The Goldstone Mode and Resonances in the Fluid Interfacial Region

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The development of a molecular theory of inhomogeneous fluids and, in particular, of the liquid-gas interface has received enormous interest in recent years; however, long standing attempts to extend the concept of the surface tension in mesoscopic approaches by making it scale dependent, while apparently plausible, have failed to connect with simulation and experimental studies of of the interface which probe the detailed properties of density correlations. Here, we show that a fully microscopic theory of correlations in the interfacial region can be developed which overcomes many problems associated with simpler mesoscopic ideas. This theory originates from recognizing that the correlation function displays, in addition to a Goldstone mode, an unexpected hierarchy of resonances which constrain severely its structural properties. Indeed, this approach allows us to identify new classes of fully integrable models for which , quite surprisingly, the tension, density profile and correlation function function can all be determined analytically, revealing the microscopic structure of correlations in all generalised van der Waals theories.

Interfaces, for example between liquids and gases or between solids and liquids, are ubiquitous in nature playing crucial roles across all of biology and in modern technologies from oil recovery to micro-fluidics. The key ingredient in our understanding of them is the nature of the surface tension; the macroscopic energy cost of separating coexisting fluid phases. Indeed, at large scales the interface behaves like a taut drum-skin with the surface tension acting always to minimize the exposed surface area. However, it has also long been recognized that the surface tension provides insight into the microscopic world since it arises directly from the imbalance between the attractive intermolecular forces either side of the interface. It was van der Waals who first developed a microscopic theory which not only predicted the coexistence of liquid and gas phases but also the structure of the interface separating them, specifically that the change from a high density liquid to a low density gas does not occur abruptly but smoothly over a molecular scale. The modern statistical mechanical theory of interfaces is based on a marriage between these large scale and microscopic approaches. However, this union has not always been easy and has been the subject of many controversies.

Consider an interface situated near the $z = 0$ plane separating coexisting bulk liquid and gas phases below a critical temperature T_c. Three microscopic quantities of particular importance are $\rho(z)$, the equilibrium density profile, $G(z, z'; q)$, the 2D Fourier transform of the density-density pair correlation function in the direction *along* the interface and its integral $S(z; q) = \int dz' \, G(z, z'; q)$, which defines the local structure factor. Integrals of $G(z, z'; q)$ are directly related to the intensity measured in scattering studies, while $S(z; q)$ is of thermodynamic importance since, at $q = 0$, it is equal to the local compressibility (the derivative of the local density w.r.t chemical potential). A key insight in the modern statistical mechanical theory is that, if the interface is not subject to external forces, the density-density correlation function must contain a Goldstone mode (GM) in the long-wavelength limit, since the interface can be translated without cost of energy [1–3]. Thus, at small wave-vectors (well below the scale of the inverse bulk correlation length), it is well established from exact sum-rules that the correlation function (and hence $S(z; q)$) diverges as $G(z, z'; q) \approx \rho'(z)\rho'(z')/\beta\sigma q^2$, with $\beta = 1/k_B T$ (which we hereafter set to unity), $\rho'(z)$ is the derivative of the density profile and σ is the surface tension. We refer to this divergence as the Wertheim-Weeks GM [2, 3]. At these long wavelengths, there is a happy marriage with the picture of the interface as a taut drum-skin. This is explicit in the mesoscopic capillary-wave description of the interface, which models it as a position dependent height $h(\mathbf{x})$ with an energy cost $H[h] = \frac{\sigma}{2} \int d\mathbf{x} \, (\nabla h)^2$, i.e. surface tension times area [4]. Equipartition immediately implies that the Fourier transform of the height-height correlation function behaves as $1/\sigma q^2$. This not only tallies perfectly with the Wertheim-Weeks GM, but has the profound consequence that the width of the interface is broadened due to its thermal fluctuations[4], a feature that has been visualized directly in colloid-polymer mixtures [5].

What happens beyond the GM (i.e. at higher wave-vectors) has received a great deal of attention in recent decades [6–20]. One popular approach borrows ideas from the theory of membranes [21] and extends the capillary-wave model by including a higher-order term, $\frac{K}{2} \int d\mathbf{x} \, (\nabla^2 h)^2$, arising from the curvature of the interface, where K is a rigidity. Clearly, this alters the expression for the height-height correlation function to $1/(\sigma q^2 + K q^4)$. With a positive rigidity, this approach has the advantage of eliminating the need to impose an explicit cut-off, and was hoped to be a short-cut to determining the properties of $G(z, z'; q)$ and $S(z; q)$ [6]. This plausible approach is, however, plagued with problems. Long-ranged dispersion forces introduce non-analytic contributions [7, 10], implying that K is not well defined. For systems with short-ranged forces, commonly used in simulation studies, attempts to identify K have also

