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Abstract

We investigate the intermediate-and longest-range decay of the total pair correlation function $h(r)$ in model fluids where the inter-particle potential decays as $-r^{-6}$, as is appropriate to real fluids in which dispersion forces govern the attraction between particles. It is well-known that such interactions give rise to a term in q^3 in the expansion of $\hat{c}(q)$, the Fourier transform of the direct correlation function. Here we show that the presence of the r^{-6} tail changes significantly the analytic structure of $\hat{h}(q)$ from that found in models where the inter-particle potential is short ranged. In particular the pure imaginary pole at $q = i\alpha_0$, which generates monotonic-exponential decay of $rh(r)$ in the short-ranged case, is replaced by a complex (pseudo-exponential) pole at $q = i\alpha_0 + \alpha_1$ whose real part α_1 is negative and generally very small in magnitude. Near the critical point $\alpha_1 \sim -\alpha_0^2$ and we show how classical Ornstein–Zernike behaviour of the pair correlation function is recovered on approaching the mean-field critical point. Explicit calculations, based on the random phase approximation, enable us to demonstrate the accuracy of asymptotic formulae for $h(r)$ in all regions of the phase diagram and to determine a pseudo-Fisher–Widom (pFW) line. On the high density side of this line, intermediate-range decay of $rh(r)$ is exponentially damped-oscillatory and the ultimate long-range decay is power-law, proportional to r^{-6}, whereas on the low density side this damped-oscillatory decay is sub-dominant to both monotonic-exponential and power-law decay. Earlier analyses did not identify the pseudo-exponential pole and therefore the existence of the pFW line. Our results enable us to write down the generic wetting potential for a 'real' fluid exhibiting both short-ranged and dispersion interactions. The monotonic-exponential decay of correlations associated with the pseudo-exponential pole introduces additional terms into the wetting potential that are important in determining the existence and order of wetting transitions.

Ode to Richard Palmer and other travellers on the imaginary axis

> *Beware this road to Hell*
> *Strange asymmetrical poles lie waiting*
> *Is it really imaginary? For*
> *Surely the integrand is odd.*
>
> *Fear the curse of Derjaguin*
> *Wonder at Casimir and Lifshitz*
> *Trust in Widom and Enderby*
> *To Verlet via critical Dantchev.*
>
> *Risking travails of Cauchy's Theorem*
> *Armed only with the RPA*

> *Taming the asymmetrical poles and*
> *Thereby saving the correlation length.*

1. Introduction

We re-visit a problem in liquid-state physics that is easy to state but has proved difficult to answer satisfactorily: How does the radial distribution function $g(r)$ of a simple, neutral fluid decay for large and intermediate values of r, the separation between the atoms or particles? Specifically we consider models of atomic (rare gas) fluids where $\phi(r)$, the interatomic pair potential, decays as $-r^{-6}$ at large separations. Such power-law decay reflects the presence of induced dipole–induced

dipole interactions, i.e. dispersion (London) forces, that are omnipresent in atomic systems and, at larger length scales, in colloidal fluids. For model fluids with short-ranged potentials, meaning $\phi(r)$ is of finite range or decays exponentially or faster, the problem is solved and the nature of the asymptotic and intermediate-range decay of $g(r)$ is well-understood [1–3]. Moreover, the asymptotic analysis has proved valuable in interpreting the results of computer simulation studies [4] where the pair potential is truncated and set to zero beyond some cut-off separation. However, in real fluids r^{-6} tails are always present.

Several authors have posed the problem. Widom [5] and later Enderby *et al* [6] proposed that $g(r) - 1$ should decay asymptotically in the same fashion as $\phi(r)$ when the latter decays as a power-law. In [6] it is argued that if the pair direct correlation function $c(r)$ decays in the standard way

$$c(r) \to -\beta\phi(r), \qquad r \to \infty, \qquad (1)$$

then from the Ornstein–Zernike (OZ) equation it follows that the total correlation function

$$h(r) \equiv g(r) - 1 \to -(\rho\chi_T)^2\beta^{-1}\phi(r), \qquad r \to \infty, \quad (2)$$

where $\beta = (k_{\mathrm{B}}T)^{-1}$ (T denotes temperature and k_{B} Boltzmann's constant), ρ is the number density and χ_T is the isothermal compressibility. Equation (1) is valid for state points away from the critical point where χ_T and ξ, the correlation length for density fluctuations, are finite. For states close to the critical point one should expect equations (1) and (2) to be valid only for $r > \xi$, with ξ diverging at the critical point. By contrast, in *dense* liquids one expects to observe the same exponentially damped oscillations that characterize the decay of $h(r)$ in theories and simulations of models with truncated pair potentials; the oscillations arise from the residual effects of packing of the atoms and these should not depend on the details of the tail of $\phi(r)$. Verlet [7] was one of the first authors to seek a unified description of the intermediate-range correlations, reflecting residual ordering in fluids, and the longest-range behaviour, reflecting directly the power-law decay of the dispersion interactions.

In 1994, the present authors together with Leote de Carvalho and Hoyle [8], hereafter referred to as Paper I, developed what we believed was a suitable unified treatment of the intermediate-and long-range decay of $h(r)$ for a simple model fluid in which the pair potential $\phi(r)$ decays as $-a_6/r^6$. Our approach was based on the pole structure of the Fourier transform $\hat{h}(q)$ in the complex-q plane. The analysis is not as straightforward as that for models with short-ranged potentials where $\hat{h}(q)$ is an even function of the wavenumber q. Dispersion interactions give rise to a q^3 term in $\hat{c}(q)$ [6, 8] and hence $\hat{h}(q)$ has both even and odd terms. We proposed an explicit approximation for $h(r)$, see equation (38) of Paper I, that adds the (oscillatory) contribution from the leading-order pole of $\hat{h}(q)$ to the slowest power-law contribution, where the latter is obtained from an expansion about the origin of an integral along the imaginary q axis. At temperature $T = 1.18T_c$, where T_c is the critical temperature, and a high liquid density $\rho^* = \rho\sigma^3 = 0.8$ the approximation provides an

excellent fit to numerical results for $h(r)$ defined by the OZ equation and the random phase approximation (RPA) for $\hat{c}(q)$, for $r \geqslant 2.2\sigma$ where σ is the atomic diameter. The results showed that the slowest decaying power-law contribution, as given by equation (2), is comparable with the exponentially decaying contribution for $r \approx 25\sigma$ and dominates completely for $r \geqslant 35\sigma$. The same approximation was less successful at a lower density $\rho^* = 0.45$ on the same isotherm, where the oscillations are more strongly damped. Our Paper I did not focus on the important issue of the decay of correlations in the neighbourhood of the critical point and, with the benefit of hindsight, we recognize that had we considered that region of the phase diagram some of the limitations of the approximations we made would have been apparent.

Recall that for model fluids with short-ranged potentials one expects conventional Ornstein–Zernike decay: $h(r) \sim r^{-1}\exp(-r/\xi)$, for $r > \xi$, in dimension $d = 3$. In mean-field treatments such monotonic decay of the pair correlation function is associated with a pure imaginary pole $q = \mathrm{i}\alpha_0$ of $\hat{h}(q)$; on approaching the critical point $\alpha_0 \equiv \xi^{-1} \to 0$. However, when the r^{-6} tail is present and $\hat{c}(q)$ has a term in q^3, it is easy to show [8] there is no pure imaginary pole and therefore the genesis of Ornstein–Zernike decay is not obvious. We return to this topic in the present paper and attempt to provide a comprehensive treatment of the asymptotic decay of correlations valid for all fluid-state points at mean-field level. It turns out that incorporating dispersion interactions shifts the pole slightly off the imaginary axis (as well as destroying the left–right symmetry of poles lying off the imaginary axis) and it is the presence of this complex pole, with its very small real part, that gives rise to monotonic Ornstein–Zernike decay of $h(r)$ at intermediate values of r. This particular pole was not identified in Paper I but it is crucial to understanding the different regimes of decay in various regions of the phase diagram.

