Infinite compressibility states in the Hierarchical Reference Theory of fluids. I. Analytical considerations

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In its customary formulation for one-component fluids, the Hierarchical Reference Theory yields a quasilinear partial differential equation (PDE) for an auxiliary quantity f that can be solved even arbitrarily close to the critical point, reproduces non-trivial scaling laws at the critical singularity, and directly locates the binodal without the need for a Maxwell construction. With the present contribution commences a short series of reports aiming at the systematic exploration of the behavior of f for thermodynamic states of diverging isothermal compressibility κ_T as the renormalization group theoretical momentum cut-off approaches zero. Focussing on purely analytical considerations first, we find three classes of asymptotic solutions compatible with infinite κ_T, characterized by uniform or slowly varying bounds on the curvature of f, by monotonicity of the build-up of diverging κ_T, and by stiffness of the PDE in part of its domain, respectively. A seeming contradiction between two of these alternatives and an asymptotic solution derived earlier [Parola *et al.*, Phys. Rev. E **48**, 3321 (1993)] is easily resolved.

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I. INTRODUCTION

Reconciling the vastly different approaches to fluid structure and thermodynamics afforded by classical integral equation (IE) formalisms and renormalization group (RG) theory, respectively, the Hierarchical Reference Theory (HRT, [1–7]) presents itself as a particularly effective instrument for studying the critical region and liquid-gas phase equilibrium in simple one-component fluids: For subcritical temperatures, $T < T_c$, the usual formulation of the theory [1, 7] yields density intervals of rigorously flat free energy and, hence, infinite isothermal compressibility κ_T the boundaries of which are readily identified with the densities ϱ_v and ϱ_l of the coexisting gas and liquid phases. The binodal so found terminates at some temperature $T = T_c$ and density $\varrho = \varrho_c$ in a liquid-gas critical point characterized by non-classical, partly Ising-like exponents [2]. And far away from the coexistence region of the phase diagram, HRT reduces to one of the standard approximations of liquid state theory, *viz.*, the popular scheme commonly known under the names of Lowest-Order γ Ordered Approximation (LOGA, [8, 9]) and Optimized Random-Phase Approximation (ORPA, [10]). HRT's unified treatment of thermodynamic states so diverse should be contrasted with the limitations inherent in approaches based on IEs alone: Close to the critical point these generally do not have a solution or else develop major deficiencies, and the binodal is accessible only by way of a Maxwell construction [11]. RG calculations alone, on the other hand, while invaluable for illuminating the scaling relations valid asymptotically close to the critical point, generally do not allow one to determine non-universal quantities such as, *e. g.*, the *loci* of the critical point and the binodal. A theory like HRT that provides comprehensive structural and thermodynamic information both close to and away from the critical point and exhibits a non-trivial scaling limit is thus clearly attractive for applications calling for high-resolution data on the behavior of a fluid in the critical region.

In the present series of reports we want to have a closer look at the solution of the HRT equations for thermodynamic states of diverging compressibility, *i. e.*, at the critical point and at phase coexistence. Our motivation for this inquiry is twofold: First of all, we aim to extend our understanding of the way in which HRT achieves its remarkable description of criticality and phase separation beyond mere invocation of its conceptual ingredients, RG theory and thermodynamic consistency (*v. i.*) in particular. Instead, it is on the level of the partial differential equation (PDE) itself and the corresponding finite difference (FD) approximations used in practical calculations that we want to understand the mechanism responsible for the suppression of van der Waals loops and the emergence of a singular limit of κ_T in an extended part of the phase diagram. A second reason for our investigation lies in our earlier work on HRT and its numerical side [12–14]: For all the merits of the theory, its practical application has been found to be troubled with two major difficulties that have been traced to the customary way of incorporating the core condition of vanishing pair distribution function for hard core reference systems, and to the numerical properties of the equations for high compressibility, respectively. The latter clearly is an issue of prime importance when focussing on phase separation and the immediate vicinity of the critical point where κ_T diverges, and its severity can only be assessed on the basis of a thorough understanding of the numerical process in relation to the properties of the HRT PDE. Evidently, such an understanding is also highly relevant to the interpretation of numerical results and the extraction of meaningful and reliable information from them.

In order to shed some light on these questions, in this first part of the present series of reports we study the solution of the PDE by analytical means to characterize and investigate the possible types of behavior that are compatible with the general properties of HRT and a singular limit of κ_T. Relegating some details to the appendix, after a short introduction to HRT itself and its conceptual basis in section II we present the PDE, identify a quantity convenient for following the build-up of infinite compressibility, and infer the asymptotic scaling relations we base our work on. Employing a suitably formalized notion of smoothness, in sections III through VI we formulate a sequence of three scenarios for the gradual build-up of infinite κ_T, clarify their preconditions, and infer some of their properties with a view to an eventual implementation by FD methods. According to their most prominent traits we refer to the classes of asymptotic solutions that we find as the "genuinely smooth" (section III), the "monotonous" (section V), and the "stiff" or only "effectively smooth" (section VI) ones, respectively. Of these, only the first seems to be compatible with an earlier analysis of HRT's scaling limit at first sight [6]; however, a closer investigation into the assumptions implicit in the simplifications made there leads to a reappraisal of those results that therefore cannot invalidate either of the remaining two candidate types of solution (section VII).