run into numerous difficulties. For example, unlike the surface tension σ, the value of K is unsatisfactorily sensitive to how the interface height $h(\mathbf{x})$ (i.e. the local separation of liquid and gas) is defined microscopically. Moreover, simple definitions, as those used in density functional theories (DFT) of wetting, fail because they lead to unphysical negative values for K [8, 14]. In addition, it is now apparent that, even with a positive rigidity K, this approach is not a short-cut to the determination of the underlying microscopic observables $G(z,z';q)$ and $S(z;q)$. In fact, the very opposite is true: One needs to know $G(z,z';q)$ in order to define a rigidity, if we wish to extend capillary-wave theory [20]. In this paper, we shall show in fact that both $G(z,z';q)$ and $S(z;q)$ contain information occurring at higher wave-vectors which cannot possibly be encapsulated using a rigidity, and which does not rely on the definition of an interface position $h(\mathbf{x})$.

I. EXISTENCE OF RESONANCES

Let us first try to identify the properties of $S(z;q)$ at higher wave-vectors using general principles. We specialize to systems with short-ranged intermolecular forces (e.g. finite-range or exponentially decaying) and specify the bulk properties first. Far from the interface, the density and structure factor take their bulk liquid ($b=l$) or gas ($b=g$) values ρ_b and $S_b(q)$ respectively. The bulk structure factor is the 3D Fourier transform of the density-density correlation function, which we assume decays monotonically in the liquid as well as gas phase in standard Ornstein-Zernike fashion, $G_b(r) \sim e^{-\kappa r}/r$ [22]. Here, κ is the inverse of the appropriate bulk liquid or gas correlation length ξ, identified formally from the condition $C_b(i\kappa)=0$, where $C_b(q)=1/S_b(q)$ is the 3D Fourier transform of the bulk direct correlation function. The bulk correlation length also determines the asymptotic exponential decay of the density profile; e.g., on the liquid side $\rho(z)-\rho_l \sim e^{-\kappa z}$, where in general the correction terms are simply higher powers of $X=e^{-\kappa z}$. We do not need to specify the details of the broadening of the interface, which would appear in the coefficients of the expansion, since this has no influence on the location of the resonances. Within DFT, the local structure factor can be determined from solution of [23, 24]

$$\int dz'\; C(z,z';q)\; S(z';q) \;=\; 1 \tag{1}$$

which is the integral of the usual Ornstein-Zernike equation for $G(z,z';q)$. Here, $C(z,z';q)$ is the 2D Fourier transform of the direct correlation function of the inhomogeneous fluid, which is determined as the second functional derivative of the intrinsic Helmholtz Free-energy functional.

In an earlier paper [18], we show how the asymptotic decay of $S(z;q)$ each side of the interface ($|z|\to\infty$ at fixed q) can be determined exactly, ignoring minor three-body contributions, as

$$S(z;q) = S_b(q) + \frac{\Delta\rho\,\rho'(z)}{q^2\,\sigma_b(q)} + \cdots \tag{2}$$

where $\Delta\rho = \rho_l - \rho_g$ and $\sigma_b(q) \propto C_b(q)\,C_b(i\sqrt{\kappa^2-q^2})$. Thus, the wave-vector dependence of the leading-order asymptotic decay is *different* on the liquid and gas side, which is not at all explicable using one single rigidity. The coefficients $\sigma_b(q)$ are determined exclusively by bulk quantities and show a rich temperature dependence, consistent with that of the total (integrated) structure factor as measured in simulation studies of truncated Lennard-Jones systems, as shown in Fig. 1. While this agreement is encouraging, many important questions remain unanswered. Do the asymptotic tails of $S(z;q)$ truly represent the interfacial behaviour? What happens nearer the interface, and how do the asymptotic behaviours swap between the liquid and gas sides? How are the two coefficients $\sigma_b(0)$ related, if at all, to the surface tension? How does one guarantee that we recover the Wertheim-Weeks GM as $q\to 0$?

Key to answering these questions and developing a fully microscopic description of correlations in the interfacial region is recognising that the local structure factor must, in general, exhibit resonances each side of the interface. More specifically, the formalism of DFT, which recall is exact in principle, implies that in addition to the GM at $q=0$ there must also be resonances at specific wave-vectors. The presence of these resonances can be understood rather easily by noting that in general, each side the interface, the general solution for $S(z;q)$ can be written as a sum of two expansions; one in the variable X (i.e. similar to the density profile), which can be obtained by expanding $C(z,z';q)$ about the liquid (say) density and a second defined as the solution to (1) but with the right hand side set to zero. The leading term of this second series decays as $e^{-\kappa_q z}$, where $\kappa_q=\sqrt{\kappa^2+q^2}$, and can be directly related to the correlation function $G(0,z;q)$ where the origin is conveniently chosen to correspond to the maximum of $\rho'(z)$ [18, 25, 26]. Note that this is not a definition of the interface position, but merely a convenient choice of the origin of co-ordinates. This means that on the liquid side $S(z;q)$ must have resonances – that is the amplification of a particular exponentially decaying term - when κ_q is an integer multiple of κ; i.e. when the wave-vector satisfies $\xi q = \sqrt{3}, \sqrt{8}, \sqrt{15}, \cdots$. Similar resonances occur on the gas side of the interface at slightly different q since the correlation length of the gas is different.

