Pole topology of the structure functions of continuous systems

Christian Tutschka[1] and Gerhard Kahl[2]
[1]*Departamento de Matemáticas, Universidad Carlos III de Madrid, Avenida de la Universidad 30, 28911-Leganés, Spain*
[2]*Institut für Theoretische Physik and CMS, TU Wien, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria*
(Received 13 February 2002; published 29 April 2002)

We develop a theory of the pole topology of the Laplace transform of the structure functions of continuous N component systems based on the Wiener-Hopf technique. We classify systems according to the spectrum of the $N\times N$ matrix $\tilde{Q}(t)$, with elements $\tilde{Q}_{ij}(t)=\delta_{ij}-2\pi\sqrt{\rho_i\rho_j}\int e^{-tr}q_{ij}(r)dr$, associated with their factor functions $q_{ij}(r)$. For the simplest nontrivial class of systems—namely, that with only two eigenvalues of $\tilde{Q}(t)$ different from one—a full and explicit analysis of the pole topology is possible. We illustrate the theory with exactly solvable examples, such as the Percus-Yevick equation for arbitrary mixtures of hard spheres (HS) and polydisperse HS and the mean spherical model for binary mixtures of adhesive spheres.

DOI: 10.1103/PhysRevE.65.051104 PACS number(s): 05.20.−y, 02.30.−f, 82.70.−y

I. INTRODUCTION

The Wiener-Hopf (WH) factorization technique has—since its invention in 1931—proved to be an immensely important method in mathematical physics. It provides one of the very few approaches to obtain exact solutions to a class of integral equations [1]. Its applicability to problems in the theory of exactly solvable statistical mechanical models was first demonstrated by Baxter [2] in 1968. Baxter not only did present in detail the function theoretic background of the method, from which a general transformation of the Ornstein-Zernike (OZ) relation between the direct and the total correlation function follows, but also illustrated the elegance of the WH technique by reexamining the Percus-Yevick (PY) solution for hard spheres (HS) (see, e.g., Wertheim [3] for a related approach).

In 1970 Baxter generalized his analysis to the case of N component systems [4]. The specific example treated in detail was the PY equation for an N component system of HS. During the 1970s several models beyond HS were solved exactly via the WH technique: Perram and Smith [5] derived a solution of the PY equation for multicomponent systems of adhesive HS (AHS), Blum and Høye [6] solved the mean spherical model (MSM) for HS Yukawa (HSY) mixtures [immediately afterwards also the examination of the MSM for the special case of mixtures of charged HS (CHS) via the WH decomposition was started [7]], and at the end of the decade Blum and Stell [8] already extended the technique to the polydisperse case: they solved the PY equation for polydisperse HS in 1979. The structure functions of the MSM for polydisperse CHS [9] and AHS [10,11] were obtained not before the late 1990s, and the thermodynamic functions of the MSM for a polydisperse system of AHS only with the turn of the century [12,13].

As shown, for instance, in [14], the WH formalism can also be used for numerical calculations of the pair distribution functions over the entire r range in a convenient way.

The main step in the WH factorization of the OZ relation is the introduction of an additional function, the so-called factor function $q_{ij}(r)$. In this paper we will be mainly concerned with the algebraic and analytic properties of this function for the following reasons. Let us denote by $\hat{h}_{ij}(k)$ and $\hat{c}_{ij}(k)$ the three-dimensional Fourier transforms of the total $h_{ij}(r)$ and the direct correlation function $c_{ij}(r)$ of an N component system, where r is the distance between the particles of species i and j, and let $\hat{H}_{ij}(k)=2\pi\sqrt{\rho_i\rho_j}\hat{h}_{ij}(k)$ as well as $\hat{C}_{ij}(k)=2\pi\sqrt{\rho_i\rho_j}\hat{c}_{ij}(k)$, with $\rho_i=c_i\rho$ the partial particle density and c_i the concentration of component i, and $\rho=\Sigma_i\rho_i$ the total particle density. Then the OZ relation becomes (in matrix notation, with E being the unit matrix)

$$[E-\hat{C}(k)][E+\hat{H}(k)]=E. \tag{1}$$

The WH factorization of Eq. (1) uses the positive definiteness of the complete direct correlation function, which translates in Fourier space to the decomposition [4] (T denotes the transpose of a matrix)