As the considerations outlined above do not take into account the initial and boundary conditions imposed on the PDE but rather concern themselves with a summary analysis of the asymptotic behavior of the various terms in the PDE and of the range of solution types compatible with these, the all-important question of which of the scenarios captures the true behavior cannot be answered in the present contribution. In part II of the present series of reports [15], however, we will present a host of numerical evidence that strongly suggests that thermodynamic states of infinite compressibility render the PDE stiff whereas its numerical integration still yields a smooth solution that is to be regarded as a mere artifact of the use of FD methods on practical discretization grids. Due to the characteristics of the stiff scenario, however, its realization also strongly affects the interpretation of numerical results and the methods of data analysis to be applied to them; part III [16] will be devoted to these questions and discuss some of the phenomena encountered on non-uniform high-resolution discretization grids.

II. BASIC RELATIONS

As a starting point, let us shortly review the concepts underlying HRT when applied to simple one-component fluids, recalling some of its central notions and establishing the equations we will base our work on; for a more detailed account of the derivation, its physical justification and relation to both the IE formalism and RG theory as well as the modifications necessary for dealing with other physical systems, most notably spin models and fluid mixtures, we refer the reader to refs. 1, 12 and further references therein. For consistency with our earlier work on HRT we employ a number of notational conventions that can be found in the appendix: Most importantly, a tilde indicates Fourier transformation, and once a symbol has been introduced we generally omit the obvious function arguments where they do not add to the understanding. The appendix also serves as a repository for some of the more cumbersome analytical expressions as well as for auxiliary definitions and relations tangential to our reasoning but necessary to make our presentation self-contained.

Working in the grand-canonical ensemble we consider a system of particles interacting *via* pair-wise additive forces taken to derive from a potential $v(r) = v^{\mathrm{ref}}(r) + w(r)$. For the sake of simplicity, the potentials are assumed ϱ independent, and we restrict the reference fluid corresponding to v^{ref} alone to a system of hard spheres of diameter σ, *i. e.*, $v^{\mathrm{ref}}(r)$ is infinite for $r < \sigma$ and vanishes otherwise. The perturbation $w(r)$ and temperature T enter the calculation only in the combination $\phi(r) = -\beta\, w(r)$, where $\beta = 1/k_B T$ and k_B is Boltzmann's constant.

Based on this splitting of v, a momentum space cutoff Q is introduced by the device of a rather artificial [17] Q dependent potential $v^{(Q)}(r)$ obtained from $v(r)$ by the elimination from w of all Fourier components $\tilde{w}(k)$ with $k < Q$, *i. e.*,

$$v^{(Q)}(r) = v^{\mathrm{ref}}(r) + w^{(Q)}(r),$$
$$\tilde{w}^{(Q)}(k) = \begin{cases} \tilde{w}(k) & : \; k > Q \\ 0 & : \; k < Q. \end{cases}$$

Clearly, the reference and target systems with potentials v^{ref} and v are obtained in the limits $Q \to \infty$ and $Q \to 0$, respectively. A rather intricate analysis of a resummed perturbation expansion for the properties of the $(Q - \Delta Q)$ system in terms of those of the Q system at the same temperature and density in the limit $\Delta Q \to 0$ [3] finally yields a non-terminating hierarchy of first-order ordinary differential equations (ODEs) in Q for the free energy $A^{(Q)}(\varrho)$ and the n particle direct correlation functions. Formally, these differential equations allow one to follow the evolution of structure and thermodynamics of the Q systems when fluctuations of ever increasing wavelength $1/Q$ are taken into account, *i. e.*, when Q goes from infinity to zero and $v^{(Q)}$ is transformed from v^{ref} into v.

Such an infinite set of coupled ODEs is, of course, hardly tractable numerically, let alone analytically. As a remedy, a closure on the two-particle level resembling LOGA/ORPA, eq. (A4) in the appendix, is customarily adopted and combined with only the first HRT equation giving the Q dependence of $A^{(Q)}$. As demonstrated in ref. 12, if HRT's ability to describe phase coexistence is not to be lost, it is vital to also incorporate a condition of thermodynamic consistency into the closure: In HRT's standard formulation this takes the form of the compressibility sum rule (A5) relating $\kappa_T^{(Q)}$ as obtained by differentiation of the free energy to the volume integral of the direct correlation function at arbitrary Q. Due to the density derivatives so introduced the ODEs at fixed ϱ give way to a single PDE in Q and ϱ for the free energy that is to be solved on the semi-infinite strip $\mathcal{D}$ where $\varrho_{\min} \le \varrho \le \varrho_{\max} \wedge \infty > Q \ge 0$. The precise choice of the initial and boundary conditions that remain to be imposed at $Q = \infty$, at $\varrho = \varrho_{\min}$, and at $\varrho = \varrho_{\max}$ is of no importance for the remainder of this work, and we refer the reader to refs. 12–14 for a more detailed discussion of this point.