The existence of these resonances, which has not been noted previously, severely constrains the relationship between the structure factor and correlation function, and in many circumstances is sufficient to determine both exactly, as we shall show below.

II. AN EXAMPLE: SQUARE-GRADIENT THEORY

As a first example, we consider a mean-field square-gradient theory based on the model Grand Potential functional [23]

$$\Omega[\rho] = \int d\mathbf{r} \left(\frac{f}{2}(\nabla\rho)^2 + \phi(\rho) \right) \tag{3}$$

where f is a constant and $\phi(\rho)$ is a double-well potential describing the coexistence of liquid and gas phases below T_c. Thermodynamic equilibrium requires that $\phi(\rho_g) = \phi(\rho_l)$, while the bulk structure factor is $S_b(q) = 1/(\phi''(\rho_b) + fq^2)$ and identifies $\xi^2 = f/\phi''(\rho_b)$. For convenience we define $\Delta\phi \equiv \phi(\rho) - \phi(\rho_b)$ which will be useful later. Minimization of the Grand Potential functional (3) leads to the well known Euler-Lagrange equation for the density profile $f\rho''(z) = \phi'(\rho)$ and, in turn, to the surface tension $\sigma = f\int dz\, \rho'(z)^2$. Although this mean-field approach does not account for the capillary-wave broadening of the interface, we will see that this plays no role in the discussion of the resonances. We now consider the general class of potentials $\phi(\rho)$ which are analytic except, perhaps, at the critical density $\rho_c = (\rho_l + \rho_g)/2$, where we just impose continuity and $\phi'(\rho_c) = 0$. For simplicity, we specialise initially to systems with a liquid-gas (Ising-like) symmetry; the effect of asymmetry is accounted for later. We can classify all such potentials via the coefficients u_n appearing in the expansion about the bulk liquid density; thus, for $\rho > \rho_c$, we write $\phi'(\rho) = f\kappa^2\delta\rho(1 + u_3\delta\rho/\Delta\rho + u_4(\delta\rho/\Delta\rho)^2 + \cdots)$ with $\delta\rho = \rho - \rho_l$. A similar expansion exists about the gas density for $\rho < \rho_c$. Within this class of models, the resonances determine that the local structure factor must always be of the form [26]

$$S(z;q) \;=\; S_b(q) \left(1 + \lambda \sum_{n=1}^{\infty} \frac{\sigma}{\sigma_n} \mathcal{R}_n(z;q) \right) \tag{4}$$

where $\lambda = \Delta\rho/\rho'(0)S_b(0)$ is a constant. The leading term

$$\mathcal{R}_1(z;q) = \frac{\rho'(0)\,\rho'(z)}{\sigma q^2} \tag{5}$$

describes the asymptotic decay (as in Eq. (2)), while for $n > 1$

$$\mathcal{R}_n(z;q) = \frac{G(0,z;q) - G(0,z;\sqrt{n^2-1}\kappa)}{1 - \dfrac{q^2\xi^2}{n^2-1}} \tag{6}$$

is the isolated contribution from each resonance. The local structure factor $S(z;q)$ has a maximum at $z = 0$ and decays towards its bulk value as $|z|$ increases, as expected. We note that $\mathcal{R}_1(z;q)$ contains an explicit GM divergence while both the numerator and denominator of $\mathcal{R}_n(z;q)$ vanish at $\xi q = \sqrt{n^2-1}$ which also has an implicit GM divergence contained within $G(0,z;q)$. The explicit GM and resonances are weighted by generalised tensions σ_n with $\sigma_1 = f\kappa(\Delta\rho)^2/2u_3$ (equivalent to $\sigma_b(0)$) which, at low temperatures, is larger than σ [18]. Higher coefficients are determined similarly [26], and satisfy the useful summation condition $1/\sigma = 1/\sigma_1 + 1/\sigma_2 + \cdots$ ensuring that $S(z;q)$ has the required Wertheim-Weeks GM mode divergence $S(z;q) \approx \Delta\rho\rho'(z)/\sigma q^2$ at small wave-vectors. Expression (4) describes the general form of the structure factor throughout the interfacial region, encompassing both the large distance behaviour (fixed q, $|z| \to \infty$) and the Wertheim-Weeks GM divergence (fixed z, $q \to 0$). A number of immediate implications follow:

A: In general, the leading order exponential decay of $S(z;q)$ comes from the explicit GM term $\mathcal{R}_1(z;q)$. However, higher-order exponentials include corrections at the resonances. For example, at $\xi q = \sqrt{3}$, the next higher-order term in $S(z;q)$ decays as $|z|e^{-2\kappa|z|}$ whose coefficient is determined by the sign of $(u_4 - \frac{2}{9}u_3^2)$.

