nature physics

SUPPLEMENTARY INFORMATION

https://doi.org/10.1038/s41567-018-0361-z

In the format provided by the authors and unedited.

The Goldstone mode and resonances in the fluid interfacial region

A. O. Parry[1] and C. Rascón[2]*

[1]Department of Mathematics, Imperial College London, London, UK. [2]GISC, Departamento de Matemáticas, Universidad Carlos III de Madrid, Leganés, Spain. *e-mail: carlos.rascon@uc3m.es

Supplementary Information

The Goldstone Mode and Resonances in the Fluid Interfacial Region

A.O. Parry, C. Rascón

Here, we provide further information regarding five aspects of our study: The derivation of the relation between $S(z;q)$ and $G(0,z;q)$ for the square-gradient functional (equations (4) to (6) in the main text), the determination of single resonance models (SRMs), the full solution for $G(z,z';q)$ for the double-cubic model, the general proof of the wavevector dependent decay of the $S_{cf}(z;q)$ (or, equivalently, $G(0,z;q)$) for systems with short-ranged forces and, finally, the correlation function structure within the Sullivan Model.

1 Resonances within square-gradient theory

Within Density Functional Theory (DFT), the equilibrium density profile and many-body correlation functions are obtained from the Grand Potential functional $\Omega[\rho] = F[\rho] - \int d\mathbf{r}\,(\mu - V(\mathbf{r}))\,\rho(\mathbf{r})$, where $\rho(\mathbf{r})$ is the density distribution, μ is the chemical potential and $V(\mathbf{r})$ is the external potential [1]. The equilibrium density profile is obtained from minimization of $\Omega[\rho]$

$$\frac{\delta\Omega[\rho]}{\delta\rho(\mathbf{r})} = 0 \tag{1}$$

while the direct correlation function of the inhomogeneous fluid

$$C(\mathbf{r},\mathbf{r}') = \frac{1}{k_B T}\,\frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \tag{2}$$

is obtained as the second derivative of the intrinsic Helmholtz Free-energy functional $F[\rho]$, which must be evaluated at the equilibrium fluid density. From $C(\mathbf{r},\mathbf{r}')$, we can then determine the equilibrium density-density correlation function $G(\mathbf{r}',\mathbf{r})$ via the solution of the Ornstein-Zernike equation

$$\int d\mathbf{r}''\, C(\mathbf{r},\mathbf{r}'')\, G(\mathbf{r}'',\mathbf{r}') \;=\; \delta(\mathbf{r}-\mathbf{r}') \tag{3}$$

Consider the mean-field square-gradient theory based on the model Grand Potential functional

$$\Omega[\rho] = \int d\mathbf{r}\,\left(\frac{f}{2}(\nabla\rho)^2 + \phi(\rho)\right) \tag{4}$$

where, for simplicity, we set $f = 1$, since this does not appear in our final results. For this model of a free liquid-gas interface located near the plane $z = 0$, the direct correlation function reduces to

$$C(\mathbf{r},\mathbf{r}') = \left(-\nabla^2_{\mathbf{r}} + \phi''(\rho(\mathbf{r}))\right)\,\delta(\mathbf{r}-\mathbf{r}') \tag{5}$$

where have set $k_B T = 1$. Thus, the 2D Fourier transform of the direct correlation function, along the interface, is the delta function operator

$$C(z,z';q) = \left(-\partial_z^2 + q^2 + \phi''(\rho(z))\right)\,\delta(z-z') \tag{6}$$

where $\rho(z)$ is the equilibrium density profile. For the local functional (4), the minimization of $\Omega[\rho]$ reduces to the Euler-Lagrange equation $\rho''(z) = \phi'(\rho)$, which is solved subject to the boundary conditions $\rho(z \to -\infty) = \rho_g$ and $\rho(z \to \infty) = \rho_l$. Thus, the Ornstein-Zernike equation for the 2D Fourier transform of the density-density correlation function reduces to the differential equation

$$\left(-\partial_z^2 + q^2 + \phi''(\rho(z))\right) G(z, z'; q) = \delta(z - z') \tag{7}$$

The local structure factor is defined as the integral

$$S(z; q) = \int dz'\, G(z, z'; q) \tag{8}$$

and, therefore, satisfies

$$\left(-\partial_z^2 + q^2 + \phi''(\rho(z))\right)\, S(z; q) = 1 \tag{9}$$

which we now seek to solve. Since the differential equation is linear, we can write $S(z; q) = S_{cf}(z; q) + S_{ps}(z; q)$ where the complementary function has the solution

$$S_{cf}(z; q) = A(q)\, G(0, z; q) \tag{10}$$

with an amplitude $A(q)$ to be determined from a boundary condition after a particular solution is specified. Note that, for positive z, the correlation function has an asymptotic expansion $G(0, z; q) \equiv \mathcal{G}(q) e^{-\kappa_q z}(1 + \mathcal{O}(X))$ in terms of $X = e^{-\kappa z}$ [6]. The amplitude $\mathcal{G}(q)$ of the correlation function will be needed in order to define the weights of the resonances in terms of the generalised tensions σ_n. To determine the particular solution, we first note that the Euler-Lagrange equation allows us to re-write $\phi''(\rho(z)) = \rho'''(z)/\rho'(z)$. However, the Euler-Lagrange equation also determines that the profile always has an exponential expansion

$$\rho(z) - \rho_l \;=\; r_0\, \Delta\rho\, e^{-\kappa z}\Big(1 + \sum_{n=1}^{\infty} r_n X^n\Big) \tag{11}$$

where the coefficients r_n are, in turn, determined by the coefficients u_n characterising the potential $\phi(\rho)$. For example,

$$r_1 = \frac{r_0 u_3}{3}, \qquad r_2 = \frac{r_0^2}{8}\left(u_4 + \frac{2}{3}u_3^2\right) \tag{12}$$

with the lead coefficient r_0 determined from integration of the first-order equation $\rho'(z) = \sqrt{2\Delta\phi(\rho)}$. This means that we can also expand

$$\phi''(\rho(z)) = \kappa^2 + \sum_{n=1}^{\infty} \alpha_n X^n \tag{13}$$

with, for example,

$$\alpha_1 = 2 r_0 u_3, \qquad \alpha_2 = r_0^2\left(3u_4 + \frac{2}{3}u_3^2\right) \tag{14}$$