$$E-\hat{C}(k)=\hat{Q}^T(-k)\hat{Q}(k), \tag{2}$$

where

$$\hat{Q}_{ij}(k)=\delta_{ij}-2\pi\sqrt{\rho_i\rho_j}\int e^{ikr}q_{ij}(r)dr \tag{3}$$

with δ_{ij} the usual Kronecker delta. The matrix $\hat{Q}(k)$ [with elements $\hat{Q}_{ij}(k)$] is analytic and nonsingular in the upper half k plane. On using the factorization (2) and the OZ relation (1) we have that

$$\hat{Q}(k)[E+\hat{H}(k)]=[\hat{Q}^T(-k)]^{-1}. \tag{4}$$

Now, since $\hat{Q}^T(-k)$ is analytic and nonsingular in the lower half k plane, the singularities of $\hat{H}(k)$ are determined by the roots of

$$\det\hat{Q}(k)=0 \tag{5}$$

in the lower half k plane. This shows that, by using the WH technique, the problem of the transform inverse of $\hat{H}(k)$ may be reduced to the determination of the singularities of $\hat{Q}(k)$ in the lower half k plane, and hence the importance of the algebraic and analytic properties of $q_{ij}(r)$.

Methods based on this observation appeared in the 1980s [15] and are nowadays known as asymptotic representations (AR) (for an historic overview, see, e.g., [16]); they represent an easy to use and yet accurate tool to compute the pair distribution functions $g_{ij}(r)$ directly from the $\hat{h}_{ij}(k)$ for intermediate and large r values. So far, AR have been presented in detail for the PY equation of binary HS [16], for the PY equation and the MSM for binary AHS [17], and for the MSM for binary HSY systems [18]. For all these models, the singularities of $\hat{H}(k)$ are an infinite sequence of poles. But the singularities are not always poles: Smith [19] has solved the MSM for a generalized Yukawa system with a branch cut in the lower half k plane.

Restricting ourselves here to cases where all the singularities are poles, the two main properties of the distribution of roots of $\det \hat{Q}(k)$ [of poles of $\hat{H}(k)$] in the lower half k plane are the following.

(i) The root k_1 closest to the real k axis determines the asymptotic behavior of $h_{ij}(r)$ for $r \to \infty$: if $-ik_1 \in \mathbb{R}$, then the $h_{ij}(r)$ converge to their asymptotic values exponentially monotonic, or if $-ik_1 \in \mathbb{C}$, then exponentially oscillatory. The crossover of these two behaviors was termed Fisher-Widom (FW) line [20]. The concept of the FW line was reintroduced by Evans respective Henderson and their colleagues in the 1990s [21,22] (and subsequent papers). They also examined the relevance of the FW line for *nonuniform* systems. The common asymptotic behavior of all partial total correlation functions was discovered by Martynov [23].

(ii) In contrast to the singularities closest to the real k axis, much less is known, from a mathematical point of view, about the overall distribution of poles, which we refer to as *pole topology*: it is only known that the complete sequence of poles is necessary to represent the thermodynamics of the system correctly [15,18], and it was conjectured that—at least for two-component systems—the poles arrange typically in two branches [16–18]. So far a proof of this conjecture was obtained only for the special case of the MSM for symmetric binary mixture of AHS [17]. A general mathematical theory is not available yet.

In this paper we start such a qualitative theory of the distribution of roots of $\det \hat{Q}(k)$ in the lower half k plane. First, we reduce the problem by considering the algebraic properties of $\hat{Q}(k)$. This part can be carried out in complete generality and is based on an examination of the eigenvalues of $\hat{Q}(k)$. Second, we deal with the much less handy analytic properties of $\hat{Q}(k)$ to derive results on the pole topology: for this part we restrict ourselves to examples of the simplest nontrivial class of systems, namely, that with only two eigenvalues of $\hat{Q}(k)$ different from one, such as the PY equation for an N component and a polydisperse mixture of HS and the MSM for binary mixtures of AHS. For these cases the function theoretic problem involved can be settled. The generalizability of these results to more complicated systems is discussed in concluding remarks.

II. POLE TOPOLOGY

A. Algebraic classification

At the outset let us change from Fourier to Laplace space. Of course, the two transforms are completely equivalent in the complex plane. There is no special reason for going over to Laplace space apart from making contact with previous papers [16–18].