B: The presence of just *one* resonance means that, even with an idealised Ising symmetry, there is no consistent separation of both the local structure factor $S(z;q)$ and correlation function $G(0,z;q)$ into bulk and excess terms, as

has been routinely assumed.

C: For a given q, the local structure factor is maximal at the origin (i.e., where $\rho'(z)$ also has a maximum), and its value $S(0;q)$ is *shielded* from information contained in the correlation function. To see this, suppose that $G(0,0;q) \approx \rho'(0)^2/\sigma q^2 + \mathcal{C}$, containing the Wertheim-Weeks GM and an additive constant. This could be generated by the low-q behaviour of a background contribution, or as an expansion arising if we suppose the surface tension in the Wertheim-Weeks GM is replaced with $\sigma + Kq^2$, with K some phenomenological rigidity, as discussed earlier. Substitution into (4) determines that

$$\frac{S(0;q)}{S_b(q)} \approx 1 + \frac{\Delta\rho\rho'(0)}{\sigma q^2 S_b(0)} \tag{7}$$

which is *independent* of the constant $\mathcal{C}$. This tells us a number of things. First, that the approximate, non-additive, separation (7) will be accurate for a wide class of models; it is indeed exact for the standard quartic Landau potential [14]. Second, that the corrections to the Wertheim-Weeks GM are determined by properties of the bulk structure factor (or bulk direct correlation function) throughout *the whole interfacial region*, and not just in the tails of $S(z;q)$, which explains the close agreement between $\sigma_{\text{HD}}(q)$ and $\sigma_b(q)$ in Fig. (1). And finally, that the leading order correction to the Wertheim-Weeks GM divergence in $S(0;q)$ is *unrelated* to the leading order correction in the Wertheim-Weeks GM divergence of the correlation function. This means that it is *impossible* to infer directly the value of any rigidity in $G(0,0;q)$ from the structure factor.

D: Integration of Eq. (4) over a macroscopic interval $[-L/2, L/2]$ determines a similar exact result for the total structure factor $S_{\text{TOT}}(q)$ as a sum of the resonances ([26]). From this, it follows that $S_{\text{TOT}}(q)$ is always well approximated by

$$\frac{S_{\text{TOT}}(q)}{S_b(q)} \approx L + \frac{(\Delta\rho)^2}{\sigma\, q^2\, S_b(0)} \tag{8}$$

This result does not rely on the density profile and, therefore, is unlikely to be affected by capillary wave fluctuation effects.

III. COUNTING THE RESONANCES

We can take the theory further and classify the potentials $\phi(\rho)$ according to the presence or absence of resonances [26]. For example, when $u_4 = 2u_3^2/9$, the resonance at $\xi q = \sqrt{3}$ is missing and further setting $u_5 = 0$ removes the next resonance at $\xi q = \sqrt{8}$. Alternatively, we can be more stringent and consider the class of single resonance models (SRMs) containing just one resonance at $\xi q = \sqrt{n^2 - 1}$ for which $S(z;q) = S_b(q)\left(1 + \lambda\,\mathcal{R}_n(z;q)\right)$. Such SRM potentials can be determined and are shown in Fig. 2.

For $n = 1$ (that is, a model with no resonances), $\phi(\rho)$ has a quartic expansion with coefficients $u_3 = 3$ and $u_4 = 2$ and corresponds precisely to the standard potential of Landau theory $\phi = -t(\rho - \rho_c)^2 + u(\rho - \rho_c)^4$ with $t \propto T_c - T$. In this case, eqs. (7) and (8) are exact, while for higher n the R.H.S. of both equations are lower bounds. For $n = 2$ (that is, a model with only a resonance at $\xi q = \sqrt{3}$, in addition to the GM), the potential is similarly quartic but the coefficients are $u_3 = 0$ and $u_4 = -4$. The potential for SRMs for higher n, however, no longer truncate [26]. In the limit $n \to \infty$, the potential recovers a double parabola (in which all the coefficients u_n are zero) and the single resonance in $\mathcal{R}_\infty(z;q)$ disappears, since it occurs at infinite wave-number. Indeed, apart from the Landau quartic potential, this is the only other model for which the structure factor does not exhibit resonances. This is all the more surprising given that these two limiting SRM potentials are the only ones for which $G(z,z';q)$ and $S(z;q)$ have been studied.

In the absence of such fine tuning, we must expect that $\sigma_1 \neq \sigma$ and that *all resonances* are present in $S(z;q)$. However, at low temperatures, the correlation length ξ is molecularly small so it may not be possible to reach wave-vectors where the explicit resonant decay of $S(z;q)$ is observable. As the temperature is increased towards T_c, the correlation length increases, which exposes the resonances [26].