The structure of $\phi''(\rho(z))$ suggests the trial solution

$$S_{ps}(z; q) = S_b(q)\left(1 + \sum_{n=1}^{\infty} a_n(q)\, X^n\right) \tag{15}$$

This indeed solves the Ornstein-Zernike equation and determines that the amplitudes $a_n(q)$ take the form

$$a_n(q) = \frac{a_{n1}}{\xi^2 q^2} + \frac{a_{n2}}{1 - \frac{q^2\xi^2}{3}} + \cdots + \frac{a_{nn}}{1 - \frac{q^2\xi^2}{n^2 - 1}} \tag{16}$$

with dimensionless numbers a_{nm} determined by the α_n and hence the u_n and r_0 (see Table 1). Thus, in general, each amplitude $a_n(q)$ contains an explicit GM and a series of resonances of increasing order in

a_{nm}		n		
	1	2	3	
	1	$-2r_0u_3$		
m	2	$-\frac{4}{3}r_0^2u_3^2$	$r_0^2\Big(u_4-\frac{2}{9}u_3^2\Big)$	
	3	$-\frac{2}{3}r_0^3u_3\Big(u_4+\frac{2}{3}u_3^2\Big)$	$\frac{2}{5}r_0^3u_3\Big(u_4-\frac{2}{9}u_3^2\Big)$	$\frac{1}{2}r_0^3\Big(u_5+\frac{3}{40}u_3u_4-\frac{1}{60}u_3^3\Big)$

Table 1: Examples of matrix elements a_{nm} determining the strength of the resonances appearing in the expansion of $a_n(q)$ (see Eq. (16)) in terms of the coefficients u_n characterising the potential $\phi(\rho)$. If a particular diagonal element $a_{nn}=0$, all the elements of that column vanish and the resonance occurring at $\xi q=\sqrt{n^2-1}$ is absent.

n. Of particular importance is each diagonal element a_{nn} since, if this is zero, so are all the elements of the column (a_{mn} with $m\geq n$), implying that a particular resonance is entirely absent. Hence, we can see already that, by setting $u_4=\frac{2}{9}u_3^2$, there is no resonance at $\xi q=\sqrt{3}$ (since $a_{22}=0$), and that, by further setting $u_5=0$, there is also no resonance at $\xi q=\sqrt{8}$ (since also $a_{33}=0$). Note that, at $\xi q=\sqrt{n^2-1}$, the local structure factor $S(z;q)$ contains a resonant contribution decaying as $\kappa\, z\, e^{-(n-1)\kappa z}S_b(q)$ whose amplitude is $a_{nn}(1-n^2)/2n$. Therefore, if $a_{nn}=0$, the resonance does not manifest itself in the decay of $S(z;q)$.

We next re-order the expansion of $S_{ps}(z;q)$ using a different basis noting that we can also write it

$$S_{ps}(z;q) \;=\; S_b(q)\left(1+\frac{\rho'(z)}{b_1(q)}+\sum_{n=2}^{\infty}\frac{G(0,z;\sqrt{n^2-1}\,\kappa)}{b_n(q)}\right) \tag{17}$$

This is just a linear re-grouping of the original exponential expansion since $\rho'(z)\propto e^{-\kappa z}(1+\mathcal{O}(X))$ and $G(0,z;\sqrt{n^2-1}\,\kappa)\propto e^{-n\kappa z}(1+\mathcal{O}(X))$. Substituting into the Ornstein-Zernike equation then determines $b_1(q)=-q^2/\alpha_1$ and that, more generally,

$$b_n(q) \;\propto\; 1-\frac{q^2\xi^2}{n^2-1} \tag{18}$$

meaning that, in this basis, each resonance is *isolated*. The amplitudes of the coefficients $b_n(q)$ are conveniently written in terms of the generalised tensions σ_n with

$$\sigma_1=\frac{\kappa\Delta\rho^2}{2u_3} \qquad \text{and} \qquad \frac{\sigma}{\sigma_n}=-\frac{\rho'(0)\,\xi^2}{\Delta\rho}\,\frac{a_{nn}}{\mathcal{G}\big((n^2-1)\kappa\big)} \qquad (n>1) \tag{19}$$

where the a_{nn} are the coefficients determined for the original exponential expansion of $S_{ps}(z;q)$. Thus, for the particular solution we have

$$S_{ps}(z;q) \;=\; S_b(q)\;+\;\frac{\Delta\rho\,\rho'(z)}{\beta\sigma_1q^2\big(1+q^2\xi^2\big)}\;+\;\mathcal{U}_{ps}(z;q) \tag{20}$$

where

$$\mathcal{U}_{ps}(z;q) \;=\; -\frac{\Delta\rho}{\rho'(0)}\sum_{n=2}^{\infty}\frac{\sigma}{\sigma_n}\,\frac{G\big(0,z;\sqrt{n^2-1}\kappa\big)}{(1+q^2\xi^2)\big(1-\frac{q^2\xi^2}{n^2-1}\big)} \tag{21}$$

Finally, the amplitude $A(q)$ of the complementary function is determined from requiring that $S(z;q)$ has a maximum at the origin $z=0$ (since our potentials are continuous and satisfy $\phi'(\rho_c)=0$). Noting that $\rho''(0)=0$ and that $\partial_zG(0,z;q)|_{z=0^+}=-1/2$, we find

$$A(q) \;=\; \frac{\Delta\rho}{\rho'(0)}\sum_{n=2}^{\infty}\frac{\sigma}{\sigma_n}\,\frac{1}{(1+q^2\xi^2)\big(1-\frac{q^2\xi^2}{n^2-1}\big)} \tag{22}$$

and hence

$$S_{cf}(z;q) \;=\; \frac{\Delta\rho}{\rho'(0)} \sum_{n=2}^{\infty} \frac{\sigma}{\sigma_n} \frac{G\big(0,z;q\big)}{(1+q^2\xi^2)\big(1-\frac{q^2\xi^2}{n^2-1}\big)} \tag{23}$$

arriving at our central result (Eq. (4) in the main text) and the identification of $\mathcal{R}(z;q)$.