We start our analysis with a classification of continuous N component systems according to the spectrum of the matrix $\tilde{Q}(t)$, with elements [cf. (3)]

$$\tilde{Q}_{ij}(t) = \delta_{ij} - 2\pi\sqrt{\rho_i \rho_j}\int e^{-tr} q_{ij}(r)\,dr. \tag{6}$$

We denote by $\{\lambda_i(t)\}_{1 \leq i \leq N}$ the spectrum of $\tilde{Q}(t)$. Then we have

$$\det \tilde{Q}(t) = \prod_{i=1}^{n} \lambda_i(t), \quad n \leq N, \tag{7}$$

where any eigenvalue of multiplicity m is counted as m of the N eigenvalues. Now, let us classify N component systems according to n. Generically, we have $n=N$, but, surprisingly enough, for several exactly solved models n is a small integer for all N (and hence also in the stochastic limit [24]): for the PY equation of HS mixtures $n \leq 2$ [8], for the MSM of mixtures of CHS $n \leq 3$ [25], and for the MSM of Lorentz-Berthelot mixtures of AHS $n \leq 5$ [10] or $n \leq 3$ [11].

For $n=1$, nothing is to be shown, since there is only one sequence of roots of $\det \tilde{Q}(t)=0$ in the left half (LH) t plane. As the first nontrivial case, let us consider the class characterized by $n=2$, that contains—in principle—all two-component systems and also the PY equation for HS mixtures with arbitrary $N \geq 2$ (including thus polydisperse HS). In particular, it was conjectured that for the solution (i) of the PY equation for N component HS [16,18], (ii) of the MSM for binary AHS [17], and (iii) of the MSM for binary HSY [18] the poles in the LH t plane arrange typically in two branches. Subsequently, we prove this conjecture for the examples (i) and (ii), as well as for the PY solution of polydisperse HS, at least as $|t| \to \infty$.

B. Analytic properties

1. PY equation for HS mixtures

Consider an N component system of HS with diameters R_i. Introduce $R_{ij} = \frac{1}{2}(R_i + R_j)$, $S_{ij} = \frac{1}{2}(R_i - R_j)$, and enumerate the components in order of increasing R_i, so that $S_{ji} > 0$. Fix $R_N = 1$. Then the solution of the PY equation for HS mixtures can be written in the form [4]

$$q_{ij}(r) = \theta(r - S_{ij})\left[\frac{a_i}{2}(r - R_{ij})^2 + (b_i + a_i R_{ij})(r - R_{ij})\right] \times \theta(R_{ij} - r) \tag{8}$$

with the Heaviside function θ and

$$a_i = \frac{1}{1-\xi_3} + \frac{3R_i\xi_2}{(1-\xi_3)^2}, \quad \frac{R_i}{1-\xi_3} = a_i R_i + 2b_i, \tag{9}$$

where

$$\xi_\alpha = \frac{\pi}{6} \sum_i \rho_i R_i^\alpha, \quad \alpha \in \mathbb{N}. \tag{10}$$

Hence, on following Blum and Stell [8], it is found that

$$\det \tilde{Q}(t) = \det D_N(t), \tag{11}$$

where

$$D_N(t) = \begin{pmatrix} 1 + \frac{6\xi_2}{(1-\xi_3)t} - \frac{6[\xi_1 - m_1(t)]}{(1-\xi_3)t^2}, & \frac{12\xi_1}{(1-\xi_3)t} - \frac{6\xi_2}{1-\xi_3} - \frac{12[\xi_0 - m_0(t)]}{(1-\xi_3)t^2} \\ -\frac{1}{t} - \frac{3[\xi_2 - m_2(t)]}{(1-\xi_3)t^2}, & 1 + \frac{6\xi_2}{(1-\xi_3)t} - \frac{6[\xi_1 - m_1(t)]}{(1-\xi_3)t^2} \end{pmatrix} \tag{12}$$

with

$$m_\alpha(t) = \frac{\pi}{6} \sum_i \rho_i e^{-tR_i} R_i^\alpha, \quad \alpha \in \mathbb{N}. \tag{13}$$