Our present analysis also makes contact with the work of other authors who have investigated the decay of $h(r)$ for states close to the critical point. Kayser and Raveché [9] considered a model where the pair potential $\phi(r)$ decays as $-r^{-(d+p)}$ for $r \to \infty$ and assumed that $h(r)$ could be decomposed into two (additive) contributions. The long-ranged piece $h_{\mathrm{LR}}(r)$ is given by equation (2) for $r > r^*$ (and is zero for $r < r^*$) whereas the 'short-ranged' piece $h_{\mathrm{SR}}(r)$ has the usual (Fisher) critical scaling form that is valid for fluids with short-ranged potentials. The separation r^* is determined by requiring $h_{\mathrm{SR}}(r) = h_{\mathrm{LR}}(r)$ at $r = r^*$ and the authors find $r^* = (p - 2 + \eta)\xi\ln(\xi/\sigma)$ where η is the critical exponent that describes the power-law decay of $h(r)$ precisely *at* the critical point. For a three-dimensional fluid $\eta \approx 0.02$ and dispersion interactions correspond to $p = 3$. Later, Dantchev [10] carried out an explicit asymptotic analysis of a d-dimensional mean-spherical model where the interaction between spins decays as $-r^{-(d+p)}$ for $r \to \infty$ with $2 < d < 4$, $2 < p < 4$ and $d + p \leqslant 6$. Dantchev expands the Fourier transform of the potential $\hat{\phi}(q)$ in powers of the wavevector q, retaining terms in q^2, q^p and q^4 only. He finds that $h(r)$ can indeed be written as a sum of 'short-ranged' and long-ranged pieces and determines explicitly the asymptotic behaviour of each. In

agreement with [9], Dantchev concludes that cross-over from 'short-ranged' to long-ranged decay occurs for $r^* = (p - 2)\xi \ln(\xi/\sigma)$; recall $\eta = 0$ in the mean-spherical model. Thus, specializing to $d = 3$ and dispersion interactions, Dantchev's analysis implies that Ornstein–Zernike (exponential) decay of $rh(r)$ is found only in the range $\xi < r < r^*$ with $r^* = \xi \ln(\xi/\sigma)$. For $r > r^*$ power-law decay should dominate. Figure 1 of [11] illustrates nicely the different regimes of decay of $h(r)$ expected for a near critical fluid.

Since Dantchev retains only a finite number of terms in the expansion of $\hat{\phi}(q)$, his analysis cannot capture the oscillations in $h(r)$ that arise in a fluid. Our present treatment, based on a liquid-state theory, incorporates oscillatory as well as Ornstein–Zernike like behaviour. For completeness we should also mention very recent work of Martynov [12] who addresses the same problem of asymptotic decay in fluids with dispersion interactions. However, he fails to identify the subtle nature of the pole structure of $\hat{h}(q)$, that is crucial to understanding the asymptotics when dispersion interactions are present.

It is well-known that medium-and long-range correlations in liquids and their mixtures determine many aspects of fluid interfacial phenomena and phase transitions—see e.g. [1, 2, 13, 14]. In particular, the decay of the density profile of a fluid and the adsorption of thick films at a substrate, and the nature of wetting transitions are governed by the same physics that determines the decay of $h(r)$. Understanding the latter is therefore a pre-requisite for a proper understanding of fluid interfaces and the solvation of colloidal particles (we shall return to some of this history in the discussion section below).

In section 2 we describe the asymptotics of $h(r)$. Sections 3 and 4 present the results of numerical calculations for a particular model fluid treated in the RPA. The pair potential is that employed in Paper I:

$$\phi(r) = \begin{cases} \infty & r \leqslant \sigma \\ -\epsilon & \sigma < r \leqslant R_c \\ -a_6/r^6 & R_c < r \end{cases} \quad (3)$$

with a_6, $\epsilon > 0$ and to ensure continuity at $r = R_c$ we set $a_6 = \epsilon R_c^6$. The RPA for this model is defined by

$$c(r) = c_{hs} - \beta\phi_{att}(r), \quad (4)$$

where c_{hs} is the (Percus–Yevick) direct correlation function of a hard-sphere fluid of diameter σ and the attractive part of the potential is

$$\phi_{att}(r) = \begin{cases} -\epsilon & r \leqslant R_c \\ -a_6/r^6 & R_c < r. \end{cases} \quad (5)$$

The Fourier transforms $\hat{c}(q)$ and $\hat{\phi}_{att}(q)$ can be calculated analytically and one finds [8] $\hat{c}(q) = \hat{c}_e(q) + \hat{c}_o(q)$, where $\hat{c}_e(q)$ is an even function of q and $\hat{c}_o(q) = aq^3$ with $a = \beta\pi^2 a_6/12$. This q^3 contribution can be seen experimentally in the small q expansion of the structure factor from neutron scattering data on liquid argon [15]. Note that the challenges in identifying the q^3 contribution from structure factor data measured in neutron scattering experiments were discussed

in [15] and in subsequent papers that we shall return to in section 5. Within the RPA there are no other odd terms. Closure approximations that go beyond the RPA could introduce higher odd powers, such as q^9—see Paper I. We shall ignore these higher-order terms in the subsequent analysis. Although the RPA is a rather crude theory of liquids it has the important advantage for the present problem of yielding an analytical expression for $\hat{c}(q)$ so that the poles of $\hat{h}(q)$ can be calculated (numerically) enabling us to test in section 3 the accuracy of the asymptotic formulae we obtain and to calculate what we denote a pseudo-Fisher–Widom line (pFW) where the damped-oscillatory exponential decay of $rh(r)$ becomes sub-dominant to *both* monotonic-exponential and power-law decay, [2, 16]. In section 4 we investigate the behaviour of the pair correlation function in the approach to the critical point, comparing the results from approximating $\hat{c}(q)$ by a power-series expansion truncated after the q^3 term with those from the full RPA solution. We conclude in section 5 with a summary of our results for the decay of $g(r)$ and a discussion of the relevance of our present results for the form of the wetting potential that determines wetting transitions in real fluids and for other interfacial phenomena.

2. Asymptotics of $h(r)$ in a fluid with dispersion interactions

We seek to extract the medium-and long-range parts of the total correlation function $h(r)$ from

$$rh(r) = \frac{1}{2\pi^2} \int_0^\infty dq \, q \sin qr \hat{h}(q) \quad (6)$$

$$= \frac{1}{2\pi^2} \text{Im}\left[\int_0^\infty dq \, q e^{iqr} \hat{h}(q) \right] \quad (7)$$

with the Fourier transform $\hat{h}(q)$ given by the Ornstein–Zernike (OZ) equation

$$\hat{h}(q) = \frac{\hat{c}(q)}{1 - \rho\hat{c}(q)}, \quad (8)$$

together with a direct correlation function of the general form

$$\hat{c} = \hat{c}_e + \hat{c}_o, \quad (9)$$

where we have omitted the dependence on q. The subscripts refer to contributions that are even functions of q and odd functions of q, respectively. Thus,

$$\hat{h} = \hat{h}_e + \hat{h}_o \quad (10)$$

$$= \frac{\hat{c}_e(1 - \rho\hat{c}_e) + \rho\hat{c}_o^2}{D} + \frac{\hat{c}_o}{D} \quad (11)$$

$$D = (1 - \rho\hat{c})(1 - \rho\hat{c}_e + \rho\hat{c}_o). \quad (12)$$

When (7) is evaluated with Cauchy's theorem, simple poles arise at complex values of $q = q_n$ defined by

$$\rho\hat{c}(q_n) = 1, \quad (13)$$

with residues determined from

$$\text{Res}\{\hat{h}\} = \frac{1}{\rho}\left[\frac{q - q_n}{1 - \rho\hat{c}(q_n) - \rho(q - q_n)\hat{c}'(q_n) + \cdots} \right]_{q \to q_n}$$

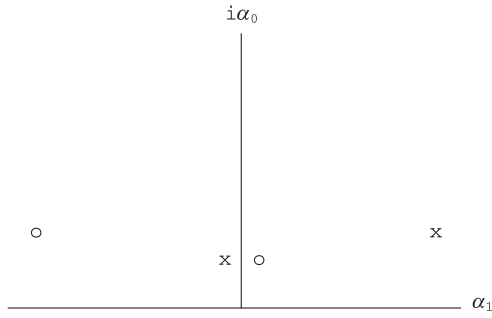$$\rightarrow \frac{-1}{\rho^2 \hat{c}'(q_n)}. \quad (14)$$

Figure 1. Schematic illustration of the pole structure of simple fluid models that contain dispersion interactions. The crosses denote poles of $\hat{h}(q)$, where $q \equiv \alpha_1 + i\alpha_0$. The circles denote $q^\# \equiv -\alpha_1 + i\alpha_0$, which are poles of $\hat{h}_e$ and $\hat{h}_o$ but not of $\hat{h}$. The illustration ignores higher-order poles contributing to short-range correlations and is for a state point that lies on the pseudo-exponential side of the pFW line, i.e. the oscillatory pole of $\hat{h}(q)$ with $\alpha_1 \approx 2\pi/\sigma$ has a larger value of α_0 than the pseudo-exponential pole lying close to the imaginary axis. If the power-law dispersion interactions are set to zero, to leave a short-ranged model, then the pair of poles $(q, q^\#)$ closest to the imaginary axis coalesce into a single pole on the imaginary axis, leaving three poles of $\hat{h}_{SR}(q)$, an even function of q—see text.