Integration over a macroscopic interval defines the total structure factor:

$$S_{\text{TOT}}(q) \;=\; \int_{-L/2}^{L/2} dz \;\; S(z;q) \tag{24}$$

from which it follows that this also has an expansion in terms of resonances

$$S_{\text{TOT}}(q) \;=\; L\, S_b(q) + \frac{(\Delta\rho)^2}{\sigma_1 q^2(1+\xi^2q^2)} + \frac{\Delta\rho}{\rho'(0)} \sum_{n=2}^{\infty} \frac{\sigma}{\sigma_n} \frac{S\big(0;q\big) - S\big(0;\sqrt{n^2-1}\,\kappa\big)}{(1+q^2\xi^2)\big(1-\frac{q^2\xi^2}{n^2-1}\big)} \tag{25}$$

which is exact for this class of square-gradient models. Following a similar argument to that explained in section § II.C, the approximation that $S(0;q) \approx \Delta\rho\,\rho'(0)/\sigma\, q^2 + C'$ where C' is an arbitrary unknown constant, leads directly to Eq. (8) in the main text as a highly accurate approximation for the total structure factor over the whole range of wave-vectors.

As mentioned in the main text, as the temperature is increased towards T_c, the correlation length ξ increases, which exposes more and more resonances. We can model this by, for example, adding a higher-order term $(\rho-\rho_c)^6$ to the standard Landau theory potential. Calculation then shows that $\sigma_1 = \sigma + \mathcal{O}(t^2)$, so that the Landau theory becomes more and more accurate as $T \to T_c$. In this case, the explicit GM term $\mathcal{R}_1(z;q)$ encompasses almost the whole Wertheim-Weeks GM divergence and the contribution from the resonances becomes negligible. However, this behaviour is specific to a mean-field treatment of the critical region. To assess the role of resonances more generally, we can use a phenomenological Fisk-Widom potential $\phi(\rho) = -t^\gamma(\rho-\rho_c)^2 + u(\rho-\rho_c)^{\delta+1}$, where γ and δ are standard bulk critical exponents which can be regarded as input parameters [2]. For example, we may use the reliable rational approximation $\gamma = 4/3$, $\delta = 5$. For the Fisk-Widom potential, $u_4 - \frac{2}{9}u_3^2 = \frac{4}{9}\delta(\delta-3)$, implying that it is only for the standard Landau quartic potential ($\delta = 3$) that the resonance at $\xi q = \sqrt{3}$ is absent. Indeed, using the rational values of the exponents quoted above, we find the universal value of the critical amplitude ratio $\sigma_1/\sigma \approx 0.7$. Since $1 = \sigma/\sigma_1 + \sigma/\sigma_2 + \cdots$, this signals the weights cannot vanish in the critical region. We note that the same value of the universal critical amplitude also applies to the potential modeling the approach to a tri-critical point ($\gamma = 1$, $\delta = 5$).

2 Single resonance models

As noted above, the condition that a resonance is absent follows from simply setting the appropriate matrix element $a_{nn} = 0$, which can be imposed for any number of resonances. More stringent is the requirement that a model contains only a single resonance, occurring (say) at $\xi q = \sqrt{n^2-1}$. If this is the case, we have $a_{kk} = 0$ for all $k \neq n$, and hence the single resonance is weighted by the entire surface tension $\sigma_n = \sigma$. Therefore, the local structure factor simplifies to

$$S(z;q) \;=\; S_b(q) \;+\; \frac{\Delta\rho}{\rho'(0)} \frac{G(0,z;q) - G\big(0,z;\sqrt{n^2-1}\,\kappa\big)}{(1+q^2\xi^2)\big(1-\frac{q^2\xi^2}{n^2-1}\big)} \tag{26}$$

In writing this, we are assuming that $n > 1$, since for $n = 1$ the "resonance" occurs at $q = 0$ and is equivalent to the explicit GM. Substituting (26) into the Ornstein-Zernike equation (9) determines that this function $S(z;q)$ is indeed a solution, provided that the two-point function satisfies

$$G(0,z;\sqrt{n^2-1}\,\kappa) \;\propto\; \phi''\big(\rho(z)\big) - \kappa^2 \tag{27}$$

Incidentally, if we were to set $n = 1$ we could then use $G(0, z; 0) \propto \rho'(z)$, as dictated by the Euler-Lagrange equation, to reduce this to $\sqrt{\Delta\phi} \propto \phi''(\rho(z)) - \kappa^2$. This can be integrated and recovers immediately the standard Landau theory quartic potential. The condition $\sigma_1 = \sigma$ then implies that

$$S(z; q) \;=\; S_b(q) \;+\; \frac{\Delta\rho\, \rho'(z)}{\beta\sigma q^2(1 + q^2\xi^2)} \tag{28}$$

as originally derived in [6]. For completion, we note that the surface tension ($\sigma = \kappa(\Delta\rho)^2/6$), profile ($\rho(z) = \rho_g + \Delta\rho \tanh\frac{\kappa z}{2}$) and the correlation function $G(z, z'; q)$ are also known analytically for this potential [10].