Discretization of the PDE for the free energy so obtained is straightforward and yields a computational scheme that can, indeed, successfully be used for $T > T_c$; for close-to-critical and subcritical temperatures, however, attempts at a direct solution invariably fail to produce any results [5, 14]. In order to remedy this situation, Tau *et al.* [7] proposed an alternative formulation in terms of an auxiliary quantity $f(Q, \varrho)$ that is essentially the first Q derivative of the free energy; just as in our previous work on HRT [12–14], in the present contribution we rely on a slightly different definition for f detailed in the appendix, *cf.* eq. (A3). Further specializing to density-independent potentials and not explicitly including the core condition that is not expected to be relevant to the subject of our study, the PDE can be written in quasilinear form,

$$\frac{\partial f}{\partial Q} = d_{00}[f; Q, \varrho] + d_{02}[f; Q, \varrho]\,\frac{\partial^2 f}{\partial \varrho^2}, \tag{1}$$

with initial and boundary conditions that directly follow from those imposed in the original formulation.

The rather lengthy expressions for the coefficients d_{00} and d_{02} of eq. (1) are to be found in the appendix, as are the defining relations for a number of auxiliaries. Among these the quantity $\varepsilon(Q, \varrho) \equiv \bar{\varepsilon}(Q, \varrho) + 1$ is of particular relevance to our reasoning: Essentially the exponential of f, it turns out proportional to the isothermal compressibility of the fully interacting system, *cf.* eq. (A6). Infinite κ_T therefore directly implies attendant divergences at $Q = 0$ in ε, $\bar{\varepsilon}$, and f, and we have to study the large-$\bar{\varepsilon}$ behavior of the PDE if we are to understand the description of the critical region afforded by HRT on the level of the PDE.

On the other hand, $f(Q, \varrho)$ is guaranteed by the construction of the HRT hierarchy to be continuous and finite for every non-vanishing cutoff Q and to coincide with its limit from above at $Q \to 0$ wherever that limit exists. In other words, for thermodynamic states (T, ϱ) within the coexistence part of the phase diagram f must take on large but finite values for sufficiently small but non-vanishing values of Q but diverge for $Q \to 0$: If $\kappa_T(\varrho)$ is infinite, for every threshold F there is a corresponding cutoff $Q_F(\varrho) > 0$ such that $f(Q, \varrho) > F$ for all $Q < Q_F(\varrho)$, or, less formally,

$$\kappa_T(\varrho) = \infty \Longleftrightarrow \begin{cases} \lim_{Q\to 0} f(Q, \varrho) = \infty \\ f(Q, \varrho) < \infty : Q\sigma > 0 \\ f(Q, \varrho) \gg 1 : Q\sigma \ll 1, \end{cases} \tag{2}$$

which is the very basis of the main arguments of the present report. Considering large $\bar{\varepsilon}(Q, \varrho)$ and assuming that f diverges more strongly than just logarithmically (*v. i.*, section V), inspection of the expressions in the appendix shows both of the coefficients of the quasilinear PDE (1) to be of first order in $\bar{\varepsilon}$ whereas f is essentially the logarithm of $\bar{\varepsilon}$:

$$\begin{aligned} d_{02} &= \mathbf{O}(\bar{\varepsilon}), \\ d_{00} &= \mathbf{O}(\bar{\varepsilon}), \\ f &= \mathbf{O}(1). \end{aligned} \tag{3}$$

The reason for using $\bar{\varepsilon} = \varepsilon - 1$ rather than the seemingly more natural ε in the above relations is the small-$\tilde{\phi}$ behavior of the coefficients d_{0i}, *cf.* part III [16] as well as appendix (A.3) of ref. 14. $\mathbf{O}$ and its companion $\mathbf{o}$ are the usual Landau symbols, and here as in the remainder of the present series of reports $x = \mathbf{O}(y^a)$ is taken to actually mean that a is the infimum of all b for which $x = \mathbf{o}(y^b)$ when the implied limit is $y \to \infty$, or else the supremum when considering $y \to 0$. Furthermore, qualification of some quantity x as "essentially" independent of some other quantity y is equivalent to the characterization of x as of order $\mathbf{O}(1)$ in y which does not rule out a weak, say, logarithmic y dependence of x.

