillations is different from the FW scenario described above.

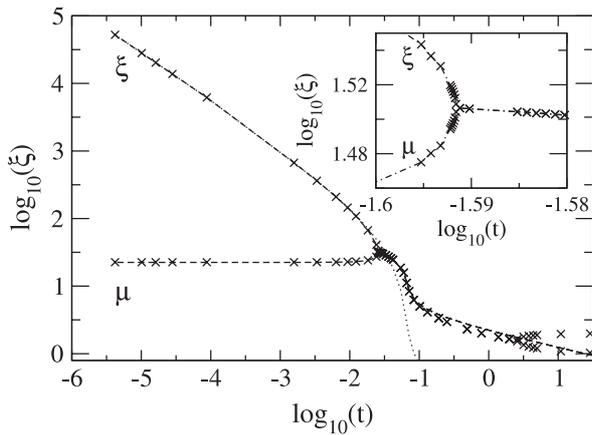


Figure 3. Correlation length on the critical isochore of the HCTY potential with $z_1 = 1$, $z_2 = 0.5$, $A = 0.0973$. The reduced temperature is $t = (T - T_c)/T_c$. Crosses: true correlation length ξ . See the text for the meaning of μ . Dashed line: correlation length obtained from the truncated expansion (9). Dotted line: Ornstein–Zernike correlation length ξ_{OZ} . Inset: enlargement in the neighbourhood of the Kirkwood temperature t_{K1} . Only the data for the true correlation length have been shown. Dot-dashed lines are a guide to the eye.

For the system considered here, in the critical region not only the leading pole $\alpha_1 = i\kappa_1$, but also the next-to-leading one $\alpha_2 = i\kappa_2$ is purely imaginary. The corresponding length $\mu = 1/\kappa_2$ has also been shown in the plot. As t increases, α_1 moves up along the imaginary axis, until α_1 and α_2 coalesce for $t = t_{\text{K1}}$. For $t \rightarrow t_{\text{K1}}^-$, the slopes of κ_1 and κ_2 as a function of t become infinite, and so do those of ξ and μ , see inset to figure 3. For $t > t_{\text{K1}}$, the two poles move off the imaginary axis as complex conjugate quantities. This is the Kirkwood scenario [12], that has already been described in detail in ionic fluids [13]. Unlike in the FW case, here the wavelength of the oscillations becomes infinite at the crossover point. Moreover, the comparison between figures 3 and 1 shows that here oscillations persist much closer to the critical point, and by the time monotonic decay takes over, ξ has increased to more than 30 times the particle diameter σ , whereas at the FW point shown in figure 1, ξ is smaller than σ , and nearly equal to its hard-sphere value. In the critical region, ξ becomes rapidly undistinguishable from ξ_{OZ} and much bigger than μ , that saturates at a finite value for $t \rightarrow 0$, and is actually almost constant in most of the region $t < t_{\text{K1}}$. However, as pointed out above, both μ and (*a fortiori*) ξ are much bigger than σ . As a consequence, even though the asymptotic behaviour of $h(r)$ for $r \rightarrow \infty$ is ultimately determined by ξ , both lengths are important to describe the correlations at relatively large values of r , up to several tens of σ , suggesting the presence of large clusters of correlated particles [1, 10]. Finally, we observe that, as t increases above t_{K1} , the decay does not remain oscillatory up to arbitrary high temperatures, but becomes again monotonic above a second Kirkwood temperature t_{K2} with $0 < \log(t_{\text{K2}}) < 1$, at which α_1 and α_2 meet again on the imaginary axis. This system then displays two Kirkwood lines, as was discussed in [15]. Obviously, the higher-temperature crossover cannot be described by the truncated expansion (9),

which is useful only at large ξ . For $t > t_{\text{K2}}$, the purely imaginary poles $\alpha_1 = i\kappa_1$ and $\alpha_2 = i\kappa_2$ move away from each other, and for $t \rightarrow \infty$ one has $\kappa_1 \rightarrow z_2^+ = 0.5$, $\kappa_2 \rightarrow z_1^- = 1$. Therefore, the decay length at high temperature is determined by the potential range as in the case of the HCY potential with $z = 1.8$ considered above.

5. Conclusions

We have carried out a study of the true correlation range ξ of a hard-core fluid with three different tail interactions, namely, the AO effective potential, an attractive Yukawa with range adjusted to model the phase diagram of a LJ fluid, and a double Yukawa with competing attractive and repulsive tails. The correlation length has been determined along the critical isochore from the critical to the high-temperature regime by studying the poles of $S(k)$ in the complex plane. In the critical region, ξ becomes identical to the Ornstein–Zernike correlation length, as expected, and as the temperature increases it crosses over to a finite value that for short-ranged tails is given by the hard-sphere correlation length ξ_{HS} , while for longer-ranged tails is determined by the potential range itself. As for the decay of the correlations as the temperature increases, the systems studied give a rather complete overview of the possible scenarios: purely monotonic decay at all temperatures (attractive LJ-like Yukawa), monotonic to oscillatory according to the FW crossover (AO), monotonic to oscillatory to monotonic according to the Kirkwood crossover (double Yukawa). As a concluding remark, we stress that in the present study we have always dealt with rapidly decreasing interactions. For power-law interactions such as the LJ itself, the asymptotic decay of the correlations will also be described by a power law, as pointed out in [14], so that the very notion of true correlation range loses its meaning. Moreover, our pole analysis rests on the simple form (1) for the direct correlation function. The overall pole structure given by more sophisticated closures could be different. However, the crossover scenarios considered above are quite general, and we expect that a different theory would mostly give quantitative rather than qualitative differences.

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