Returning to the more general case $n > 1$, we note that for $z > 0$ the function $G(0, z; \sqrt{n^2 - 1}\,\kappa)$ satisfies its own Ornstein-Zernike equation

$$\left(-\partial_z^2 + \kappa^2(n^2 - 1) + \phi''(\rho(z))\right) G(0, z; \sqrt{n^2 - 1}\,\kappa) \;=\; 0 \tag{29}$$

Substituting here the identification (27) yields the non-linear fourth-order equation

$$2\Delta\phi\, \phi'''' + \phi'\phi''' \;=\; (\phi'' - \kappa^2)\left(\phi'' + \kappa^2(n^2 - 1)\right) \tag{30}$$

that must be satisfied if the model potential is to have a single resonance. The boundary conditions here are $\Delta\phi(\rho_l) = \phi'(\rho_l) = \phi'(\rho_c) = 0$ and $\phi''(\rho_l) = \kappa^2$. Consider, for example, the class of truncated polynomial potentials of order N in $\delta\rho$ or equivalently for the derivative

$$\phi'(\rho) \;=\; \kappa^2\delta\rho\left(1 + u_3\frac{\delta\rho}{\Delta\rho} + \cdots + u_N\Big(\frac{\delta\rho}{\Delta\rho}\Big)^{N-2}\right) \tag{31}$$

Matching the coefficient of the highest power either side of (30) is only possible if N satisfies

$$2N^2 - 11N + 12 = 0 \tag{32}$$

Remarkably, this gives an integer solution $N = 4$ implying that only quartic polynomials are allowed if $\Delta\phi(\rho)$ is truncated, leaving only the values of u_3 and u_4 to be determined. Substituting into (30) and matching yields the two conditions

$$u_3(n^2 - 1) = 0, \qquad 3u_4(4 - n^2) = 2u_3^2 \tag{33}$$

This leaves us with two options: If $u_3 \neq 0$, then we are restricted to $n = 1$ and $u_4 = 2u_3^2/9$. The condition $\phi'(\rho_c) = 0$ then gives $u_3 = 3$ and $u_4 = 2$, which is nothing other than the Landau quartic potential derived above. However, if $u_3 = 0$ but $u_4 \neq 0$ then the above requirements (33) are consistent with $n = 2$. The condition $\phi'(\rho_c) = 0$ then implies $u_4 = -4$. The density profile for this potential, which yields a single resonance at $\xi q = \sqrt{3}$, can be determined analytically as

$$\rho(z) \;=\; \rho_b \;\mp\; \Delta\rho\,\frac{(2 + \sqrt{2})e^{-\kappa|z|}}{3 + 2\sqrt{2} + e^{-2\kappa|z|}} \tag{34}$$

with the minus (plus) sign applying on the liquid (gas) side of the interface, while for the surface tension we find

$$\sigma \;=\; \frac{1}{3}\left(1 - \frac{1}{2\sqrt{2}}\right)\kappa\,(\Delta\rho)^2 \tag{35}$$

For this quartic potential, the relationship between the structure factor and the correlation function reduces to

$$S(z; q) \;=\; S_b(q) \;+\; \frac{\Delta\rho}{\rho'(0)}\,\frac{G(0, z; q) - G(0, z; \sqrt{3}\kappa)}{(1 + q^2\xi^2)\big(1 - \frac{q^2\xi^2}{3}\big)} \tag{36}$$

These explicit results are a hint that the SRM with $n = 2$ is, like the standard Landau potential, a new example of a fully analytically integrable model for $G(z, z'; q)$ and $S(z; q)$, which indeed it is. The results

will be discussed elsewhere but are similar to those obtained for the double-cubic model, which is discussed explicitly below.

SRMs also exist for $n = 3, 4, 5 \cdots$ and the potential, when expanded about the liquid density (say), has a scaling form $\Delta\phi(\rho) \propto \delta\rho^2\, W(x)$ where $x \equiv \alpha\,(\delta\rho/\Delta\rho)^n$ and the scaling function $W(x)$ has the expansion

$$W(x) \;=\; 1 \,+\, x \,-\, \frac{(n^2-4)}{4}\, x^2 \,-\, \frac{(n^2-1)(n^2-4)}{48\, n^4}\, x^3 \,+\, \cdots \tag{37}$$

which is valid for $n \geq 1$. It is apparent that $\Delta\phi(\rho)$ truncates at quartic order in $\delta\rho$ for $n = 1$ and $n = 2$, as discussed above. Even when $\Delta\phi(\rho)$ does not truncate, curtailing $W(x)$ at cubic order is indistinguishable from the solution for $\Delta\phi(\rho)$ found by numerically solving (30). The value of the pure number α can then be determined from the condition that $\phi'(\rho_c) = 0$.

In the limit of $n \to \infty$, the single resonance potential approaches the shape of a simple double parabola $\Delta\phi(\rho) = \kappa^2(\rho-\rho_l)^2/2$ (and similarly on the gas side $\Delta\phi(\rho) = \kappa^2(\rho-\rho_g)^2/2$). In this case, the relationship between $S(z;q)$ and $G(0,z;q)$ reduces to

$$S(z;q) = S_b(q) + \frac{\Delta\rho}{\rho'(0)}\,\frac{G(0,z;q)}{(1+q^2\xi^2)} \tag{38}$$

which, like the result (28) for the Landau quartic potential, does not display any resonance. These, however, are the only models (together with piece-wise combinations of them) for which resonances are entirely absent. As a check, we note that the explicit solutions for $S(z;q)$ and $G(0,z;q)$ within the double parabola model are completely consistent with the relation (38) [6].