In order to understand the properties of the solution of the PDE around some point $(Q, \varrho) \in \mathcal{D}$ we still need to supplement eq. (3) with an analogous characterization of the behavior of the remaining term on the right hand side of eq. (1), *viz.*, $\partial^2 f/\partial\varrho^2$. Lacking any *a priori* information to guide us, in this report we adopt the simple *ansatz*

$$\frac{\partial^2 f}{\partial \varrho^2} = \mathbf{O}(\bar{\varepsilon}^r), \qquad r \ge 0, \tag{4}$$

a choice that is sufficiently general to admit a consistent description both of the behavior of the exact solution and of the computational process yielding a numerical approximation of it. Inserting eqs. (3) and (4) into the PDE (1), comparison of both sides of the equation immediately yields

$$\begin{gathered} \frac{\partial f}{\partial Q} = \mathbf{O}(\bar{\varepsilon}^s), \\ s = \max(1, 1 + r) = 1 + r; \end{gathered} \tag{5}$$

only for $r = 0$ is there the added possibility of a cancellation of the leading terms on the right hand side of eq. (1) that might give rise to an s less than unity, including $s = r = 0$. At any rate, neither r nor s may be negative.

Equipped with eqs. (3) through (5) we are now in a position to gain a better understanding of the PDE's workings; and although the analytical expressions presented and orders cited below hinge on the assumption (4), most of our conclusions are expected to remain qualitatively valid even for more general situations, *cf.* section V in part II [15].

III. SIMPLISTIC SMOOTH SOLUTION SCENARIO

From the PDE itself the Q and ϱ scales characteristic of the variations of $f(Q,\varrho)$ in the integration domain $\mathcal{D}$ are hardly apparent; in particular, we cannot say *a priori* whether they remain bounded from below in an essentially $\bar{\varepsilon}$ and, hence, temperature independent way throughout $\mathcal{D}$ or else scale like some inverse power at least of $\bar{\varepsilon}$ and so become arbitrarily small in part of $\mathcal{D}$ whenever the temperature falls below T_c. Restricting ourselves to analytical considerations, in this report we will study and present arguments for both of these types of solution, referring to them as smooth and non-smooth, respectively. Clearly, this distinction is highly relevant to the numerics and therefore of immediate practical interest: After all, smoothness implies that finite difference (FD) schemes are in principle well applicable to the PDE at hand whereas otherwise local truncation errors will generally be unbounded and at least an estimate of the global error incurred must be obtained *a posteriori* in order to gauge the significance of any information extracted from FD approximations of the PDE.

For this section turning to the assumption of f being smooth in the sense stated — an assumption that we will repeatedly refer to as leading to the "simplistic," or "genuinely smooth," scenario —, we immediately conclude that $r=s=0$: If the Q and ϱ scales set by f are bounded from below in the manner indicated, for any linear differential operator L we can choose $\bar{\varepsilon}$ independent step sizes ΔQ and $\Delta\varrho$ such that an FD approximation of Lf becomes accurate throughout $\mathcal{D}$. As the estimate so obtained is just a linear combination of f values sampled few ΔQ and $\Delta\varrho$ apart, Lf is bound to scale like f and is thus of order $\mathbf{O}(1)$ in $\bar{\varepsilon}$. Specializing to $L\equiv\partial^2/\partial\varrho^2$ and to $L\equiv\partial/\partial Q$ we immediately conclude that $r=0$ and $s=0$, respectively. — As an application we note for future reference that growth of f in proportion to an inverse power of the cutoff, $f\propto 1/Q^a$ at fixed ϱ with $a>0$, always falls into the class of genuinely smooth solutions: Obviously, $\partial f/\partial Q$ then goes like $1/Q^{a+1}$, *i. e.*, $\partial f/\partial Q\sim f^{(a+1)/a}$ which is of order $\mathbf{O}(1)$ in the exponential of f; and as the form of f is then independent of Q, so are the density scales characteristic of the variation of the solution.

The main advantage afforded by the presupposition of smoothness is that it allows us to understand on the level of the PDE the build-up of infinite f and κ_T close to the critical point and in the coexistence region of the phase diagram: Let us assume that, at some fixed and sufficiently small cutoff Q, $f(Q,\varrho)$ is a function of ϱ like that sketched in fig. 1: continuously differentiable for all densities, convex and large for densities in a range with approximate boundaries ϱ_1 and ϱ_2 but rather small elsewhere. Focussing on the region of large f and, hence, very large $\bar{\varepsilon}$ where asymptotic reasoning along the lines of eqs. (3) through (5) is applicable, we find the PDE coefficient d_{00} to be dominated by terms related to the Q dependence of the Fourier transforms of the potential and of the reference system direct correlation function,

$$d_{00}\sim-\frac{\partial(\tilde{\phi}/\tilde{\mathcal{K}})}{\partial Q}\,\frac{\tilde{\mathcal{K}}^2\,\bar{\varepsilon}^2}{\varepsilon}\,\frac{\tilde{\phi}_0^2}{\tilde{\phi}^4}\qquad\text{for }\tilde{\phi}\,\varepsilon\gg1,\tag{6}$$

cf. eq. (A1). This expression is expected to be negative for most cutoffs less than the position of the first minimum of $\tilde{\phi}$, and certainly for very small Q; it is by this standard that the cutoff under consideration must be "sufficiently small" as stated before. — Trivially, we also see from eq. (A1) that d_{02} is non-positive throughout $\mathcal{D}$, and negative for $\bar{\varepsilon}\neq0$, as $\tilde{\phi}_0$ must be positive for the PDE to be stable at all, *cf.* section 2.4.1 of ref. 14 as well as refs. 1, 7.