From (9), (12), (13) it follows that the even and odd residues are each precisely one half the total residue:

$$\text{Res}\{\hat{h}_e\} = \text{Res}\{\hat{h}_o\} = \tfrac{1}{2}\text{Res}\{\hat{h}\}. \qquad (15)$$

In addition, we note from the second factor in (12), that $\hat{h}_e$ and $\hat{h}_o$ both possess an additional pole at $q = q^\# \equiv -q^*$, where superscript $*$ denotes the complex conjugate—see figure 1. For this pole one can readily show that

$$\text{Res}\{\hat{h}_e\} = -\text{Res}\{\hat{h}_o\} = \frac{-1}{2\rho^2\left(\hat{c}'_e(q^\#) - \hat{c}'_o(q^\#)\right)}. \qquad (16)$$

Below we shall typically refer to residues in the form

$$R_n \equiv q_n\text{Res}\{\hat{h}\}, \qquad (17)$$

$$R_n^\# \equiv 2q_n^\#\text{Res}\{\hat{h}_e\}. \qquad (18)$$

The symmetry of the relationship between these poles leads to the result that R_n is the complex conjugate of $R_n^\#$.

We have already demonstrated numerically (within an explicit RPA calculation) in Paper I that for all fluid states there should be a pole of $\hat{h}$ lying in the top-right quadrant of the complex q plane; namely $q_{osc} \equiv \alpha_1 + i\alpha_0$ with $\alpha_1 \approx 2\pi/\sigma$, where σ is the atomic diameter which hereafter will be taken as our unit of length. This pole gives rise to exponentially damped-oscillatory decay of $rh(r)$. An important point to note is that the presence of dispersion forces (the inclusion of odd symmetry) prevents $q_{osc}^\# = -\alpha_1 + i\alpha_0$ from being a pole of $\hat{h}$. One can see this reflected in (16); i.e. for this pole the total residue $\text{Res}\{\hat{h}_e\} + \text{Res}\{\hat{h}_o\} = 0$ in complete contrast to the pole in the right quadrant which is of the class (15). We also remark in Paper I that the odd symmetry contribution prevents the existence of any pole lying precisely on the imaginary axis. Hence, a mathematical problem arises in trying to identify non-oscillatory, exponentially decaying correlations. Physically we

should expect such OZ decay to manifest itself near the critical point. Recall that for short-ranged forces, without dispersion force contributions, OZ decay of $rh(r)$ is associated with a pure imaginary pole $i\alpha_0$ and the 'true' correlation length ξ is $1/\alpha_0$ with $\alpha_0 \to 0$ on approaching the critical point. In order to gain insight into this issue, we expand $\hat{c}(q)$ in powers of q about $q = 0$, up to and including order q^3. We shall refer to this as a generalized Ornstein–Zernike (GOZ) expansion truncated beyond order q^3:

$$\hat{c}(q) = c_e^{(0)} + c_e^{(2)}q^2 + aq^3, \qquad (19)$$

where the coefficients of the even symmetry component are defined by taking successive derivatives evaluated at the origin $c_e^{(0)} = \hat{c}(0), c_e^{(2)} = \hat{c}''(0)/2$. The limiting value is linked to the $q = 0$ limit of the structure factor of the fluid $S(0) = 1/[1 - \rho\hat{c}(0)] = \rho\beta^{-1}\chi_T$ and we can define a GOZ 'second moment' correlation length ξ_2 from

$$\xi_2^2 \equiv -\rho c_e^{(2)}S(0) = R^2 S(0), \qquad (20)$$

where R is the usual persistence length. To the same order as (19) a pole of $\hat{h}(q)$ is a solution of

$$S^{-1}(0) = \rho c_e^{(2)}q_n^2 + \rho a q_n^3 + \cdots, \qquad (21)$$

or, defining $a_1 \equiv -a/c_e^{(2)}$,

$$1 = -(q_n\xi_2)^2(1 - a_1q_n + \cdots). \qquad (22)$$

Note that a_1 is a (microscopic) length. Substituting $q_n \equiv \alpha_1 + i\alpha_0$ and working only to leading-order in the real and imaginary parts, yields

$$\alpha_0\xi_2 = 1 \qquad (23)$$

$$2\alpha_1\xi_2^2 = -a_1. \qquad (24)$$

Equation (23) implies that the GOZ 'second moment' correlation length is equal to the 'true' exponential decay length $\xi = \alpha_0^{-1}$ to this order, as anticipated, but (24) requires substantial further explanation. Firstly, note that physical values of a_1 are positive, so that this pole of $\hat{h}$ lies in the *left* quadrant. Secondly, in this expansion about the mean-field critical point, α_1 is of order $\sigma\alpha_0^2$ and so this pole tends asymptotically to the imaginary axis in the approach to the critical point. For this reason we shall refer to it as the pseudo-exponential pole (q_{pexp}). Of course this pole will be present at other state points; it was not identified in Paper I. Note also that in the limit $a_1 \to 0$, where the dispersion interactions vanish, $\alpha_1 \to 0$ and we recover the pure imaginary pole.

When one attempts to use Cauchy's theorem with (7) to evaluate the contributions to $rh(r)$ from both the oscillatory and pseudo-exponential poles one appears to run into insuperable difficulties due to the asymmetrical nature of the pole distribution. Instead, the only viable option seems to be to close the contour around the upper right quadrant alone, thereby capturing the damped-oscillatory structure at

wavelengths σ or smaller, but leaving an integral along the imaginary axis (see equation (16) of Paper I):

$$I \equiv \frac{1}{2\pi^2} \text{Im} \left[\int_0^\infty d(i\alpha_0)(i\alpha_0)e^{-\alpha_0 r} \hat{h}(i\alpha_0) \right] \tag{25}$$

$$= \frac{1}{2\pi^2} \int_0^\infty dy \, e^{-yr} iy \hat{h}_o(iy), \tag{26}$$

$$= \frac{a}{2\pi^2} \int_0^\infty dy \, y^4 \frac{e^{-yr}}{D(iy)}, \tag{27}$$

where we note that only the odd contribution $\hat{h}_o$ contributes and that hereafter we have specialized to the RPA where $\hat{c}_o(q) = aq^3$, see section 1. This class of integral is well-behaved because of the exponential cut-off at large y and is often evaluated by successive integration by parts, equivalent to expanding $1/D$ as a Taylor series in y from the origin. The leading-order contribution follows trivially from noting that $1/D(0) = S^2(0)$ and the next few terms are readily obtained from the Taylor series [6]:

$$\frac{2\pi^2}{a} I_{\text{plaw}} = \frac{I_5 S^2(0)}{r^5} - \frac{I_7 S^3(0)\rho \hat{c}_e''(0)}{r^7}$$

$$+ \frac{I_9}{r^9} \left[\frac{S^3(0)\rho \hat{c}_e''''(0)}{12} + \frac{3S^4(0)\rho^2 \left(\hat{c}_e''(0)\right)^2}{4} \right] + \cdots \tag{28}$$

where subscript plaw denotes power-law and $I_n = (n-1)!$. In Paper I we argued that combining the first (slowest) term in this series with the damped-oscillatory contribution from the pole at q_{osc} should constitute a good approximation for $rh(r)$. However, from the present analysis it is immediately apparent that this power-series expansion fails to capture the contribution to I arising from the presence nearby of the q_{pexp} pole. In fact, the integrand of (27) is proportional to $\hat{h}_o$ and hence, as discussed previously, is equally affected by the $q_{\text{pexp}}^{\#}$ pole in the right quadrant. Our conjecture, which is tested numerically in section 3, is that the integral I must also yield a non-oscillatory exponentially decaying correlation that can be accurately defined by expanding the denominator of the integrand of (27) about q_{pexp} and $q_{\text{pexp}}^{\#}$. From the geometry illustrated in figure 1, this alternative expansion is given by

$$D(iy) = (iy - q_{\text{pexp}})(iy - q_{\text{pexp}}^{\#})\rho^2 \left(\hat{c}_e' + \hat{c}_o'\right)_{q_{\text{pexp}}}$$

$$\times \left(\hat{c}_e' - \hat{c}_o'\right)_{q_{\text{pexp}}^{\#}} + \cdots. \tag{29}$$