IV. FULLY INTEGRABLE MODELS

By considering the occurrence of the resonances, we can identify models that are fully analytically integrable; that is, potentials for which the profile, surface tension, correlation function $G(z,z';q)$ and structure factor $S(z;q)$ can be determined analytically. Only one non-trivial example of this was known previously, corresponding to the Landau quartic potential for which Zittartz first determined $G(z,z';q)$ using spectral methods [1]. The only other example is the double parabola model, which similarly does not contain resonances [14].

However, our approach identifies many model potentials (in fact, an infinite number) which are fully integrable, all of which include resonances. Among these are the SRM with $n=2$ and the trigonometric potential $\Delta\phi(\rho) \propto \sin^2(\pi(\rho-\rho_g)/\Delta\rho)$. This latter potential generates an infinite number of resonances at $\xi q = \sqrt{n^2-1}$ for even n. However, the example which is most pertinent to fluids, away from the critical regime, is the double-cubic model with $u_3=2$ (and all other coefficients zero). This potential is particularly useful because the value of $\sigma_1 = f(\Delta\rho)^2\kappa/4$ is larger than the equilibrium tension σ as applies to real fluids at low temperatures [18]. This model contains all resonances of $S(z;q)$, and can be readily generalised to encompass liquid-gas asymmetry. The behaviour of $G(z,z';q)$ for this double-cubic potential is shown in Fig. (2) and illustrates the smooth development of the Wertheim-Weeks GM divergence as the wave-vector is reduced. The analytical results show that $G(z,z';q)$ also contains a *new resonance* at $\xi q = \sqrt{5/4}$ when the particles are on the same side of the interface [26]. Similar behaviour is found in other integrable models. For example, in the SRM with $n=2$, the correlation function (like the structure factor) contains a GM and a single resonance at $\xi q = \sqrt{3}$. We have shown that, for more general types of potential, the correlation function must have resonances when $\xi q = \sqrt{(m^2-4)/4}$ for $m = 3, 4\cdots$; again when both particles are on the same side of interface. This includes the same resonances contained in $S(z;q)$ (when m is even) and also a new set occuring at $\xi q = \sqrt{5/4}, \sqrt{21/4}, \ldots$ (when m is odd).

The results for $G(z,z';q)$ show that, similar to the robust approximation (7), the correlation function at the interface is always well approximated by

$$\frac{G(0,0;q)}{G_b(0;q)} \;\approx\; 1 \;+\; \frac{\rho'(0)^2}{\sigma q^2 G_b(0;0)} \tag{9}$$

Here $G_b(z;q) = e^{-\kappa_q|z|}/2f\kappa_q$ is the 2D Fourier transform of the bulk correlation function (along the $x-y$ plane) so that $G_b(0;q)$ corresponds to the 2D Fourier transform when the particles are co-planar. Indeed, (9) is the *exact* result for the Landau quartic potential *and* trigonometric model. Thus, at the origin (and only at the origin), the approximate rule of factoring out a bulk background *and* a multiplicative correction to the GM describes accurately the correlation function and structure factor over the whole range of wave-vectors (see Fig. 3).

V. THE SULLIVAN MODEL AND THE BULK ENHANCEMENT EFFECT

As a second example, we present results for the well-known Sullivan DFT model of the free-interface, based on a local approximation of the repulsive hard-sphere contribution and a non-local, mean-field, treatment of an attractive Yukawa intermolecular potential [27–30]. This more microscopic description of the interfacial region will allow us to see some limitations of square-gradient theory and finally introduce liquid-gas asymmetry. We will in fact consider a broad class of Sullivan-like models in which the model chemical potential for bulk hard spheres $\mu_h(\rho)$ is considered an arbitrary function. To begin, we again consider systems with an Ising symmetry. In this case, the analysis of the square-gradient theory generalises in a straightforward manner. Indeed, the central result (4) for the expansion of $S(z;q)$ becomes

$$S(z;q) \;=\; S_b(q)\left(\gamma(z) + \lambda\sum_{n=1}^{\infty}\frac{\sigma}{\sigma_n}\,\mathcal{R}_n(z;q)\right) \tag{10}$$

which only differs from (4) in one regard: The first term on the RHS is modified to $S_b(q)\,\gamma(z)$ where $\gamma(z) = \mu_h'(\rho_b)/\mu_h'(\rho(z))$ [26].