3 The function $G(z,z';q)$ for the double-cubic potential

The potential for the double-cubic model is given by

$$\Delta\phi(\rho) = \begin{cases} \dfrac{\kappa^2}{2}\,(\rho-\rho_l)^2\left(1+\dfrac{4}{3}\,\dfrac{\rho-\rho_l}{\Delta\rho}\right) & \text{for } \rho > \rho_c \\[2ex] \dfrac{\kappa^2}{2}\,(\rho-\rho_g)^2\left(1-\dfrac{4}{3}\,\dfrac{\rho-\rho_g}{\Delta\rho}\right) & \text{for } \rho < \rho_c \end{cases} \tag{39}$$

which satisfies $\phi'(\rho_c) = 0$ as required. The density profile follows from solution of the Euler-Lagrange equation:

$$\rho(z) = \begin{cases} \rho_l - \dfrac{3}{4}\,\Delta\rho\,\mathrm{sech}^2\,\dfrac{\kappa(z-z_0)}{2} & \text{for } z > 0 \\[2ex] \rho_g + \dfrac{3}{4}\,\Delta\rho\,\mathrm{sech}^2\,\dfrac{\kappa(z+z_0)}{2} & \text{for } z < 0 \end{cases} \tag{40}$$

with $\kappa z_0 = \ln\frac{\sqrt{3}-1}{\sqrt{3}+1}$. The surface tension $\sigma = \int dz\,\rho'(z)^2$ is then easily computed:

$$\sigma = \frac{9-2\sqrt{3}}{30}\,\kappa\,(\Delta\rho)^2 \tag{41}$$

which, as noted in the main text is smaller than $\sigma_1 = \kappa\,(\Delta\rho)^2/4$. Substituting the profile into $\phi''(\rho)$ leads to the Ornstein-Zernike equation

$$\left(-\partial_z^2 + 1 + q^2 - 3\,\mathrm{sech}^2\,\frac{|z|-z_0}{2}\right)\, G(z,z';q) \;=\; \delta(z-z') \tag{42}$$

where, for ease of presentation, we have set $\kappa = 1$ or, equivalently, hereafter measure all lengths in units of ξ. This equation is very similar to the differential equation for $G(z,z';q)$ for the Landau quartic potential –

indeed, the only differences are the amplitude of the sech^2 term (which is 6 for the Landau potential) and the presence of a phase-like term z_0. Zittartz [10] obtained $G(z,z';q)$ for the Landau potential by recasting it as a simple Schrödinger equation for which the spectrum is known exactly [3]. Similar, and indeed more direct, methods apply here, allowing us to obtain $G(z,z';q)$ for the double-cubic model and actually for many other potentials $\phi(\rho)$. If $z \geq z' \geq 0$ (i.e. the particles are on the liquid side), we find that

$$G(z,z';q) \;=\; \alpha(q)\;\psi_-(z)\,\psi_+(z') \;+\; \beta(q)\;\psi_-(z)\,\psi_-(z') \tag{43}$$

while if $z' \geq 0 \geq z$ (i.e. they are on opposites sides of the interface)

$$G(z,z';q) \;=\; \gamma(q)\;\overline{\psi}_+(z)\,\psi_-(z') \tag{44}$$

where

$$\begin{aligned}
\psi_-(z) &= e^{-\kappa_q z}\left(\tau^3 + 2\kappa_q\tau^2 + (1+\tfrac{8}{5}q^2)\tau + \tfrac{8}{15}\kappa_q q^2\right)\\
\psi_+(z) &= e^{\kappa_q z}\;\left(\tau^3 - 2\kappa_q\tau^2 + (1+\tfrac{8}{5}q^2)\tau - \tfrac{8}{15}\kappa_q q^2\right)\\
\overline{\psi}_+(z) &= e^{\kappa_q z}\;\left(\bar\tau^3 - 2\kappa_q\bar\tau^2 + (1+\tfrac{8}{5}q^2)\bar\tau - \tfrac{8}{15}\kappa_q q^2\right)
\end{aligned} \tag{45}$$

and

$$\tau = \tanh\frac{z-z_0}{2}, \qquad \bar\tau = \tanh\frac{z+z_0}{2}, \qquad \kappa_q = \sqrt{1+q^2} \tag{46}$$

Recall we have set $\kappa = 1$, but the explicit dependence on the correlation length ξ is trivially re-instated dimensionally, if required. The amplitudes of the correlation function in the different regions are determined by

$$\begin{aligned}
\alpha(q) &= \frac{225}{q^2\kappa_q(5-4q^2)(3+4q^2)}\\
\beta(q) &= \frac{225\,(5+4q^2)}{4q^2\kappa_q(5-4q^2)(3+4q^2)\epsilon(q)}\\
\gamma(q) &= -\frac{225}{8q^2\epsilon(q)}
\end{aligned} \tag{47}$$

Here,

$$\epsilon(q) = \left(5 + 4\,q^2 + \frac{12}{\sqrt{3}}\kappa_q\right)\left(\frac{10}{\sqrt{3}} + \frac{12}{\sqrt{3}}\,q^2 + \kappa_q(5+4q^2)\right) \tag{48}$$

is a smooth monotonically increasing function of q that displays no divergences. Notice that, in the limit $q \to 0$, the functions $\psi_-(z)$, $\psi_+(z)$ and $\overline{\psi}_+(z)$ are all simply proportional to $\rho'(z)$. Indeed, it is straightforward to check that the explicit expression for $G(z,z';q)$ is in perfect keeping with the anticipated Wertheim-Weeks GM divergence as $q \to 0$, which can be established independently. Notice that, when z and z' are on the same side, the correlation function shows a new resonance at $\xi q = \sqrt{5}/2$, appearing as a singularity in $\alpha(q)$ and $\beta(q)$, and that there are no explicit resonances at $\xi q = \sqrt{3}, \sqrt{8}, \cdots$ which, recall, *are* present in the local structure factor. Similar to our discussion of $S(z;q)$, this means, for example, that at $\xi q = \sqrt{5}/2$ the function $G(z,z';q)$ has multiplicative corrections to higher-order exponentially decaying terms. Note, however, that there are no resonances in the amplitude $\gamma(q)$ determining the correlation function between particles across the interface.