Thus, to leading-order, we can write

$$\frac{1}{D(iy)} = \frac{\rho^2}{\alpha_0^2 + \alpha_1^2} \left[\frac{R_{\text{pexp}} R_{\text{pexp}}^{\#}}{(y - \alpha_0)^2 + \alpha_1^2} \right], \tag{30}$$

where α_0 and α_1 refer to the pseudo-exponential pole of $\hat{h}$. This yields an approximate expression for I proportional to the product of two residues (or equivalently the pseudo-exponential pole residue times its complex conjugate):

$$\frac{2\pi^2}{a} I_{\text{pexp}} = \rho^2 |\text{Res}\{\hat{h}\}|^2 e^{-\alpha_0 r} \int_0^\infty dy \, y^4 \frac{e^{-(y-\alpha_0)r}}{(y - \alpha_0)^2 + \alpha_1^2}. \tag{31}$$

Provided the integrand is relatively sharply peaked about $y = \alpha_0$ this will yield a non-oscillatory exponential contribution.

Thus we arrive at what one might define as a pseudo-Fisher–Widom (pFW) line, i.e. the line in phase space in which the imaginary part of q_{pexp} is equal to the imaginary part of q_{osc}. On the side of the pFW line closest to the liquid–vapour critical point the non-oscillatory exponential contribution, with inverse decay length α_0 given by the imaginary part of q_{pexp}, is longer ranged than the usual damped-oscillatory correlations associated with q_{osc} and wavelength $\approx \sigma$. We have yet again introduced the caveat 'pseudo', this time to remind readers that the true asymptotic correlations are power-law and these will often hide the physics associated with the pseudo-exponential poles, particularly on the other (high density) side of the pFW line where the non-oscillatory exponential decay of $rh(r)$ is sub-dominant at all values of r.

The conjecture that we shall test numerically below is that whenever one is on the non-oscillatory side of the pFW line, a good approximation to the medium-range and long-range correlations will be to simply add the leading-order contributions from all three different classes of physics, i.e. we investigate the accuracy of the approximation

$$rh(r) = \frac{1}{\pi} \text{Im} \left[iR_{\text{osc}} e^{iq_{\text{osc}} r} \right] + I_{\text{pexp}} + I_{\text{plaw}}, \tag{32}$$

where R_{osc} is the residue of the oscillatory pole. On the other side of the pFW line one can neglect I_{pexp}. Note that in this approach it is not appropriate to continue the expansions for I_{pexp} and I_{plaw} beyond leading-order, since the simple sum in (32) requires a good separation between the parts of the integrand that are estimated by the respective expansions. In this regard, it is instructive to also apply the expansion about the mean-field critical point introduced earlier, this time to estimate I_{pexp}. One readily finds from (29) that

$$D(i\alpha_0) \rightarrow 4\alpha_1^2 \alpha_0^2 \left(\rho c_e^{(2)}\right)^2 = 4D(0)\alpha_1^2 \xi^2, \tag{33}$$

which evaluates (30). One can then ask for an estimate of the integral (27) in terms of a pure exponential, from the part of the integrand captured by I_{pexp},[3]:

$$\int_0^\infty dy \, y^4 \frac{e^{-yr}}{D(iy)} \approx \frac{\pi |\alpha_1| \alpha_0^4 e^{-\alpha_0 r}}{D(i\alpha_0)}. \tag{34}$$

The resulting cross-over interpolation to the integral I throughout the GOZ region of the mean-field critical point is

$$I \approx \frac{aS^2(0)}{2\pi^2} \left[\frac{I_5}{r^5} + \frac{\pi}{2a_1} \frac{e^{-r/\xi}}{\xi^4} \right]. \tag{35}$$

Note that the second term in equation (35) does not depend on the coefficient a. Indeed this term reduces to $\exp(-r/\xi)/(4\pi\rho R^2)$, the standard OZ result for $rh(r)$, as one would expect in the limit $a \rightarrow 0$.

The above arguments have assumed a simple fluid model where correlations are captured at least qualitatively by the RPA. Namely, there are never more than two poles of $\hat{h}(q)$ lying close to the real axis and these poles lie in different quadrants of the upper-half complex wavenumber

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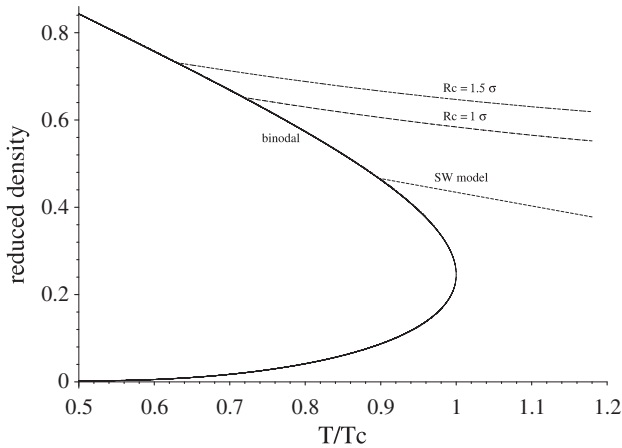[3] Note that $\int_{-\infty}^\infty dx \frac{\alpha_1^2}{x^2 + \alpha_1^2} = \pi|\alpha_1|$.

Figure 2. The pseudo-Fisher–Widom line in the proximity to liquid–vapour coexistence, calculated from the RPA. The full line denotes the binodal (coexistence curve) which, in the RPA, obeys corresponding states. The dashed lines labelled with values of R_c show the pFW lines of our present model (3)–(5). For state points below a given pFW line damped-oscillatory decay is sub-dominant to *both* monotonic-exponential and power-law decay. The dashed line labelled SW model is the FW line of the standard square-well model (with $R_c = 1.5\sigma$), calculated from the RPA. We note that the latter has the same unscaled critical temperature as for $R_c \approx 1.2\sigma$ in the present model, so that pFW lines do not display corresponding states (even approximately).
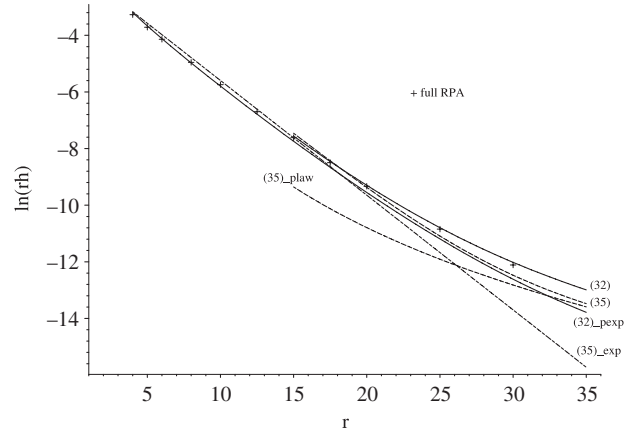