The function $\gamma(z)$ is larger than 1 for all finite z, but approaches unity as $T \to T_c$, in which case the results of the Sullivan model recover those of square-gradient theory. The effect of $\gamma(z)$ is two-fold: Firstly, it leads to the enhancement of a bulk-like contribution, which is maximal at the origin. Secondly, it decays to unity exponentially at large $|z|$ and mixes with the explicit GM term (controlled by σ_1) to recover the asymptotic decay (2). With these provisos, the rest of the analysis is unchanged, including the classification of single resonance and fully integrable

models, but now based on properties of the function $\mu_h(\rho)$ rather than the potential $\phi(\rho)$. Most importantly, this allows us to understand the generalizations of the extremely accurate approximations (7), (8) and (9) (which we stress also remain exact for some model functions $\mu_h(\rho)$). These are now modified to

$$\frac{S(0;q)}{S_b(q)} \approx \gamma(0) + \frac{\Delta\rho\rho'(0)}{\sigma q^2 S_b(0)} \tag{11}$$

$$\frac{S_{\rm TOT}(q)}{S_b(q)} \approx \int dz\, \gamma(z) + \frac{(\Delta\rho)^2}{\sigma\, q^2\, S_b(0)} \tag{12}$$

and

$$\frac{G(0,0;q)}{G_b(0;q)} \approx \gamma(0)^2 + \frac{\rho'(0)^2}{\sigma q^2 G_b(0;0)} \tag{13}$$

The presence of the corrections introduced by the function $\gamma(z)$ serves to underline again why there is no simple additive separation into bulk and excess quantities within the correlation function structure. Indeed, the enhancement effect means that neither $S(0;q)$ nor $G(0,0;q)$ approach their bulk values as q increases, not even when the GM contribution is irrelevant.

Finally, we turn to the inclusion of liquid-gas asymmetry which is now a relatively minor amendment. For example, the local structure factor at the origin (defined again as the location of the maximum of the density profile derivative) generalises to

$$S(0;q) \approx f(q)\,\gamma_g\, S_g(q) + \big(1-f(q)\big)\,\gamma_l\, S_l(q) + \frac{\Delta\rho\,\rho'(0)}{\sigma q^2}\left(f(q)\,\frac{S_g(q)}{S_g(0)} + \big(1-f(q)\big)\,\frac{S_l(q)}{S_l(0)}\right) \tag{14}$$

where $\gamma_b = \mu_h'(\rho_b)/\mu_h'(\rho(0))$ and $f(q) = \Delta\kappa_g(q)/\big(\Delta\kappa_g(q) + \Delta\kappa_l(q)\big)$, with $\Delta\kappa_b(q) = \sqrt{\kappa_b^2+q^2} - \kappa_b$. This result encapsulates an accurate approximation for the weighting of different bulk-like and GM contributions where there is an arbitrary liquid-gas asymmetry. In Fig. 4, we illustrate how well this approximation, which contains no free parameters, works using the accurate Carnahan-Starling equation of state for $\mu_h(\rho)$.

VI. SUMMARY

In this paper we have shown that, by recognizing the presence of resonances, a very rich perspective emerges regarding correlation function structure for interfaces in systems with short-ranged forces. Indeed, this allows us to essentially solve analytically for the correlation function in generalised van der Waals DFTs and eliminates the need for the introduction of a rigidity, highlighting properties that cannot be explained using such a simple mesoscopic concept. Our predictions for the local structure factor and correlation function can certainly be tested in Ising model simulation studies, similar to those described in [31], which have better statistics compared to molecular simulations. Our analysis of the resonances generalises in a straightforward manner to more sophisticated non-local DFT treatments [32]. However, when the bulk correlation length is large, the predictions of the square-gradient theory will be accurate. It may also be possible to incorporate long-ranged forces but, similarly, they become irrelevant in the critical region [33] and we expect that the local structure factor displays universal features that are correctly captured by models with short-ranged forces discussed here. Resonances will also occur for interfaces in binary liquid mixtures and more generally still, will occur at other types of interface, such as the solid-liquid, even when a GM is absent.

VII. METHODS

Methods, including the derivation of the relationship between $S(z;q)$ and $G(0,z;q)$, the classification of single resonance models and the explicit solution for $G(z,z'q)$ in a model with an infinite hierachy of resonances can be found in [26].

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Author Contributions

A.O.P. conceived problem and subsequent joint theoretical development. C.R. performed joint theoretical development and numerical computations.

Competing Interests statement

None

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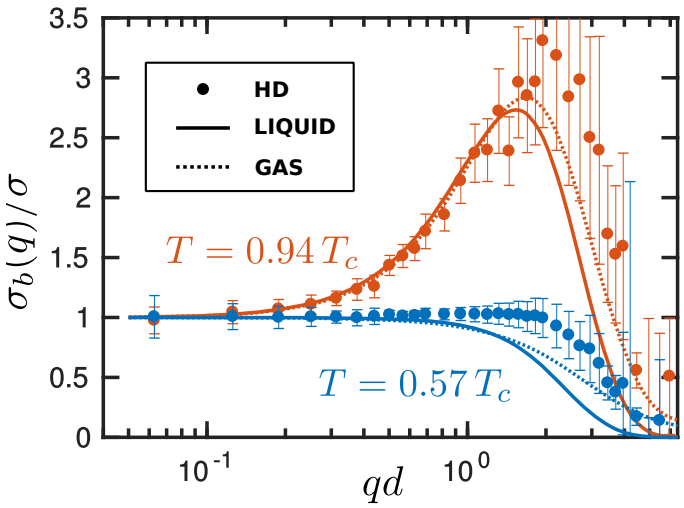