Now use Eq. (11) to write $\det \tilde{Q}(t) = 0$ in the form of a quadratic equation in e^{-t},

$$\sum_{k=0}^{2} d_k(t) e^{-kt} = 0, \tag{14}$$

where the coefficients $d_k(t)$ are found upon using Eqs. (12) and (10) to be

$$d_0(t) = u(t)^2 - v(t)w(t), \tag{15}$$

$$d_1(t) = -\frac{12w(t)\mu_0(t)}{(1-\xi_3)t^2} + \frac{12u(t)\mu_1(t)}{(1-\xi_3)t^2} - \frac{3v(t)\mu_2(t)}{(1-\xi_3)t^2}, \tag{16}$$

$$d_2(t) = \frac{36[\mu_1(t)^2 - \mu_0(t)\mu_2(t)]}{(1-\xi_3)^2 t^4}, \tag{17}$$

with

$$u(t) = 1 + \frac{6\xi_2}{(1-\xi_3)t} - \frac{6\xi_1}{(1-\xi_3)t^2}, \tag{18}$$

$$v(t) = -\frac{6\xi_2}{1-\xi_3} + \frac{12\xi_1}{(1-\xi_3)t} - \frac{12\xi_0}{(1-\xi_3)t^2}, \tag{19}$$

$$w(t) = -\frac{1}{t} - \frac{3\xi_2}{(1-\xi_3)t^2}, \tag{20}$$

and $\mu_\alpha(t) = e^t m_\alpha(t)$. Denote the two solutions of Eq. (14) by $\chi_{1,2}(t)$. Then we find for the two sets of roots of $\det \tilde{Q}(t)$ in the LH t plane, written as $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$ (the latter sequence contains the roots closer to the imaginary axis)

$$e^{-t_k^{(1)}} = \omega_1(t_k^{(1)}), \tag{21}$$

$$e^{-t_k^{(2)}} = \omega_2(t_k^{(2)}), \tag{22}$$

where the functions $\omega_{1,2}(t)$ are defined via the solutions $\chi_{1,2}(t)$ so that the roots closer to the imaginary axis are elements of $\{t_k^{(2)}\}$.

Since the coefficients $d_k(t)$, which build up the right-hand side of Eqs. (21) and (22), are not very handy functions in t (and in the $2N$ system parameters), we consider instead the leading order asymptotic behavior of the $\omega_{1,2}(t)$ as $|t| \to \infty$ in the LH t plane. Upon using definitions (15), (16), and (17), it is found via (18), (19), and (20) that

$$e^{-t_k^{(1)}} \asymp \left. \frac{t^2 \left(1 - \xi_3 + \frac{3}{2}\xi_2\right) e^{-2tS_{N(N-1)}}}{2\pi \rho_{N-1} S_{N(N-1)}^2} \right|_{t=t_k^{(1)}}, \tag{23}$$

$$e^{-t_k^{(2)}} \asymp -\left. \frac{t^2}{2\pi \rho_N \left(\frac{1}{1-\xi_3} + \frac{3\xi_2}{2(1-\xi_3)^2}\right)} \right|_{t=t_k^{(2)}}, \tag{24}$$

as $|t| \to \infty$ in the LH t plane. This is our principal result. It shows that the two sequences $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$ are exponentially separated [in the sense that the quotient of the right-hand side (RHS) of Eqs. (23) and (24) is an exponential function in t for any given set of system parameters]. In addition, it states for $\{t_k^{(1)}\}$ that the number of roots inside a box with a subset of $\{t_k^{(1)}\}$ in its interior, decreases with increasing $S_{N(N-1)}$, and that both $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$ move closer to the imaginary axis as ρ increases. Of course, the detailed structure of the distribution of roots is clearly outside the realm of this asymptotic analysis.

2. PY equation for polydisperse HS

In the probabilistic description of polydisperse systems of HS, introduced by Salacuse [24], the particles are uniquely characterized by their diameters R, where R is distributed according to a continuous probability density $f(R)$. In the thermodynamic limit the systems have a composition given by $f(R)$, and contain (with probability one) a countable infinity of distinct particles. Hence an N particle polydisperse system can be interpreted as an N component system with $\rho_i=\rho/N$. It is this fact that allows $D_N(t)$ [and so $\det\tilde{Q}(t)$] to be generalized from the N component to the polydisperse case. Based on Eqs. (11), (12), and the law of large numbers, it is found that $\det\tilde{Q}(t)$ of the PY solution for polydisperse HS is given by [8,24]