Figure 3. Numerical results for the total correlation function $h(r)$ calculated from the RPA, compared with liquid-state asymptotics developed in section 2. Symbols denote (numerically) 'exact' results from the RPA of our model (3)–(5) at $R_c = 1.5\sigma$, for the state point on the critical isochore at $T/T_c = 1.1$ corresponding to $S(0) = 4.01$. The upper full line labelled (32) is the result of equation (32), which includes the leading-order power-law contribution I_{plaw}. The lower full line labelled (32)_pexp is the contribution I_{pexp} alone. Note that for this state point the oscillatory pole q_{osc} makes a negligible contribution over the entire range plotted, $r > 4\sigma$. The dashed curve labelled (35) shows the result of the cross-over interpolation formula (35), combining the monotonically decaying exponential approximation, the straight dashed line (35)_exp, and the leading-order power-law approximation (35)_plaw. Note that results are plotted as a function of r/σ, the reduced separation.

plane. All other poles are much further from the real axis. The longest-range correlations are the power-law terms contained in the integral I through a power-series expansion about the origin, while an expansion about q_{pexp} and $q^{\#}_{\text{pexp}}$ is needed to capture medium-range, non-oscillatory, exponentially decaying correlations. The cross-over in the decay lengths of the oscillatory and pseudo-exponential pole contributions defines a pseudo-FW line. These conjectures imply that the physics of a model with dispersion forces is similar to that of a model where the interatomic forces are strictly short ranged, despite the dramatically more complex mathematics required to describe it. In particular, the imaginary part of the pseudo-exponential pole continues to play the role of an inverse bulk correlation length well beyond the strict critical region (not correctly captured by the RPA). In the next two sections we shall demonstrate numerically the validity of these conjectures for the model fluid introduced in Paper I. This model and the RPA that we employ are described in section 1. In the final section we present a general overview of mean-field correlations in simple fluids, including their relevance to wetting phenomena and colloidal physics.

3. Results of calculations of pair correlation functions and cross-over

Figure 2 shows results of calculations of the pFW line and the liquid–vapour coexistence curve (binodal), from the RPA treatment of the model fluid defined by (3)–(5) for different values of R_c. In this plot, all states below a given pFW line are associated with asymptotic

decay for which damped-oscillatory exponential decay is sub-dominant to *both* monotonic-exponential and power-law contributions. It is straightforward to show that within the RPA the reduced critical density $\rho_c\sigma^3 = 0.245\,7358$ is independent of the choice of $\phi_{\text{att}}(r)$ and, for a given choice of $c_{\text{hs}}(r)$, the binodal obeys corresponding states exactly. In contrast, figure 2 implies that the pFW line does not obey even an approximate corresponding states. Rather, the presence of dispersion interactions favours the dominance of monotonic-exponential decay over damped-oscillatory correlations and when combined with increasing R_c, the range of an intermediate attractive square-well, the pFW line shifts to higher densities. The results presented in the remainder of this section are restricted to the choice $R_c = 1.5\sigma$; in particular, we reconsider figure 5 of Paper I which used this same choice to compare the full RPA solution to results of asymptotic theory but omitting the monotonic-exponential term I_{pexp} introduced in the previous section. First it is instructive to choose a state point on the critical isochore that is sufficiently close to the RPA critical point to enable an unambiguous test of the validity of the asymptotic analysis leading to (32) and (35).

Figure 3 shows numerical results for the logarithm of $rh(r)$ at reduced temperature $T/T_c = 1.1$ on the critical isochore ρ_c. The oscillatory pole makes no observable contribution over the entire range of the plot. Thus, here we are testing our ability to separate power-law correlations from monotonic-exponential decay. The symbols plotted are

full numerical solutions of the RPA[4], while the various curves display the results of the asymptotic theory developed in section 2. One point to emphasize is that numerically the power-law expansion (28) behaves as if it has zero radius of convergence about $\alpha_0 = 0$ and hence $r = \infty$. For a finite value of r one can only include a finite number of terms in this expansion before it breaks down. Moreover, if the expansion is restricted to leading-order there remains an unphysical region at low values of r. In figure 3 this manifests itself by an increasing upturn in the dashed curve labelled (35)_plaw as r is reduced below 15σ and the more terms from (28) that one includes the sooner this unphysical region is reached. In contrast, the term I_{pexp} in (32) is best suited to this intermediate range; see the solid curve labelled (32)_pexp. In the region where the leading-order power-law contribution is not unphysical ($r > 15\sigma$ in figure 3), we see that ansatz (32) that adds the two contributions is a remarkably good approximation—see solid curve labelled (32). The small discrepancy is due presumably to double-counting involved in combining an expansion about the origin of the complex plane with an expansion about the pair of pseudo-exponential poles[5]. This approach will fail if the domains of these expansions overlap significantly. Accordingly, for $r > 30\sigma$ in figure 3 it is more appropriate to replace the expansion about the pseudo-exponential poles with additional terms from the power-law expansion (28) and the larger the value of r the more terms one can use before the convergence breaks down. The dashed lines in figure 3 display the result of the cross-over interpolation formula (35) combining the leading-order power-law contribution and the exponential decay (the straight dashed line); we shall return to this formula in section 4 below.

Having confirmed and elucidated the validity of our asymptotic theory for the simultaneous presence of power-law and monotonic-exponential contributions, we return to figure 5 of Paper I. This figure chose to contrast two state points at $T/T_c = 1.18$: (a) $\rho^* = 0.8$ and (b) $\rho^* = 0.45$. From figure 2 one notes that these states lie almost equidistant on opposite sides of the pFW line for $R_c = 1.5\sigma$. Accordingly, for case (a) we do not expect any significant contribution from the pseudo-exponential pole in (32). As mentioned in the Introduction this was indeed confirmed in Paper I where the sum of the first
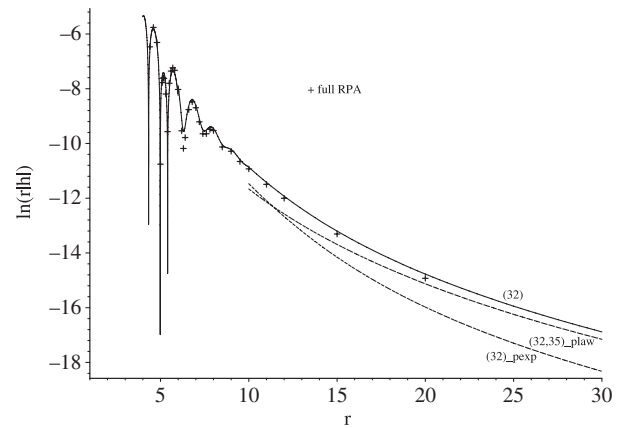
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[4] $\hat{c}(q)$ is given explicitly in section 3.2 of paper I the formally infinite sum in the expression (36) of paper I being restricted to the first 200 terms. The OZ equation (8) can be then be inserted into (6) to give $rh(r)$ by direct numerical evaluation, provided one introduces a smooth cut-off at an appropriate value of q beyond the region of physical relevance to the required range of r. We found it convenient to divide the integral into blocks and expand the integrand of each block as a series of at least 100 polynomials, prior to integration. The entire numerical procedure was tested for stability and lack of sensitivity to the parameters adopted, as well as a direct comparison with the previously published results in figure 5(b) of Paper I that had been obtained with a different method now obsolete with the passage of time.

[5] In fact, one can correct for this analytically in the GOZ limit of the RPA. Since $\alpha_1^2 \ll \alpha_0^2$ the limit $y \to 0$ of (30) is very close to $\alpha_1^2/[\alpha_0^2 D(i\alpha_0)]$, which in the GOZ limit (33) becomes $1/4D(0)$. Thus the expansion (29) about the pseudo-exponential poles generates almost precisely 1/4 of the expansion about the origin. To correct for this over-counting one only need replace the final term in (32) by $(3/4)I_{\text{plaw}}$. This improved approximation is almost indistinguishable from the full RPA results plotted in figure 3. The power-law term remains unphysical at smallest r and now there is a hint that additional power-law terms might be relevant at largest r, but in the intermediate regime the improved version of (32) is essentially exact.