With this knowledge of the signs of d_{00} and d_{02} we now turn to the remaining term on the right hand side of eq. (1): Evidently, $\partial^2f/\partial\varrho^2$ is negative throughout most of the density interval of large f, and positive on either side as f falls to small values. On the other hand, according to fig. 1 the maximum of f is rather flat so that $|\partial^2f/\partial\varrho^2|$ is quite small there. Assuming this curvature so small that the d_{02} term in eq. (1) does not reverse the sign of the right hand side, we immediately conclude that $\partial f/\partial Q<0$ where f is large. As the physically relevant limit proceeds towards $Q=0$ from above, negative $\partial f/\partial Q$ means that f further increases as the final result is approached, which provides a simple explanation of the way in which the PDE implements the gradual build-up of infinite κ_T as fluctuations of ever larger wavelength are taken into account.

This line of thought, however, depends not only on the emergence of an intermediate solution like that sketched in fig. 1 at sufficiently small Q but also on the stability of the general form of its outline as the cutoff goes to zero: In particular, the build-up is likely to break down once flatness is lost in the central part of the interval $[\varrho_1,\varrho_2]$. A closer look at the d_{02} term immediately reveals that it acts to stabilize this feature of the form of f: Taken by itself, d_{00} strongly favors f to grow most rapidly close to its maximum. This, however, is prevented by the considerable increase in the negative density curvature of the solution it would entail: The correspondingly large contribution $d_{02}\left(\partial^2f/\partial\varrho^2\right)>0$ to $\partial f/\partial Q$ effectively counteracts d_{00} and so ensures that $f(Q,\varrho)$, $\varrho_1\lesssim\varrho\lesssim\varrho_2$, remains flat even as it grows, just as postulated at the outset. Close to ϱ_1 and ϱ_2, on the other hand, the *rôle* of the d_{02} term is quite different: There the curvature $\partial^2f/\partial\varrho^2$ turns positive so that both terms on the right hand side of eq. (1) now contribute to the growth of f, thereby rendering the transition to small f ever more abrupt as Q progresses towards zero. By the same token, intermediate minima in the density range of large

f are also dissolved by the d_{02} term, which relaxes the precondition of conformance with fig. 1 somewhat.

In summary, on the basis of the analytical properties of the various terms of the PDE alone we have thus arrived at a satisfactory and intuitively appealing mental picture of the mechanism responsible for the emergence of infinite κ_T and clear phase boundaries: Once the form of f resembles that of fig. 1 at low enough cutoff so that eqs. (3) through (5) apply, for $\varrho_1 \lesssim \varrho \lesssim \varrho_2$ the solution proceeds to ever larger f in a stable manner as Q approaches zero. At the same time ϱ_1 and ϱ_2 become ever more sharply defined and eventually develop into the densities ϱ_v and ϱ_l of the coexisting gas and liquid, respectively. Right at ϱ_v and ϱ_l, however, anything but continuous inverse compressibility is hard to accomodate, which agrees well with the known coincidence of the HRT binodal and spinodal for space dimensionality $d = 3$ [6]. The key *rôle* played by the d_{02} term in stabilizing the solution and locating the densities of the pure phases once more highlights the importance of thermodynamic consistency that caused the transition from ODEs to a PDE involving partial derivatives with respect to ϱ in the first place: Indeed, it should come as no surprise that application of an approximation incompatible with the afore-mentioned compressibility sum rule yields pathological results with ill-defined ϱ_v and ϱ_l as well as negative compressibility [12].

In the absence of evidence to the contrary, it is then tempting to subscribe to the seemingly natural assumption of a smooth solution: Not only does this provide the basis for understanding the most salient features of HRT as just discussed, but it is also what has been found in an early analysis of HRT's scaling limit [6], *cf.* section VII below. Unfortunately, however, this view of the PDE's character in the asymptotic region is not entirely unproblematic. Postponing discussion of numerical effects to part II [15], the conceptual difficulties derive from the requirement that not only r but s, too, must vanish, *v. s.*: According to the remark following eq. (5), $r = s = 0$ is compatible with the asymptotic relations (3) through (5) only if the right hand side of eq. (1) is affected by massive cancellation so that the sum of two terms of order $\mathbf{O}(\bar{\varepsilon})$ each is reduced to order $\mathbf{O}(1)$; and indeed do the relevant signs — $d_{02} \leq 0$ throughout $\mathcal{D}$ [eq. (A1)], $d_{00} < 0$ for small Q [eq. (6)], and $\partial^2 f/\partial\varrho^2 < 0$ for $\varrho_1 \lesssim \varrho \lesssim \varrho_2$ (fig. 1) — allow such a cancellation. On the other hand, the rapid growth of the coefficient functions $d_{0i} = \mathbf{O}(\bar{\varepsilon})$ places rather stringent constraints on the shape of f at constant cutoff: In particular, for $s = 0$ eqs. (1) and (3) to (5) show that $f = \mathbf{O}(1)$ must deviate by terms of order $\mathbf{O}(1/\bar{\varepsilon})$ only from an exact solution $\hat{f}(Q, \varrho)$ of the non-linear ODE