$$\det\tilde{Q}(t)=\det D_\infty(t)\equiv\det\begin{pmatrix} 1+\frac{6\xi_2}{(1-\xi_3)t}-\frac{6[\xi_1-m_1(t)]}{(1-\xi_3)t^2} & \frac{12\xi_1}{(1-\xi_3)t}-\frac{6\xi_2}{1-\xi_3}-\frac{12[\xi_0-m_0(t)]}{(1-\xi_3)t^2} \\ -\frac{1}{t}-\frac{3[\xi_2-m_2(t)]}{(1-\xi_3)t^2} & 1+\frac{6\xi_2}{(1-\xi_3)t}-\frac{6[\xi_1-m_1(t)]}{(1-\xi_3)t^2} \end{pmatrix}, \tag{25}$$

with the generalized moments (cf. [26])

$$m_\alpha(t)=\frac{\pi}{6}\rho\int f(R)e^{-tR}R^\alpha\,dR,\quad \alpha\in\mathbb{N}, \tag{26}$$

and the moments

$$\xi_\alpha=m_\alpha(0),\quad \alpha\in\mathbb{N}. \tag{27}$$

A frequently used standard distribution for $f(R)$ is the Γ distribution. But as already stated in [27], the latter one gives for arbitrarily large particles nonzero probabilities, which is unphysical, whereas realistic distributions should have only finite support. Hence, we choose $f(R)$ to be a beta distribution, which satisfies this requirement,

$$f(R)=\frac{1}{B(a,b)}R^{a-1}(1-R)^{b-1}I_{(0,1)}(R),\quad a,b\in\mathbb{R}_+, \tag{28}$$

where $I_{\mathcal{A}}$ is the indicator function of the set $\mathcal{A}$, and $B(a,b)=\int_0^1 x^{a-1}(1-x)^{b-1}\,dx$ is known as beta function. In the following we restrict ourselves to $a,b\in\mathbb{N}\backslash\{0\}$. Then the beta function simplifies to $B(a,b)=[(a-1)!(b-1)!]/(a+b-1)!$.

Now we have, as for the case of HS mixtures, that $\det\tilde{Q}(t)=\det D_\infty(t)$, and that $D_\infty(t)$ is formally identical with $D_N(t)$. Hence, the two sequences of roots of $\det\tilde{Q}(t)=0$, $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$, are formally given by Eqs. (21) and (22), where in the functions $d_k(t)$ the ξ_α and $m_\alpha(t)$ of Eqs. (10) and (13) are replaced by their generalizations (27) and (26).

In general, even for $a,b\in\mathbb{N}\backslash\{0\}$, the solutions $\omega_{1,2}(t)$ are complicated functions in t. Thus, let us again consider the asymptotic behavior of the $\omega_{1,2}(t)$ as $|t|\to\infty$ in the LH t plane. We find via Eqs. (28), (26), and (25) [and by using the definitions (15)–(17)] that for $a,b\in\mathbb{N}\backslash\{0\}$,

$$e^{-t_k^{(1)}}\asymp\frac{(-1)^b 2B(a,b)}{\pi\rho\, b!}\left(1-\xi_3+\frac{3}{2}\xi_2\right)t^{b+4}\Bigg|_{t=t_k^{(1)}}, \tag{29}$$

$$e^{-t_k^{(2)}}\asymp-\frac{(-1)^b B(a,b)}{2\pi\rho(b-1)!\left(\frac{1}{1-\xi_3}+\frac{3\xi_2}{2(1-\xi_3)^2}\right)}t^{b+2}\Bigg|_{t=t_k^{(2)}}, \tag{30}$$

as $|t|\to\infty$ in the LH t plane. As for HS mixtures, the two sequences of roots $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$ are shifted towards the imaginary axis with increasing particle density ρ. However, for the solution of the PY equation for polydisperse HS, these two branches of roots are now polynomially separated.

3. MSM for binary AHS

So far, we analyzed the pole topology of the PY equation for an N component system of HS and polydisperse HS. We found for both cases two branches of poles, that are asymptotically separated for any given set of system parameters. The sequences separate exponentially fast for HS mixtures, whereas for polydisperse HS $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$ separate polynomially fast as $|t|\to\infty$ in the LH t plane.