Figure 1. Comparison of the coefficients $\sigma_l(q)$ and $\sigma_g(q)$, at two different temperatures, with the effective wave-vector dependent surface tension $\sigma_{\rm HD}(q)$ obtained from an excess-like contribution to the total (integrated) structure factor $S^{ex}(q) = (\Delta\rho)^2/q^2\sigma_{\rm HD}(q)$ after a background term is extracted (approximately, the volumes of the liquid and gas multiplied by their respective bulk structure factor). Data taken from the simulation studies of Höfling and Dietrich (HD) involving $5{\cdot}10^5$ truncated Lennard-Jones particles with core diameter d [15]. The coefficients $\sigma_b(q) \propto C_b(q)C_b(i\sqrt{\kappa^2 - q^2})$ were calculated using only simulation data results for the bulk liquid and gas quantities, respectively.

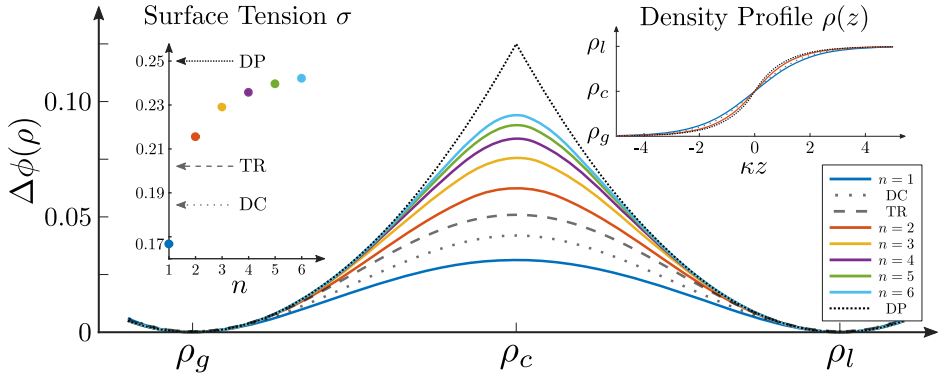


Figure 2. Potentials $\Delta\phi(\rho)$ in units of $f\kappa^2\,(\Delta\rho)^2$, together with the corresponding density profiles $\rho(z)$ and tensions σ (in units of $f\kappa(\Delta\rho)^2$) for models whose structure factor $S(z;q)$ displays a single resonance at $\xi q = \sqrt{n^2 - 1}$. The case $n = 1$ (a pure GM divergence) corresponds to the standard Landau quartic potential. As n increases the potential approaches the form of a double parabola (DP). The Double-Cubic (DC) and trigonometric (TR) potentials are also shown.

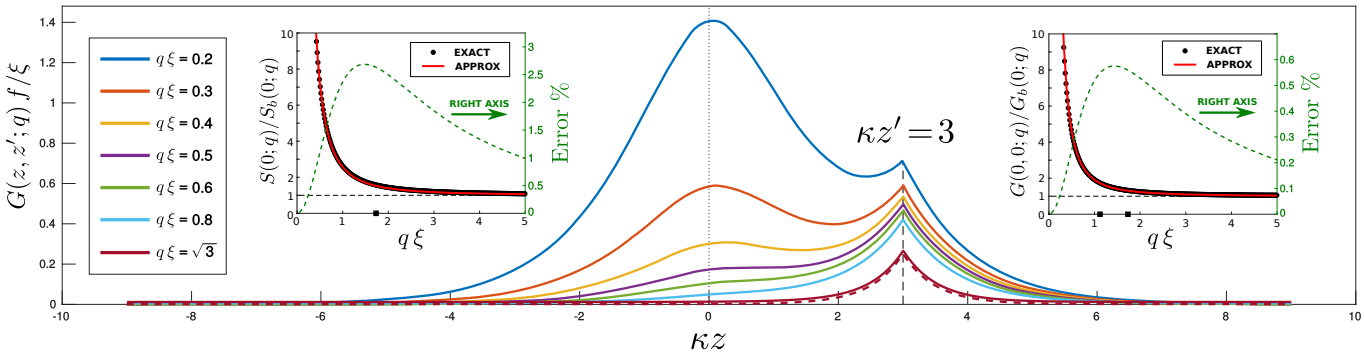


Figure 3. Correlation function $G(z,z';q)$ for the double-cubic potential for different wave-vectors q and fixed $\kappa z' = 3$. A prominent GM is apparent near the origin at small wave-vectors. For larger values of q, $G(z,z';q)$ becomes more bulk-like and is almost indistinguishable from it (dashed lines) for $q\xi = \sqrt{3}$ (the first resonance in $S(z;q)$). Inset: Exact results for $S(0;q)$ and $G(0,0;q)$ (see [26]) compared with the multiplicative approximations (7) and (9), respectively. These remain accurate over the whole range of wave-vectors. For example, the maximum error is about 2.5% for $S(0;q)$ and only about 0.6% for $G(0,0;q)$. The squares in the horizontal axes locate the resonances, which do not show any noticeable feature in the functions $S(0;q)$ or $G(0,0;q)$.