$$\frac{\partial^2 \hat{f}}{\partial \varrho^2} = -\frac{d_{00}[\hat{f}; Q, \varrho]}{d_{02}[\hat{f}; Q, \varrho]}. \tag{7}$$

Let us now suppose that the initial and boundary conditions imposed on the HRT PDE actually lead to such a near-solution of the above ODE at some sufficiently small Q, assessment of the likelihood of which falls outside the scope of this report. In this case consistency with $s = 0$ requires the residue $f - \hat{f}$ of eq. (7) to vanish as $1/\bar{\varepsilon}$ when Q further progresses towards zero, but we have not been able to support this behavior of the solution on the basis of the explicit expressions (A1) for the d_{0i} and their properties. Whereas the cancellation necessary for the genuinely smooth scenario thus certainly cannot be ruled out, it clearly poses much more stringent preconditions than the stable mechanism of growth discussed before, and both its genesis and stability remain unclear at this point.

IV. REFINED ANALYSIS

If the strong point of the simplistic scenario just discussed is the insight into HRT's description of phase separation it provides, its main conceptual difficulty lies in the uncertain standing of the cancellation requirement without which vanishing exponent s cannot be accomodated. On the other hand, nowhere did we actually make use of $s = 0$ in explaining the growth of f, the stability of the pattern displayed in fig. 1, or the emergence of clear phase boundaries ϱ_v and ϱ_l. It thus seems pertinent to attempt to salvage the advantages of the simplistic picture in a less restricted setting by eliminating the assumption of vanishing s. But rather than separately discussing the case of $r = 0$, $s = 1$ we now turn to the full generality afforded by eqs. (4) and (5). Of course, if $\partial^2 f/\partial\varrho^2$ is of order $\mathbf{O}(\bar{\varepsilon}^r)$ in $\bar{\varepsilon}$ with $r > 0$, at fixed cutoff f must be a rapidly oscillating function of ϱ and we can only hope to adapt the simplistic scenario if f resembles fig. 1 when averaged over oscillations.

Let us now consider the evolution of $f(Q, \varrho)$ for a fixed density ϱ within the region of large $\bar{\varepsilon}$, *i. e.*, for $\varrho_1 < \varrho < \varrho_2$: Combining eq. (5) with the definition (A2) of $\bar{\varepsilon}$ we find

$$\frac{\partial f}{\partial Q} = \mathbf{O}(\bar{\varepsilon}^s) = \mathbf{O}(e^{fs'}),$$
$$s' = s\,\tilde{u}_0^2.$$

Here the modified exponent s' takes into account the deviation of $\tilde{u}_0(Q) \propto \hat{\phi}(Q)$ from unity; for $Q \to 0$, s and s' do, of course, coincide by virtue of the normalization condition $\tilde{u}_0(0) = 1$. We now define an auxiliary quantity

$$\begin{aligned} d_0(Q) &= \frac{d_{00}[f; Q, \varrho] + d_{02}[f; Q, \varrho]\ \left(\partial^2 f/\partial\varrho^2\right)}{e^{fs'}} \\ &= \mathbf{O}(1), \end{aligned} \tag{8}$$

where the order cited is obtained under the assumption that no cancellation of the kind required in the simplistic model occurs. Obviously, the evolution of f is now governed by

$$\frac{\partial f}{\partial Q} = d_0\, e^{fs'}, \tag{9}$$

which is completely equivalent to the PDE (1) as existence of a solution $f(Q,\varrho)$ implies existence of d_0 [we choose to ignore the complications brought about by the possibility of eq. (1) only having a weak solution]. Furthermore, the signs of d_0 and $\partial f/\partial Q$ always coincide.