Now let us apply our technique to an exactly solvable model with an attractive interaction. One of the simplest extensions of the PY solution for N component HS is the MSM for N component AHS [10], characterized by one additional set of parameters, the interaction strength (or stickiness) γ_{ij}. We examine the pole topology of the MSM for binary AHS. The treatment of the case $N=2$ gives also the opportunity to put the results of [17] for the simplified case of the MSM for symmetric binary AHS into context.

Consider an N component system of AHS with diameters R_i and stickiness $\gamma_{ij}=\gamma_{ji}\in\mathbb{R}_+$ between particles of species i and j [5]. Enumerate the components in order of increasing R_i, so that $S_{ji}\geqslant 0$, and fix again $R_N=1$. Apply the WH technique in the usual way. Then the solution of the MSM for an N component system of AHS in terms of $q_{ij}(r)$ is [10]

$$q_{ij}(r)=\theta(r-S_{ij})\left[\frac{a_i}{2}(r-R_{ij})^2+(b_i+a_iR_{ij})(r-R_{ij})+\Gamma_{ij}\right]\times\theta(R_{ij}-r) \tag{31}$$

with

$$a_i=\frac{1-12\zeta_i}{1-\xi_3}+\frac{3R_i\xi_2}{(1-\xi_3)^2},\quad \frac{R_i}{1-\xi_3}=a_iR_i+2b_i, \tag{32}$$

where the ξ_α are given by Eq. (10) and

$$\zeta_i=\frac{\pi}{6}\sum_k \rho_k\Gamma_{ik}R_k,\quad \Gamma_{ij}=\gamma_{ij}R_{ij}^2. \tag{33}$$

On substituting Eq. (31) into Eq. (6), it is found that (cf. [17])

$$\tilde{Q}_{ij}(t)=\delta_{ij}+2\pi\sqrt{\rho_i\rho_j}[e^{-tR_{ij}}f_{ij}^{(0)}(t)+e^{-tS_{ij}}f_{ij}^{(1)}(t)] \tag{34}$$

with

$$f_{ij}^{(0)}(t)=\frac{a_i}{t^3}+\frac{a_iR_j+\frac{R_i}{1-\xi_3}}{2t^2}+\frac{\Gamma_{ij}}{t}, \tag{35}$$

$$f_{ij}^{(1)}(t)=\frac{a_iR_j}{t^2}+\frac{R_iR_j}{2(1-\xi_3)t}-f_{ij}^{(0)}(t). \tag{36}$$

Now let us examine the distribution of roots of $\det\tilde{Q}(t)$ for the case $N=2$. Then, as in the proof for HS, we have that $\det\tilde{Q}(t)=0$ can be rewritten as algebraic equation of degree 2 in e^{-t}, $\Sigma_{k=0}^{2}d_k(t)e^{-kt}=0$, where the coefficients $d_k(t)$ follow from Eq. (34),

$$d_0(t)=1+2\pi[\rho_1f_{11}^{(1)}(t)+\rho_2f_{22}^{(1)}(t)] +4\pi^2\rho_1\rho_2[f_{11}^{(1)}(t)f_{22}^{(1)}(t)-f_{12}^{(1)}(t)f_{21}^{(1)}(t)], \tag{37}$$

$$d_1(t)=2\pi[\rho_1f_{11}^{(0)}(t)e^{2tS_{21}}+\rho_2f_{22}^{(0)}(t)] +4\pi^2\rho_1\rho_2\{f_{22}^{(0)}(t)f_{11}^{(1)}(t)-f_{12}^{(0)}(t)f_{21}^{(1)}(t) +[f_{11}^{(0)}(t)f_{22}^{(1)}(t)-f_{21}^{(0)}(t)f_{12}^{(1)}(t)]e^{2tS_{21}}\}, \tag{38}$$

$$d_2(t)=4\pi^2\rho_1\rho_2e^{2tS_{21}}[f_{11}^{(0)}(t)f_{22}^{(0)}(t)-f_{12}^{(0)}(t)f_{21}^{(0)}(t)]. \tag{39}$$

Thus, the two sets of roots of $\det\tilde{Q}(t)=0$ are formally given by Eqs. (21) and (22), where Eqs. (37)–(39) are used as definitions for the coefficients $d_k(t)$.