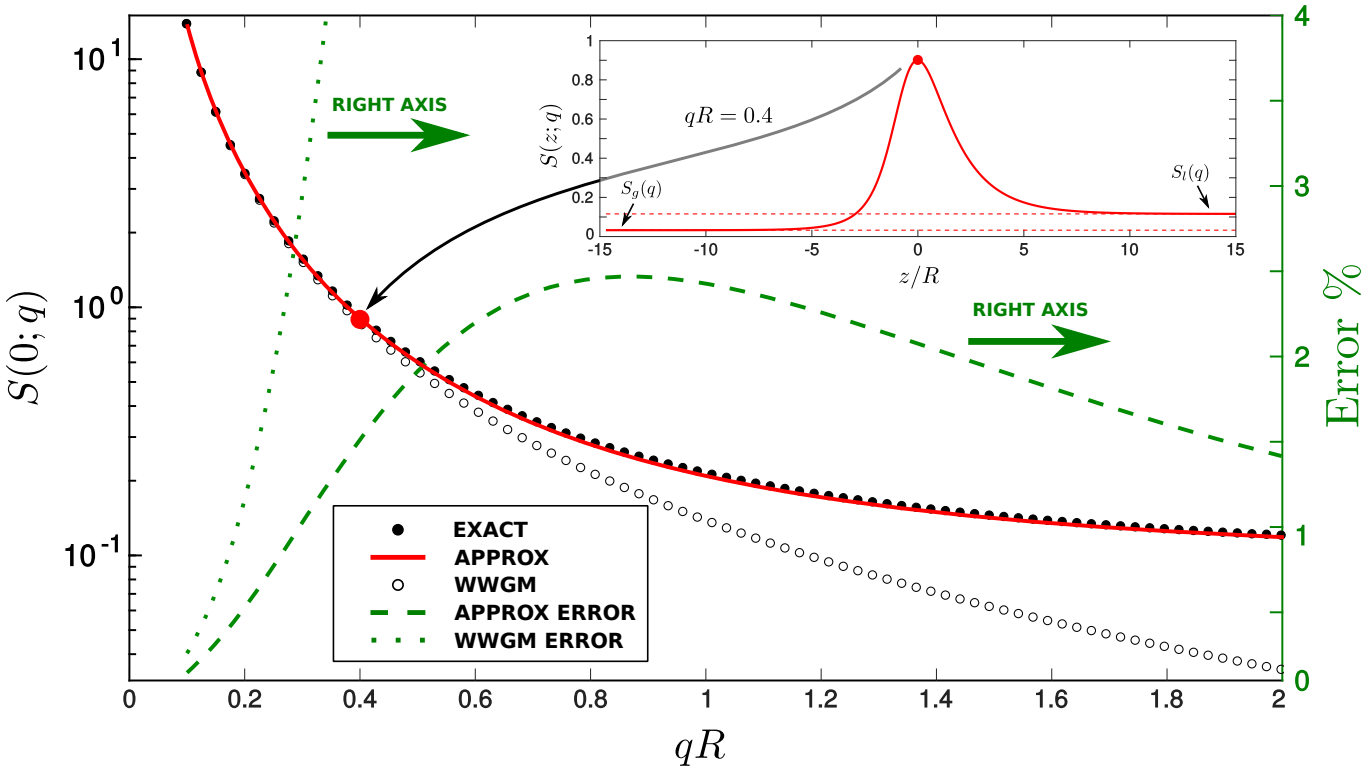


Figure 4. Sullivan models results for the structure factor $S(0;q)$ using the Carnahan-Starling equation of state for hard-spheres at $T/T_c = 0.72$, for which the ratio of the true correlation lengths $\xi_l^T/\xi_g^T \approx 2.1$, representing strong liquid-gas asymmetry. The structure factor is measured in units of R^2/α. The main figure illustrates the extraordinary accuracy of the approximation (14) (red line) compared with the numerical solution of the OZ equation (black dots) over the whole range of wave-vectors. As expected, the Wertheim-Weeks Goldstone mode (WWGM) (empty dots) is only valid when q is much smaller than the inverse of the bulk correlation lengths. Relative errors are shown in green. The error of the approximation is less than 2.5% and vanishes at small and large values of q. Inset: Numerically determined local structure factor $S(z;q)$ for $qR = 0.4$. As z increases, this varies from the bulk gas $S_g(q)$ to the bulk liquid $S_l(q)$ limits, showing a maximum near the origin (red dot).