If only for the moment we assume s' constant, eq. (9) can be formally integrated to yield the solution at all Q given the initial condition that f be f_1 at cutoff Q_1, *viz.*,

$$f(Q) = -\frac{1}{s'}\ln\left(e^{-f_1 s'} + s'\int_Q^{Q_1} d_0(q)\,\mathrm{d}q\right). \qquad (10)$$

This result is valid only if $s' \propto s\,\tilde{\phi}^2$ does not vanish, *i. e.*, if $s > 0$ and $\tilde{\phi} \neq 0$. The latter condition effectively restricts our arguments to cutoffs somewhat below $Q_{\tilde{\phi},1}$, the smallest of the zeros $Q_{\tilde{\phi},i}$ ($i = 1, 2, \ldots$, $Q_{\tilde{\phi},i} < Q_{\tilde{\phi},i+1}$) of the Fourier transform $\tilde{\phi}$ of the potential; in the limit $Q \to 0$ that we are interested in this certainly poses no problem (but see part III [16]). With this proviso, eq. (10) clearly shows f to be finite if and only if the argument of the logarithm in the formal solution is positive, and to be infinite if and only if the argument of the logarithm vanishes. As pointed out earlier, the construction of HRT guarantees finite f for non-vanishing cutoff whereas infinite isothermal compressibility implies a singular limit of f for $Q \to 0$. Under the stated assumptions we thus immediately conclude that

$$\begin{aligned} -\int_{Q_1}^{Q} d_0(q)\,\mathrm{d}q &< \frac{e^{-fs'}}{s'} \qquad \text{for } 0 < Q_1 < Q, \\ -\int_{0}^{Q} d_0(q)\,\mathrm{d}q &= \frac{e^{-fs'}}{s'} \qquad \text{for } \kappa_T = \infty, \end{aligned} \qquad (11)$$

the direct analogue of eq. (2); for the thermodynamic states of interest both sides of the above relations are positive if $Q - Q_1$ is comparable to Q.

The remainder of our analytical considerations on the nature of the PDE for low cutoff in the critical region will be based on eq. (11). As $e^{-fs'}/s'$ is strictly monotonous in s', interval arithmetic is trivial and allows us to tackle in a straightforward way the problem of the Q dependence of s' brought about by the non-constancy of $\tilde{\phi}$ and $\tilde{u}_0$: Given the $\bar{\varepsilon}$ independent and rather slow variation of $s'/s \propto \tilde{\phi}^2$ as a function of Q, for any cutoff interval considered the range of s' values is easily found and translated into an interval of $e^{-fs'}/s'$. Arguments based upon eq. (11) like those we will present shortly are thus easily modified to take into account the non-constancy of s' simply by applying the least restrictive bound for any of the s' values in the Q interval under consideration, an operation taken for granted throughout the remainder of this series of reports.

V. MONOTONOUS GROWTH AND LOGARITHMIC SINGULARITY

According to its definition (8), barring cancellation of the kind discussed at the end of section III the integrand d_0 on the left hand side of eq. (11) is of order $\mathbf{O}(1)$ in $\bar{\varepsilon}$. On the other hand, for f to be a monotonous function of Q in the asymptotic region, its reduced slope d_0 must always be negative there so that $-\int_{Q_1}^{Q} d_0(q)\,\mathrm{d}q = \mathbf{O}(1)\,(Q - Q_1)$. As Q_1 is an essentially free parameter to be chosen from $(0, Q]$, eq. (11) shows a quantity scaling like Q to be bounded from above by another one of order $\mathbf{O}(\bar{\varepsilon}^{-s})$, *i. e.*, $\mathbf{O}(Q) < \mathbf{O}(\bar{\varepsilon}^{-s})$. This prompts us to consider a power law relation between Q and $\bar{\varepsilon}$, say,

$$Q = \mathbf{O}(\bar{\varepsilon}^{-t}), \quad t \geq s,$$

corresponding to only a rather weak, *viz.*, logarithmic singularity of f at $Q = 0$. In this case, however, eq. (3) no longer holds due to the cutoff dependence of the prefactors in eq. (A1); to leading order we find

$$\begin{aligned} d_{02} &= \mathbf{O}(\bar{\varepsilon}^{1-2t}), \\ d_{00} &= \mathbf{O}(\bar{\varepsilon}^{1-t}), \\ f &= \mathbf{O}(1) \end{aligned}$$

instead. Combining the above with the PDE (1) we immediately arrive at a modified balance equation, *viz.*,

$$\mathbf{O}(\bar{\varepsilon}^{s}) = \mathbf{O}(\bar{\varepsilon}^{1-t}) + \mathbf{O}(\bar{\varepsilon}^{1-2t})\,\mathbf{O}(\bar{\varepsilon}^{r}). \qquad (12)$$

If the leading terms on the right hand side of eq. (12) do not cancel, eq. (5) is thus to be replaced by the relation $s = \max(1-t, 1-2t+r)$ with $r \geq 0$ and $t \geq s \geq 0$. For $r > t$, however, the assumption of monotonous growth of f leads to inconsistencies: In this case, the right hand side of the PDE (1) is asymptotically dominated by the d_{02} term. As rapid oscillations in the ϱ direction at fixed Q provide the only way for $\partial^2 f/\partial\varrho^2$ to become exponentially large compared to f itself, the second density derivative of f is bound to be oscillatory in the density range $\varrho_1 < \varrho < \varrho_2$ just as well. Unlike f, however, $\partial^2 f/\partial\varrho^2$ must change its sign at every swing, which immediately carries over to $\partial f/\partial Q$ and d_0 due to the asymptotic dominance of the d_{02} term, contrary to the assumption of $d_0(q)$ being negative for all $q < Q$.