With one particle at the origin, the analytic expression for the correlation function on the liquid side reduces to

$$G(0,z;q) \;=\; \frac{\tau^3 + 2\kappa_q\tau^2 + (1+\frac{8}{5}q^2)\tau + \frac{8}{15}q^2\kappa_q}{4\,q^2\left(\frac{1}{3} + \frac{4}{5\sqrt{3}}\kappa_q + \frac{4}{15}q^2\right)}\;\; e^{-\kappa_q z} \tag{49}$$

Integration of $G(0,z;q)$ determines $S(0;q)$ exactly

$$S(0;q) = \frac{\frac{2}{3} + \frac{4}{15}\,q^2 + \sqrt{\frac{1+q^2}{3}} - \frac{1}{5}\,q^2\,J(q)}{q^2\left(\frac{1}{3} + \frac{4}{5}\sqrt{\frac{1+q^2}{3}} + \frac{4}{15}\,q^2\right)} \tag{50}$$

where

$$J(q) = \int_0^\infty dz\ \ e^{-\sqrt{1+q^2}\,z}\,\tanh\left(\frac{z-z_0}{2}\right) \tag{51}$$

is itself a hypergeometric function. Similarly, integration of $G(z,z';q)$ determines $S(z;q)$. However, one can determine $S(z;q)$ much more easily by substituting $G(0,z;q)$ into our central result, the expression (4) in the main paper. This is a convenient approach because the sum is dominated by the first resonance at $\xi q = \sqrt{3}$. Indeed, the partial sum $\frac{\sigma}{\sigma_1} + \frac{\sigma}{\sigma_2} \approx 0.976$ implies that the contribution coming from the higher resonances is negligible, as the whole sum over the remaining terms must be equal to unity.

4 Particular and general solutions of the inhomogeneous Ornstein-Zernike equation

The explicit solution for $S(z;q)$ within square-gradient theory described above can be placed in a more general setting. Following the arguments described in [5], a particular solution of the Ornstein-Zernike equation, satisfying

$$\int dz'\ C(z,z';q)\,S_{ps}(z';q)\ =\ 1 \tag{52}$$

can be found each side of the interface by expanding the direct correlation function about the bulk density in a functional Taylor expansion. Since the density is assumed to decay in powers of $X = e^{-\kappa z}$ (on the liquid side, say), the particular solution must have an expansion $S_{ps} = S_l(q)(1 + \sum_{n=1} a_n(q)X^n)$, similar to that of the density profile - no other length scales can appear. The first two terms in this expansion describe the asymptotic decay, as shown in eqn. (2) of the main text. However, $S_{ps}(z;q)$ is not the general solution to the Ornstein-Zernike equation. Since the Ornstein-Zernike equation is linear in S, the general solution can be written $S(z;q) = S_{ps}(z;q) + S_{cf}(z;q)$, where the complementary function satisfies

$$\int dz'\ C(z,z';q)\,S_{cf}(z';q) =\ 0 \tag{53}$$

This implies immediately that each side of the origin $S_{cf}(z;q)$ decays in a similar manner to $G(0,z;q)$ – which is indeed the origin of the relation between $S(z;q)$ and $G(0,z;q)$ described for square-gradient theory. Here we merely wish to show that, in general, this implies the existence of resonances. In particular, we wish to determine the leading-order asymptotic decay $S_{cf}(z;q) \propto e^{-\lambda_0 z}$ (on the liquid side say). For large z, we can again expand the direct correlation function about the liquid density $C(z,z';q) = C_b(|z-z'|;q) + \mathcal{O}(\rho(z)-\rho_l)$, where $C_b(|z-z'|;q)$ is the 2D Fourier transform of the bulk liquid direct correlation function. Thus, the lengthscale λ_0 is determined from solution of

$$\int dz'\ C_b(|z-z'|;q)\ e^{-\lambda_0 z'}\ =\ 0 \tag{54}$$

which can be identified as a Laplace transform reducing to the condition

$$C_b\left(\sqrt{q^2-\lambda_0^2}\right) = 0 \tag{55}$$

Since, by definition, the zero of the Fourier transform of the direct correlation function $C_b\,(i\kappa) = 0$ identifies the (liquid) inverse bulk correction length, it follows that

$$\lambda_0\ =\ \sqrt{\kappa^2+q^2} \tag{56}$$

This is the general result for systems with short-ranged forces provided the decay is monotonic. The wave-vector dependent decay then implies that there must be resonances when κ_q is an multiple of κ since then the particular solution and complementary function are no longer independent. This means that, in general, the coefficients $a_n(q)$ in the expansion of $S_{ps}(z;q)$ each diverge at $q=0$ and at every resonance up to $\xi q = \sqrt{n^2-1}$. Given that $S(z;q)$ can only diverge at $q=0$, these resonances must be cancelled by $S_{cf}(z;q) \propto G(0,z:q)$ which, in turn, strongly constrains the relation between the structure factor and the correlation function.

5 Resonances within the Sullivan Model

The Sullivan model is based on the Helmholtz free-energy functional [7, 8, 9, 5]

$$\mathcal{F}[\rho] = \int d\mathbf{r}\, f_h\big(\rho(\mathbf{r})\big) \,+\, \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2\; \rho(\mathbf{r}_1)\, w(|\mathbf{r}_1-\mathbf{r}_2|)\, \rho(\mathbf{r}_2) \tag{57}$$

where $f_h(\rho)$ is the free-energy density for bulk hard-spheres, and the derivative $df_h(\rho)/d\rho = \mu_h(\rho)$ is the local hard-sphere chemical potential, which is a monotonically increasing function of ρ. The first term in (57) is a local density approximation for the repulsive hard-sphere contribution, and the intermolecular potential has a Yukawa form