Figure 4. Numerical results for the total correlation function $h(r)$ calculated from the RPA, compared with liquid-state asymptotics developed in section 2. Symbols denote (numerically) 'exact' results from the RPA of our model (3)–(5) at $R_c = 1.5\sigma$, for the state point belonging to figure 5(b) of paper I: $T/T_c = 1.18$ at a reduced density $\rho* = 0.45$, corresponding to $S(0) = 0.476$. The full line is calculated from equation (32); for $r < 6\sigma$ the power-law term is excluded since in this range the expansion about the pseudo-exponential poles provides a very accurate estimate of the integral I in (27). The two dashed curves show the individual contributions to (32), i.e. the leading-order power-law (32, 35)_plaw and the term I_{pexp} labelled (32)_pexp; for this state point the oscillatory pole makes a negligible contribution over the range $r > 10\sigma$. Note that results are plotted as a function of r/σ, the reduced separation.

and third terms provided an excellent fit. There is a simple cross-over at around $r = 25\sigma$ between damped-oscillatory decay and the leading-order power-law decay. However, for the lower density the monotonic-exponential correlations, given by I_{pexp} and now lying intermediate between damped-oscillatory and power-law decay, that were omitted in Paper I should be important. In figure 4 this expectation is confirmed. For $r < 6\sigma$ the leading-order power-law contribution is unphysical and is excluded, while the sum of the leading-order damped-oscillatory and pseudo-exponential contributions is extremely accurate. For $r > 6\sigma$ the full curve in figure 4 shows the result of (32) and we note that with I_{pexp} included there is no longer an intermediate region where the asymptotic formula breaks down. One should compare the quality of the fit to the full numerical RPA results in figure 4 with that given in figure 5(b) of Paper I; the former is much superior. We do observe some small discrepancy presumably due to our combining two expansions, which gets progressively worse at larger r such that when $r > 15\sigma$ it is more appropriate to replace the expansion about the pseudo-exponential poles with more terms in the expansion (28) about $q = 0$. Although it would be possible to adjust, as a function of r, the number of power-law terms used to fit the intermediate region $6\sigma < r < 15\sigma$, we conclude from the structure of the integrand of (27) that such a procedure is unphysical and that we have truly identified a monotonic-exponential decay in this region. Of course, the closer one gets to the pFW line the less easy it is to identify this type of decay, because of the increasing encroachment of the damped-oscillatory behaviour indicative of a dense liquid state.
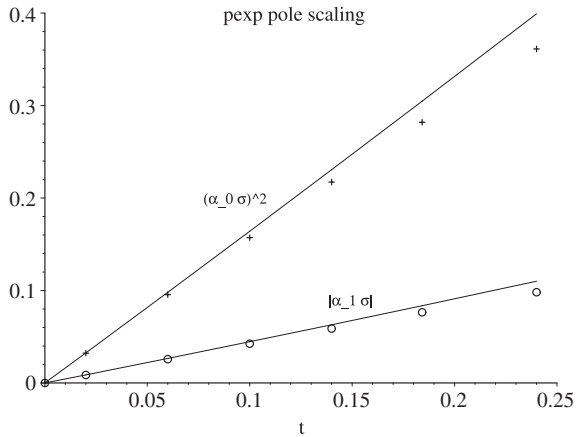
Figure 5. Scaling properties of the pseudo-exponential pole in the approach (along the critical isochore) to the critical point calculated for our model (3)–(5) at $R_c = 1.5\sigma$. The symbol O denotes $|\alpha_1\sigma|$, the modulus of the real part, and symbol + denotes $\alpha_0^2\sigma^2$, the square of the imaginary part, calculated numerically from the RPA, while the curves are the GOZ predictions defined by (20), (23), (24). The near linear behaviour of α_0^2 is appropriate to the mean-field divergence of the correlation length $\xi = 1/\alpha_0$. $t \equiv T/T_c - 1$.

4. Results of mean-field calculations of pair correlations in the approach to the critical point

In the approach to the mean-field (MF) critical point the correlation length $\xi = \alpha_0^{-1}$, describing the monotonic-exponential decay and the amplitude of the power-law dispersion contribution $\sim S^2(0)$, diverge while the damped-oscillatory decay remains short ranged and hence increasingly irrelevant for the asymptotics. The points plotted in figure 5 trace the behaviour of the real and imaginary parts of the pseudo-exponential pole in the approach to the RPA critical point, along the critical isochore calculated for $R_c = 1.5\sigma$. The curves show the associated GOZ predictions. As is appropriate to MF, we expect $\xi \sim t^{-1/2}$ and therefore $\alpha_0^2 \sim t$, for $t \equiv T/T_c - 1 \to 0$ and this is indeed observed. The GOZ prediction (20), (23) for α_0^2 is obeyed for $t \leqslant 0.06$ implying that the 'true' correlation length ξ and the GOZ 'second moment' correlation length ξ_2 are almost the same in this region. As $t \to 0$ the two correlation lengths become identical. The plot of the real part of the pole α_1 shows that the other GOZ prediction $|\alpha_1| \sim \alpha_0^2$ from (20), (24) is also valid over an extended region from the critical point. Our calculations therefore indicate that the pseudo-exponential pole approaches asymptotically close to the imaginary axis as $t \to 0$ and therefore the decay of $rh(r)$ becomes that of a pure exponential, i.e. OZ decay is recovered.

The competition between the exponential decay and the power-law decay of correlations is described by the cross-over interpolation formula (35). In figure 3 we plot the ingredients of this cross-over behaviour for the state point at $T/T_c = 1.1$ on the critical isochore. The straight dashed line labelled (35)_exp provides a compromise straight-line fit in the range over which the pseudo-exponential poles dominate, while the leading-order power-law labelled (32, 35)_plaw tends only slowly to the asymptotic form. In between, we see

that (35) describes a cross-over interpolation, rather than a good fit to the full RPA results. Note that (35) contains the same unphysical power-law correlations at $r < 15\sigma$, as discussed previously. Only at larger values of r can one use the cross-over interpolation to determine a rough boundary to the exponential decay, beyond which the power-law dominates. This boundary at r^* is therefore defined by requiring the two terms in (35) to be equal at r^*:

$$\frac{I_5}{r^{*5}} = \frac{\pi}{2a_1}\frac{e^{-r^*/\xi}}{\xi^4}. \quad (36)$$

Defining $x \equiv r^*/\xi$ and $A \equiv \pi\xi/48a_1$ (36) reduces to solving the equation

$$x - 5\ln x = \ln A. \quad (37)$$

If the right-hand side is greater than $5 - 5\ln 5$ then this equation has two solutions, of which only the larger value is physical. From figure 5 we note that a_1 is approximately $\sigma/2$ and so there will be a cross-over for all $\alpha_0\sigma < 2.75$ i.e. $\xi > 0.36\sigma$, which more than encompasses the entire length of the saturated liquid curve below the pFW line in figure 2. Thus, below the pFW line it is only for very dilute gas states with very short correlation lengths that there will be no solution to equation (37) and hence no intermediate-range monotonic-exponential decay.

In close proximity to the critical point the above analysis reproduces the result obtained by Dantchev for the mean-spherical model [10] mentioned in section 1. As ξ diverges the cross-over moves to infinity, such that exactly at the critical point the dispersion interactions are totally irrelevant. More specifically, as $\xi \to \infty$ we find from (37) that the cross-over separation

$$r^* = \xi(\ln(\xi/\sigma) + 5\ln\ln(\xi/\sigma) + \cdots), \quad (38)$$

which agrees with equation (3.14) of [10] pertaining to dispersion interactions in $d = 3$. Let us also emphasize that because of the very weak divergence of the logarithm, there is a relatively restricted range $\xi < r < \xi\ln(\xi/\sigma)$ over which the monotonic-exponential decay is dominant.

5. Discussion

This paper has focused on understanding the nature of the decay, at intermediate and longest range, of the pair total-correlation-function $h(r)$ in model fluids that exhibit dispersion interactions. We have identified a pseudo-exponential pole of $\hat{h}(q)$ that was not identified in the analysis carried out in Paper I.