Finally, let us again analyze the asymptotic behavior of the solutions $\omega_{1,2}(t)$ as $|t|\to\infty$ in the LH t plane. Let Γ be the matrix with elements Γ_{ij}. Assume $\det\Gamma\neq 0$. Then, upon using definitions (37)–(39) in Eqs. (21) and (22), it is found that

$$e^{-t_k^{(1)}}\asymp\begin{cases} -\left.\dfrac{\Gamma_{22}te^{-2tS_{21}}}{2\pi\rho_1\det\Gamma}\right|_{t=t_k^{(1)}} & \text{if } S_{21}\in(0,\tfrac{1}{2}),\\ -\left.\dfrac{(\rho_1\Gamma_{11}+\rho_2\Gamma_{22})t}{4\pi\rho_1\rho_2\det\Gamma}\left(1+\sqrt{1-\dfrac{4\rho_1\rho_2\det\Gamma}{(\rho_1\Gamma_{11}+\rho_2\Gamma_{22})^2}}\right)\right|_{t=t_k^{(1)}} & \text{if } S_{21}=0,\end{cases} \tag{40}$$

$$e^{-t_k^{(2)}}\asymp\begin{cases} -\left.\dfrac{t}{2\pi\rho_2\Gamma_{22}}\right|_{t=t_k^{(2)}} & \text{if } S_{21}\in(0,\tfrac{1}{2}),\\ -\left.\dfrac{(\rho_1\Gamma_{11}+\rho_2\Gamma_{22})t}{4\pi\rho_1\rho_2\det\Gamma}\left(1-\sqrt{1-\dfrac{4\rho_1\rho_2\det\Gamma}{(\rho_1\Gamma_{11}+\rho_2\Gamma_{22})^2}}\right)\right|_{t=t_k^{(2)}} & \text{if } S_{21}=0,\end{cases} \tag{41}$$

as $|t|\to\infty$ in the LH t plane. Hence we have two cases.

(i) For $S_{21}\in(0,\frac{1}{2})$, the two sequences of roots $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$ are exponentially separated (as for HS mixtures), and also the number of roots in a given box with a subset of $\{t_k^{(1)}\}$ in its interior decreases with increasing S_{21}. The two branches are shifted toward the imaginary axis with increasing ρ.

(ii) For $S_{21}=0$ (i.e., equally sized particles), the quotient of the RHS of (40) and (41) is a constant function in t for any given set of parameters. In particular, there is only one branch of roots for (where $c_1^{(1,2)}$ denotes the two solutions for the concentration c_1),

$$c_1^{(1,2)}(\Gamma)=\frac{\Gamma_{22}}{\operatorname{tr}\Gamma-2\dfrac{\Gamma_{12}}{\Gamma_{22}}(\Gamma_{12}\mp\sqrt{-\det\Gamma})}. \tag{42}$$

If we assume $\gamma_{12}=0$, then Eq. (42) simplifies to

$$c_1(\Gamma)=\frac{1}{1+\frac{\Gamma_{11}}{\Gamma_{22}}}, \tag{43}$$

so that if we interpret the stickiness as a function of the reciprocal temperature (see, e.g., [28]), then Eq. (43) describes a line in the concentration-temperature plane, where there is only one branch of roots. One-component HS are recovered in Eq. (43) via $\gamma_{11}=0$ ($c_1=1$) or $\gamma_{22}=0$ ($c_1=0$), and one-component AHS via $\gamma_{22}=\gamma_{11}$ ($c_1=\frac{1}{2}$). Moreover, if we specialize Eqs. (40) and (41) to the case of symmetric binary AHS, $\gamma_{22}=\gamma_{11}$ and $\gamma_{12}=\mu\gamma_{11}$, then the results (38) and (39) in [17] are reproduced. Finally, the usual shift of the branches toward the imaginary axis with increasing ρ is also encountered.

III. CONCLUDING REMARKS

We started a theory of the pole topology of the structure functions of continuous N component systems based on the WH technique. Our method consists of two stages. First, we determine the number of eigenvalues n ($\leqslant N$) of $\widetilde{Q}(t)$ different from 1, and reduce the problem of the overall distribution of the poles to an analysis of the solutions of an algebraic equation in e^{-t} of degree n. As an immediate consequence of this algebraic stage, we find at most n poles on the negative real axis in the t plane.