$$w(r) \;=\; -\frac{\alpha}{4\pi r R^2}\; e^{-r/R} \tag{58}$$

where $-\alpha = \int d\mathbf{r}\, w(r)$ is the integrated strength and the range is R. Hereafter, without loss of generality, we set $R=1$ or, equivalently, measure all lengths in units of R. Minimization of the grand potential functional leads to the Euler-Lagrange equation for the density profile

$$\mu \;=\; \mu_h\big(\rho(\mathbf{r})\big) \,+\, \int d\mathbf{r}'\, \rho(\mathbf{r}')\; w(|\mathbf{r}-\mathbf{r}'|) \tag{59}$$

which, on taking the Laplacian of both sides, reduces to

$$\nabla^2 \mu_h\big(\rho(\mathbf{r})\big) \;=\; \mu_h\big(\rho(\mathbf{r})\big) \,-\, \mu \,-\, \alpha\, \rho(\mathbf{r}) \tag{60}$$

and, thus, for a planar interface,

$$\frac{d^2\mu_h}{dz^2} \;=\; \mu_h\big(\rho(z)\big) \,-\, \mu \,-\, \alpha\, \rho(z) \tag{61}$$

which is also similar to the ODE for the profile in square-gradient theory. The surface tension σ, which can be written [8]

$$\sigma \;=\; \frac{1}{\alpha}\int dz\, \left(\frac{d\mu_h}{dz}\right)^2, \tag{62}$$

is similar to the square gradient result.

We now show how the correlation function structure within the Sullivan Model can be mapped onto that of square-gradient theory allowing us to extend directly the analysis of the resonances. The direct correlation function is given by

$$C(\mathbf{r},\mathbf{r}') \;=\; \mu_h'\big(\rho(\mathbf{r})\big)\, \delta(\mathbf{r}-\mathbf{r}') \,+\, w(|\mathbf{r}-\mathbf{r}'|) \tag{63}$$

where $\mu_h'(\rho) = d\mu_h/d\rho$. This has the 2D Fourier transform [9, 4]

$$C(z,z';q) \;=\; \mu_h'\big(\rho(z)\big)\, \delta(z-z') \,-\, \frac{\alpha\, e^{-\sqrt{1+q^2}\,|z-z'|}}{2\sqrt{1+q^2}} \tag{64}$$

We begin with the local structure factor. In [5], it was shown that the Ornstein-Zernike equation reduces, after taking two derivatives w.r.t z, to

$$\left(-\partial_z^2 + q^2 + 1 - \alpha\frac{d\rho}{d\mu_h}\right)\Big(S(z;q)\,\mu_h'\big(\rho(z)\big)\Big) \;=\; 1 + q^2 \tag{65}$$

This simple ODE identifies the bulk structure factors $S_b(q) = 1/C_b(q)$ in the liquid ($b = l$) and gas ($b = g$) phases as

$$S_b(q) = \frac{S_b(0)}{1 + \dfrac{q^2\xi_b^2}{1 + q^2R^2}} \tag{66}$$

where

$$S_b(0) = \frac{1}{\mu_h'(\rho_b) - \alpha} \tag{67}$$

and identifies the Ornstein-Zernike correlation lengths ξ_b as

$$\frac{R}{\xi_b} \;=\; \sqrt{\frac{\mu_h'(\rho_b)}{\alpha} - 1} \tag{68}$$

where we have reinstated the lengthscale R. It follows that the function $H(z;q)$ defined as

$$H(z;q) \equiv \frac{S(z;q)\,\mu_h'\big(\rho(z)\big)}{1 + q^2} \tag{69}$$

solves the ODE

$$\left(-\partial_z^2 + q^2 + 1 - \alpha\frac{d\rho}{d\mu_h}\right)H(z;q) \;=\; 1 \tag{70}$$

the structure of which is identical to that for $S(z;q)$ in square-gradient theory. If we, therefore, define $H^{(2)}(z,z';q)$ as the Greens' function satisfying

$$\left(-\partial_z^2 + q^2 + 1 - \alpha\frac{d\rho}{d\mu_h}\right)H^{(2)}(z,z';q) \;=\; \delta(z - z') \tag{71}$$

so that

$$H(z;q) = \int dz'\; H^{(2)}(z,z';q) \tag{72}$$

we see that $H(z;q)$ and $H^{(2)}(z,z';q)$ are related in precisely the same way that $S(z;q)$ and $G(0,z;q)$ within square-gradient theory, provided that $d\rho/dz$ is replaced by $d\mu_h/dz$. It follows that, if we specialise to a class of free-energy densities $f_h(\rho)$ that have an Ising symmetry, we can write

$$H(z;q) = H_b(q) + \frac{\Delta\mu_h\,\dot\mu_h(z)}{\tilde\sigma_1\,q^2}\frac{H_b(q)}{H_b(0)} + \frac{\Delta\mu_h}{\dot\mu_h(0)}\sum_{n=2}^{\infty}\frac{\tilde\sigma}{\tilde\sigma_n}\,\frac{H^{(2)}\big(0,z;q\big) - H^{(2)}\big(0,z;\sqrt{n^2-1}\,\kappa\big)}{(1 + q^2(\xi^T)^2)\big(1 - \frac{q^2(\xi^T)^2}{n^2-1}\big)} \tag{73}$$

where $\dot\mu_h(z) \equiv d\mu_h(\rho(z))/dz$, $\Delta\mu_h = \mu_h(\rho_l) - \mu_h(\rho_g)$, $\xi^T \equiv 1/\kappa = \sqrt{\xi_b^2 + R^2}$ is the true bulk correlation length, and $H_b(q) = 1/(\kappa^2 + q^2)$. The coefficients $\tilde\sigma_n$ satisfy the summation $\sum 1/\tilde\sigma_n = 1/\tilde\sigma$, where $\tilde\sigma = \alpha\,\sigma$.