The presence of this complex pole, which lies close to but not on the imaginary axis, is key to understanding OZ decay of correlations in this class of fluids and therefore plays an important role in determining $h(r)$ for states approaching the critical region. The analysis of section 4, based on the RPA treatment, elucidates the cross-over from OZ decay to power-law behaviour (2) at mean-field level. The resulting cross-over formula (35) is equivalent to that derived by Dantchev [10] in an explicit calculation for the mean-spherical model. Both

analyses omit critical fluctuation effects. Dantchev discusses how his analysis might be modified for models where the critical exponent $\eta \neq 0$. He concludes that the cross-over separation r^* should be given, at lowest order, by $r^* = (p-2+\eta)\xi \ln(\xi/\sigma)$ in agreement with the earlier conjecture of Kayser and Raveché [9]. Thus for dispersion forces in $d = 3$ where $p = 3$ and $\eta \approx 0.02$ there is little change in the estimate of r^*. Although our present analysis cannot capture the subtleties of true critical phenomena, we believe that it provides new insight into the genesis of OZ behaviour and cross-over to power-law decay of $h(r)$ for finite values of the correlation length ξ.

As stated in section 1, in Paper I we paid most attention to a high density state $\rho^* = 0.8$, $T = 1.18T_c$ which we now know is well above the pFW line (see figure 2) so that the pseudo-exponential pole is of no significance. Nevertheless, it is important to put the record straight by pointing out the shortcomings of the approximations introduced in Paper I. The weakness lies in the evaluation of the integral (25) along the imaginary axis. In Paper I only the power-law contribution I_{plaw} (28) was considered since no pseudo-exponential pole was identified. It follows that equation (23) in Paper I omits any contribution arising from the pseudo-exponential pole of $\hat{h}(q)$ close to the imaginary axis; recall that this pole lies in the left quadrant whereas the sum in equation (23) of Paper I is over poles in the right quadrant only. The statement below equation (23) of Paper I is incorrect. Hoyle [17] points this out and indicates there could be additional exponentially decaying terms. However, he does not identify the pseudo-exponential pole.

What is the relevance of our analysis for real (atomic) fluids? Considerable effort has been expended on extracting a q^3 term in the expansion of $\hat{c}(q)$ from measurements of the structure factor of rare gas fluids. Much of this work was stimulated by the influential paper of Reatto and Tau [18] who investigated the effects of including an Axilrod–Teller three-body contribution in the interatomic potential function. They find that the coefficient of the q^3 term acquires an additional contribution proportional to $\beta\nu\rho$, where ν is the amplitude of the Axilrod–Teller potential. Subsequent experimental work finds strong evidence for a q^3 term in $\hat{c}(q)$. Benmore *et al* [19] performed careful small-angle neutron diffraction measurements, at fixed (room) temperature, of the static structure factor of Kr at low (gaseous) densities in order to determine $\hat{c}(q)$ at small q. From least squares fits of their data to a cubic polynomial (see (19)) they demonstrated that the coefficient a_6 of the $-r^{-6}$ term in the pair potential could be extracted and, by considering the density dependence, an estimate of ν could be obtained. Bonetti *et al* [20] performed small-angle neutron scattering experiments on Kr, but now for states in the vicinity of the critical point. These experiments also confirm the existence of the q^3 term but could not deduce the amplitude ν of the Axilrod–Teller potential. Experimental neutron diffraction data at low q on *liquid* Kr is well-fitted by accurate liquid-state theories, such as the modified-hypernetted-chain and hierarchical-reference-theory, applied to the Aziz–Slaman pair potential augmented by the Axilrod–Teller three-body potential [21, 22]. Reatto and Tau [18] also considered the effects of retardation; for sufficiently large

separations the leading-order $-r^{-6}$ decay of the pair potential $\phi(r)$ crosses over to $-r^{-7}$ decay. The authors point out that such behaviour demands that a $q^4 \ln q$ term replaces the q^3 term in the limit of $q \to 0$. Clearly this complicates the analysis. However, Reatto and Tau estimate that retardation effects should only become significant for $q \leqslant 0.5$ nm^{-1}; q^3 behaviour should be observable in the range $1 < q < 4$ nm^{-1}, which is well within the range accessible to neutron experiments. Our present analysis details the consequences of having a q^3 term in $\hat{c}(q)$ for the decay in real space of the pair correlation function $h(r)$. Of course, with sufficiently accurate experimental data one could Fourier transform the measured structure factor and obtain $h(r)$ directly and in principle one could test the theories described here. In practice, it remains a challenging task to obtain a sufficiently accurate pair correlation function at intermediate and long range to observe the ultimate power-law decay.

For colloidal systems it is possible to measure $h(r)$ directly in real space by tracking particle coordinates using confocal laser scanning microscopy. Current experiments, with three-dimensional images, provide accurate data out to about 7 oscillations in $h(r)$, see e.g. [23] for data from colloid–polymer mixtures, but larger separations pose severe challenges.

Our results have significant repercussions for the physics of interfacial phenomena. Indeed, much of the theoretical foundation of colloid and interface science was based on the quantum mechanical prediction of power-law (dispersion or London [24]) forces [25]. On the other hand, the earlier ground-breaking paper of van der Waals [26] on the liquid–vapour interface is a density functional treatment that does not capture the complications of dispersion interactions and power-law correlations. The latter are usually a sign of fluctuations present at multiple length scales (as in fluid critical phenomena) and remarkably Casimir was able to derive the power-law nature (and the amplitude) of dispersion forces directly from relativistic quantum-field theory that assumes a 'seething' vacuum [27]. Lifshitz and co-workers were later to develop a high-temperature-field theory specifically tailored to the calculation of dispersion force contributions to the stability of interfacial (wetting) films [28]. That the physical significance of the general asymptotic theory of liquid-state physics is dramatic for wetting phenomena (for classic reviews see [29–31]) is now well-recognized [1, 13, 14]. Fluid mediated correlations between the two interfaces of a thick planar film are controlled by the same set of correlation lengths as define the asymptotic and medium-range behaviour of the radial distribution function of the wetting phase [13, 14]. Thus the equilibrium growth of thick films (adsorption) and the presence/order of wetting transitions are extremely sensitive to the details of asymptotic structure. Here we focus on adsorption from bulk gas so that correlation lengths refer to the liquid phase.

The basic physics was first recognized by the Russian School of Frumkin and Derjaguin [32] who emphasized the ultimate dominance of power-law dispersion interactions. The best known case is the transition to complete wetting from off bulk coexistence where the relevant contribution to the wetting or interface potential $V(\ell)$ can be written, for non-retarded

interactions, as $a\ell^{-2} + \delta\mu\ell\Delta\rho$, where ℓ is the film thickness, $\delta\mu$ is the deviation of the chemical potential of the bulk gas from its value at coexistence, $a > 0$ and $\Delta\rho = \rho_l - \rho_v$, the difference in densities of coexisting liquid and gas. The equilibrium film thickness $\ell_e \sim (\delta\mu)^{-1/3}$ as $\delta\mu \to 0$, a result that is confirmed for real fluids [29–31]. However, as is also well-known the existence and order of wetting transitions are controlled partly by sub-dominant correlations when the dispersion forces act to thicken the film at all thicknesses. These so-called structural contributions to the wetting potential (that enters the interface Hamiltonian) decay exponentially, with decay lengths defined by the imaginary parts of the poles of $\hat{h}(q)$ in figure 1. At leading-order the oscillatory pole $q_{\mathrm{osc}} = \alpha_1 + i\alpha_0^{\mathrm{osc}}$ with $\alpha_1 \approx 2\pi/\sigma$ leads only to an oscillatory modulation of the asymptotic decay which can safely be ignored due to strong damping of the oscillatory amplitude from the presence of capillary-wave fluctuations (in contrast, capillary-wave fluctuations in three-dimensional systems cannot renormalize a power-law decay and will typically only weakly modify a monotonic-exponential decay) [13, 14]. However, the wetting potential contains contributions proportional to the square of the density deviations, arising from interference between interfaces on each side of the adsorbed film, and so the oscillatory pole also generates a monotonic-exponential correlation with decay length $1/2\alpha_0^{\mathrm{osc}}$. The pseudo-exponential pole generates standard MF exponential correlations with decay lengths $1/\alpha_0^{\mathrm{pexp}}$ and $1/2\alpha_0^{\mathrm{pexp}}$. It is known that these correlations can all play a qualitative role in wetting transitions, depending on the relative sizes of the respective decay lengths and the sign of the amplitude with which they contribute to the wetting potential. The form of the resulting, multi-regime, wetting potential belonging to models with short-ranged interactions only has been known for some time [13] and has been confirmed directly from density functional calculations [14]. In these papers the subtlety of incorporating dispersion interactions into theories that describe properly short-and intermediate-range correlations was emphasized. One particular aspect, see section IV of [14], concerned the issue of monotonic, exponentially decaying contributions to the wetting potential $V(\ell)$. Since the pseudo-exponential pole had not been identified in Paper I, the origin of such contributions, i.e. those that constitute the 'standard' MF wetting potential used in theories of wetting transitions near the critical point for models with short-ranged interactions, was not understood when dispersion interactions were included. Note that equation (25) in [14] includes only a contribution from the oscillatory pole, along with power-law dispersion terms. Here, having now identified the pseudo-exponential pole, we can finally resolve this issue, in particular, with reference to the pFW lines in figure 2. Recall that these lines are relevant since it is the liquid phase that constitutes the adsorbed film.