The second, analytic stage consists in the mathematical analysis of the qualitative features of these n solutions in the LH t plane. In general, they are arbitrarily complicated functions in t (and in the systems parameters). Going beyond the trivial case $n=1$, we provided for $n=2$ an asymptotic analysis for three exactly solvable examples. For the PY equation of N component HS we found that the two sequences of poles $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$ separate exponentially fast as $|t|\to\infty$ in the LH t plane, whereas for the solution of the PY equation for polydisperse HS (with a composition given by a beta distribution), $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$ are polynomially separated. For the case of the MSM for binary AHS we found two different asymptotic behaviors: If $S_{21}\in(0,\frac{1}{2})$, then the two sequences are again exponentially separated, whereas if $S_{21}=0$ (equally sized particles), then the quotient of the RHS of the two equations which determine $\{t_k^{(1)}\}$ and $\{t_k^{(2)}\}$, Eqs. (40) and (41), is a constant function in t. For the latter case we found conditions such that only one branch of poles exists.

Finally, from a mathematical point of view we can say that, although we could give elementary proofs for the above examples, an analysis for arbitrary n will have to apply computer mathematics in a nontrivial way. From a physical point of view our results might be of value in a thermodynamic interpretation of the pole topology [18]. We hope that this contribution will inspire further research in this direction.

ACKNOWLEDGMENTS

We thank Bob Evans, Karl Grill, and Roman Schnabl for useful conversations. C.T. is grateful to the Austrian Science Foundation (FWF) for financial support (Grant No. J2076). This research was also funded by the FWF under Project Nos. P13062-TPH and P14371-TPH.

[1] B. Noble, *Methods Based on the Wiener-Hopf Technique* (Chelsea, New York, 1988).
[2] R.J. Baxter, Aust. J. Phys. **21**, 563 (1968).
[3] M.S. Wertheim, J. Math. Phys. **5**, 643 (1964).
[4] R.J. Baxter, J. Chem. Phys. **52**, 4559 (1970).
[5] J.W. Perram and E.R. Smith, Chem. Phys. Lett. **35**, 138 (1975).
[6] L. Blum and J.S. Høye, J. Stat. Phys. **19**, 317 (1978).
[7] L. Blum, J. Stat. Phys. **22**, 661 (1980).
[8] L. Blum and G. Stell, J. Chem. Phys. **71**, 42 (1979); **72**, 2212 (1980).
[9] D. Gazzillo, A. Giacometti, and F. Carsughi, J. Chem. Phys. **107**, 10 141 (1997).
[10] C. Tutschka and G. Kahl, J. Chem. Phys. **108**, 9498 (1998).
[11] D. Gazzillo and A. Giacometti, J. Chem. Phys. **113**, 9837 (2000).
[12] M. Ginoza, Mol. Phys. **99**, 1613 (2001).
[13] C. Tutschka and G. Kahl, Phys. Rev. E **64**, 031104 (2001).
[14] E. Arrieta, C. Jedrzejek, and K.N. Marsh, J. Chem. Phys. **95**, 6806 (1991).
[15] J.W. Perram and E.R. Smith, J. Phys. A **13**, 2219 (1980).
[16] G. Kahl and G. Pastore, J. Phys. A **24**, 2995 (1991).
[17] C. Tutschka, G. Kahl, and E. Riegler, Mol. Phys. **100**, 1025 (2002).
[18] C. Tutschka, G. Kahl, and G. Pastore, Phys. Rev. E **63**, 061110 (2001).
[19] E.R. Smith, Mol. Phys. **38**, 823 (1979).
[20] M.E. Fisher and B. Widom, J. Chem. Phys. **50**, 3756 (1969).
[21] J.R. Henderson and Z.A. Sabeur, J. Chem. Phys. **97**, 6750 (1992).
[22] R. Evans, J.R. Henderson, D.C. Hoyle, A.O. Parry, and Z.A. Sabeur, Mol. Phys. **80**, 755 (1993).
[23] G.A. Martynov, *Fundamental Theory of Liquids: Method of Distribution Functions* (Adam Hilger, Bristol, 1992).
[24] J.J. Salacuse, J. Chem. Phys. **81**, 2468 (1984).
[25] L. Blum and J.S. Høye, J. Phys. Chem. **81**, 1311 (1977).
[26] P. Sollich, P.B. Warren, and M.E. Cates, Adv. Chem. Phys. **116**, 265 (2001).
[27] L. Bellier-Castella, H. Xu, and M. Baus, J. Chem. Phys. **113**, 8337 (2000).
[28] G. Stell, J. Stat. Phys. **63**, 1203 (1991).