Finally, we turn to the relation between the Green's function $H^{(2)}(z,z';q)$ and the density-density correlation function $G(z,z';q)$. Applying the Laplacian operator to the OZ equation reduces it to Eq. (71) identifying that

$$\alpha\,H^{(2)}(z,z';q) \;=\; \mu_h'\big(\rho(z)\big)\,\mu_h'\big(\rho(z')\big)\;G(z,z';q) \qquad\qquad (z \neq z') \tag{74}$$

Substitution into (73) then reduces it to our central result for the Sullivan model

$$S(z;q) = S_b(q)\,\gamma(z) + \frac{\Delta\rho\,\rho'(z)}{\sigma_1\,q^2}\frac{S_b(q)}{S_b(0)} + \frac{\Delta\rho}{\rho'(0)}\,\frac{S_b(q)}{S_b(0)}\sum_{n=2}^{\infty}\frac{\sigma}{\sigma_n}\,\frac{G\big(0,z;q\big) - G\big(0,z;\sqrt{n^2-1}\,\kappa\big)}{\big(1 - \frac{q^2(\xi^T)^2}{n^2-1}\big)} \tag{75}$$

where

$$\gamma(z) \;=\; \frac{\mu_h'(\rho_b)}{\mu_h'(\rho(z))} \tag{76}$$

Apart from this additional factor $\gamma(z)$ in front of the first term, this is identical to the result for the square-gradient theory. Note that it is the true correlation length that appears in the resonance contributions $\mathcal{R}_n(z;q)$. The counting of resonances and the classification of potentials is then identical to the square-gradient theory with $1-\alpha\, d\rho/d\mu_h$ playing the role of $\phi''(\rho)$. Thus, there exist single resonance models, for which specific resonances are absent, as well as models which are fully analytically integrable. Indeed, this allows us to immediately write the highly accurate approximations for the local structure factor, total structure factor and correlation function at the origin (where $\dot{\mu}_h(z)$ reaches its maximum):

$$\frac{S(0;q)}{S_b(q)} \;\approx\; \gamma(0) \;+\; \frac{\Delta\rho\rho'(0)}{\sigma q^2 S_b(0)} \tag{77}$$

$$\frac{S_{\rm TOT}(q)}{S_b(q)} \;\approx\; \int dz\, \gamma(z) \;+\; \frac{(\Delta\rho)^2}{\sigma\, q^2\, S_b(0)} \tag{78}$$

and

$$\frac{G(0,0;q)}{G_b(0;q)} \;\approx\; \gamma(0)^{\,2} \;+\; \frac{\rho'(0)^2}{\sigma q^2 G_b(0;0)} \tag{79}$$

Finally, we turn attention to the inclusion of the liquid-gas asymmetry where, as an example, we discuss the local structure factor at the origin $S(0;q)$. Each side of the origin, the local structure $S(z,q)$ has a particular solution written as an expansion similar to (75) but with different bulk structure factors and coefficients σ_n on the liquid and gas sides. This expansion captures the locations of the resonances which now occur at different wave vectors each side of the interface. Continuity of $S(z,q)$ is achieved simply by adding an appropriate complimentary function proportion to $G(0,z;q)$, the amplitude of which is different on the liquid and gas asides. This complementary function is very well approximated by $\rho'(z)\, e^{-\Delta\kappa_b(q)|z|}$, where $\Delta\kappa_b(q)=\sqrt{\kappa_b^2+q^2}-\kappa_b$, and κ_b is the inverse true bulk correlation length on the liquid (l) and gas (g) sides. This approximation encapsulates the correct small q and large z behaviours, and leads to

$$S(0;q) \;\approx\; f(q)\,\gamma_g\, S_g(q) + \big(1-f(q)\big)\,\gamma_l\, S_l(q) + \frac{\Delta\rho\,\rho'(0)}{\sigma q^2}\left(f(q)\,\frac{S_g(q)}{S_g(0)} + \big(1-f(q)\big)\,\frac{S_l(q)}{S_l(0)}\right) \tag{80}$$

identifying the appropriate weighting factor $f(q) \;=\; \Delta\kappa_g(q)/\big(\Delta\kappa_g(q)+\Delta\kappa_l(q)\big)$, which is wave-vector dependent. This result also identifies the weighting of the separate bulk enhancements γ_g and γ_l, defined as $\gamma_b = \mu_h'(\rho_b)/\mu_h'(\rho(0))$.

References

[1] R. Evans. The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids. *Adv. Phys.*, 28:143, 1979.

[2] S. Fisk and B. Widom. Structure and Free Energy of the Interface between Fluid Phases in Equilibrium near the Critical Point. *J. Chem. Phys.*, 50:3219, 1969.

[3] L.D. Landau and E.M. Lifshitz. *Quantum Mechanics*. Addison-Wesley, 1958.

[4] A. O. Parry and R. Evans. Correlation functions in the approach to complete drying at a wall liquid interface. *Mol. Phys.*, 65:455, 1988.

[5] A. O. Parry, C. Rascón, and R. Evans. The local structure factor near an interface; beyond extended capillary-wave models . *J. Phys.: Condens. Matter*, 28:244013, 2016.

[6] A. O. Parry, C. Rascón, G Willis, and R. Evans. Pair correlation functions and the wavevector-dependent surface tension in a simple density functional treatment of the liquid–vapour interface . *J. Phys.: Condens. Matter*, 26:355008, 2014.

[7] D. E. Sullivan. Van der Waals model of adsorption. *Phys. Rev. B*, 20:3991, 1979.

[8] D. E. Sullivan. Surface-tension and contact-angle of a liquid-solid interface. *J. Chem. Phys.*, 74:2604, 1981.

[9] P. Tarazona and R. Evans. Long ranged correlations at a solid-fluid interface. A signature of the approach to complete wetting. *Mol. Phys.*, 47:1033, 1982.

[10] J. Zittartz. Microscopic Approach to Interfacial Structure in Ising-like Ferromagnets. *Phys. Rev.*, 154:529, 1967.