If the wetting transition is between two macroscopically thick films then it will be controlled by power-law dispersion contributions to $V(\ell)$ at leading-order and beyond [31]; this is the model favoured by the Russian School. If the transition is between a microscopically thin film and a macroscopically thick film, then it is likely that exponentially decaying correlations are involved, along with the leading-order power-law decay. At high temperatures, below the pFW line in figure 2 the dominant exponential correlation has a decay length $1/\alpha_0^{\mathrm{pexp}}$. Only for saturated liquid states at low temperatures lying on the binodal above the pFW line will sub-dominant exponential correlations with decay length $1/2\alpha_0^{\mathrm{osc}}$ become relevant. The MF wetting potential relevant to essentially all liquid–vapour systems in the presence of a spectator 'wall' should therefore take the form

$$V(\ell) = a\ell^{-2} + b\ell^{-3} + c\exp(-2\alpha_0^{\mathrm{osc}}\ell) + d\exp(-\alpha_0^{\mathrm{pexp}}\ell)$$
$$+ e\exp(-2\alpha_0^{\mathrm{pexp}}\ell), \tag{39}$$

where the amplitudes c, d and e are partly renormalized by capillary-wave fluctuations. Equation (39) should be contrasted with equation (25) of [14] which omits the final two terms arising from the pseudo-exponential pole. This form assumes that the infinitely repulsive part of the potential preventing negative adsorption is described by one of the sub-dominant terms, otherwise even higher-order correlations or an explicit short-ranged wall–fluid potential would have to be included for the thin film regime. Furthermore, by analogy with the results for $rh(r)$ in figures 3 and 4, we expect the power-law contributions to $V(\ell)$ to become unphysical before the thin film limit is reached. One must also note the recent advance of Parry *et al* [33] who have developed a systematic method of generating sub-dominant terms in the interface Hamiltonian for models with short-ranged (Ising like) interactions that implies subtle non-local modifications that go beyond a simple capillary-wave renormalization of the amplitudes. Setting these various complications aside, (39) can be considered as the general wetting potential for a 'real' fluid with dispersion interactions. One could examine the validity of (39) by performing explicit MF density functional theory calculations of $V(\ell)$ following the strategy adopted for a cut and shifted Lennard-Jones fluid adsorbed at a planar substrate that exerts an external potential of finite range [14], but now employing models that include dispersion interactions. The set of decay lengths extracted from both the oscillatory and pseudo-exponential poles and the accompanying FW lines would form the basis for such an analysis. Care is required at the cross-over between different regimes, where two decay lengths are equal; in particular, if the fit to the wetting potential requires exchanging the signs of two amplitudes then they must simultaneously pass through infinity at this temperature [14, 34]. The comparison between cross-over lines in models with dispersion interactions and the square-well model, shown in figure 2, implies that the presence of dispersion interactions significantly reduces the region of the phase diagram in which the sub-dominant structural decay from the oscillatory pole, i.e. the term $c\exp(-2\alpha_0^{\mathrm{osc}}\ell)$, is important.

Acknowledgments

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References

[1] Evans R, Leote de Carvalho R J F, Henderson J R and Hoyle D C 1994 *J. Chem. Phys.* **100** 591
[2] Evans R, Henderson J R, Hoyle D C, Parry A O and Sabeur Z A 1993 *Mol. Phys.* **80** 755
[3] Martynov G A 1992 *Fundamental Theory of Liquids: Method of Distribution Functions* (Bristol: Hilger) chapter 5
[4] Dijkstra M and Evans R 2000 *J. Chem. Phys.* **112** 1449
[5] Widom B 1964 *J. Chem. Phys.* **41** 74
[6] Enderby J E, Gaskell T and March N H 1965 *Proc. Phys. Soc.* **85** 217
[7] Verlet L 1968 *Phys. Rev.* **165** 201
[8] Leote de Carvalho R J F, Evans R, Hoyle D C and Henderson J R 1994 *J. Phys.: Condens. Matter* **6** 9275
[9] Kayser R F and Raveché H J 1984 *Phys. Rev.* A **29** 1013
[10] Dantchev D 2001 *Eur. Phys. J.* B **23** 211
[11] Dantchev D, Krech M and Dietrich S 2003 *Phys. Rev.* E **67** 066120
[12] Martynov G A 2008 *Theor. Math. Phys.* **156** 1356
[13] Henderson J R 1994 *Phys. Rev.* E **50** 4836
[14] Henderson J R 2005 *Phys. Rev.* E **72** 051602
[15] Matthai C C and March N H 1982 *Phys. Chem. Liq.* **11** 207
[16] Fisher M E and Widom B 1969 *J. Chem. Phys.* **50** 3756
[17] Hoyle D C 1996 *PhD Thesis* University of Bristol (unpublished)
[18] Reatto L and Tau M 1992 *J. Phys.: Condens. Matter* **4** 1
[19] Benmore C J, Formisano F, Magli R, Bafile U, Verkerk P, Egelstaff P A and Barocchi F 1999 *J. Phys.: Condens.*
Matter **11** 3091 These authors also provide a comprehensive summary of earlier experiments and analyses
[20] Bonetti M, Calmettes P and Bervillier C 2003 *J. Chem. Phys.* **119** 8542
[21] Barocchi F, Chieux P, Magli R, Reatto L and Tau M 1993 *J. Phys.: Condens. Matter* **5** 4299
[22] Guarini E, Magli R, Tau M, Barocchi F, Casanova G and Reatto L 2001 *Phys. Rev.* E **63** 052201
[23] Royall C P, Louis A A and Tanaka H 2007 *J. Chem. Phys.* **127** 044507
[24] London F 1937 *Trans. Faraday Soc.* **33** 8b
[25] Churaev N V 2003 *Adv. Colloid Interface Sci.* **104** xv (see the introduction to this issue that is devoted to B V Derjaguin and references therein)
[26] van der Waals J D 1893 *Verh. K. Akad. Wet.* 1 **1** 8
Rowlinson J S 1979 *J. Stat. Phys.* **20** 197 (Engl. Transl.)
[27] Casimir H B G 1948 *Proc. K. Ned. Akad. Wet.* 51 793
Maclay G J, Fearn H and Milonni P W 2001 *Eur. J. Phys.* **22** 463 review
[28] Dzyaloshinskii I E, Lifshitz E M and Pitaevskii L P 1960 *Sov. Phys.—JETP* **37** 161
[29] Dzyaloshinskii I E, Lifshitz E M and Pitaevskii L P 1961 *Adv. Phys.* **10** 165
[30] Sullivan D E and Telo da Gama M M 1986 *Fluid Interfacial Phenomena* ed C A Croxton (Chichester: Wiley) chapter 2
[31] Dietrich S 1988 *Phase Transitions and Critical Phenomena* vol 12, ed C Domb and J Lebowitz (London: Academic)
[32] Frumkin A 1938 *Zh. Fiz. Khim.* **12** 337
Frumkin A 1938 *Acta Physicochim. URSS* **9** 313 (German Transl.)
Roth R 2005 private communication. (Engl. Transl.)
[33] Parry A O, Romero-Enrique J M, Bernardino N R and Rascón C 2008 *J. Phys.: Condens. Matter* **20** 505102
[34] Aukrust T and Hauge E H 1987 *Physica* A **141** 427