We are thus left with the possibility of $r \leq t$, $s = 1 - t$; combining this with the conditions $r \geq 0$, $s \geq 0$, and $t \geq s$ and eliminating t we find the admissible exponent ranges to be

$$\begin{aligned} 0 &\leq r \leq 1, \\ 0 &\leq s \leq \min(\tfrac{1}{2}, 1-r) \leq \tfrac{1}{2}. \end{aligned}$$

For $r = t$, on the other hand, there is the added possibility of cancellation of the leading terms on the right hand side of eq. (12), in which case s may be reduced to a value less than $1 - t$; again eliminating t from the relations $0 \leq r = t$, $0 \leq s \leq 1 - t$, and $t \geq s$ we then find

$$\begin{aligned} 0 &\leq r \leq 1, \\ 0 &\leq s \leq \min(r, 1-r) \leq \tfrac{1}{2}. \end{aligned}$$

All in all, non-vanishing exponent s is compatible with monotonous growth of f only in the case of a merely logarithmic singularity at $Q = 0$, and in this case there is an upper bound of $\frac{1}{2}$ for s that holds irrespective of whether the leading terms on the right hand side of eq. (12) cancel. Furthermore, in this monotonous growth scenario $\mathbf{O}(Q) < \mathbf{O}(\bar{\varepsilon}^{-s})$, *v. s.*, so that finally $Q^2\,\bar{\varepsilon}$ must tend to a finite, possibly vanishing limit as $Q \to 0$.

VI. EFFECTIVE SMOOTHNESS FROM STIFFNESS

An obvious alternative is obtained by giving up the monotonicity assumption and allowing d_0 to alternate in sign: This opens up the possibility of a partial cancellation of the positive and negative contributions to the integral in eq. (11), and the average of d_0 no longer has to be of order $\mathbf{O}(1)$ in $\bar{\varepsilon}$ even though its modulus still is. As we will now show, this situation implies that the HRT PDE turns stiff for thermodynamic states of infinite compressibility, with $r > 0$ and $s > 1$. In numerical applications, on the other hand, discretization of the PDE on practical grids by necessity induces an artificial smoothing of the numerical solution that is then characterized by vanishing effective exponents r_{eff} and s_{eff} provided the computation is able to reach the limit $Q \to 0$ at all.

Stiffness of the PDE in that part of $\mathcal{D}$ where the divergence of κ_T is built up follows from eq. (11): In the scenario outlined above, the bound $e^{-fs'}/Qs' = \mathbf{O}(\bar{\varepsilon}^{-s})/Q$ on the mean of $-d_0$ over the interval $(0, Q]$ implies that d_0 is a rapidly oscillating function of Q both amplitude and period of which scale like $1/\bar{\varepsilon}^s Q = \mathbf{O}(\bar{\varepsilon}^{-s})$ [there is also the possibility of a non-monotonous logarithmic divergence, $Q \sim \bar{\varepsilon}^{-t}$ with $0 < t < s$, that may be accounted for by replacing s with $s - t > 0$]. For $\bar{\varepsilon} \gg f \gg 1$ we immediately see from eq. (9) that $f(Q, \varrho)$ naturally decomposes into a large and, most likely, monotonously growing regular part, and a very small part with scaling properties very much like those of d_0. — As far as the variation of f at fixed cutoff is concerned, for non-zero r there are similar oscillations in ϱ on density scales of order $\mathbf{O}(\bar{\varepsilon}^{-r/2})$, where r and s obey eq. (5). But vanishing r would require the evolution of f in Q at densities at fixed separation to remain synchronous over many, *viz.*, on the order of $Q\,\bar{\varepsilon}^s$ undulations of the function; this seems highly unlikely, and $r = 0$ must be unstable in the setting under discussion. The solution of the PDE is then characterized by exponents $r > 0$ and $s = r + 1 > 1$, where the possibility of a weak Q and ϱ dependence of r and s must also be anticipated.

The scenario just discussed differs from the simplistic considerations of section III and the monotonous growth dealt with in section V in two important ways: Firstly, the singularity of f may be stronger than before as there is now no need for the massive cancellation required by the smooth solution, nor does boundedness of the mean of d_0 imply boundedness of the mean slope of f. Secondly, non-vanishing exponents r and s mean that the scales characteristic of the variation of f and, hence, the grid spacings ΔQ and $\Delta\varrho$ appropriate for the discretization of the PDE become arbitrarily small as diverging isothermal compressibility is built up, which obviously has grave repercussions for the applicability of FD methods to the PDE at hand.

This last point is worth considering in some detail: Clearly, for the FD equations to be a good approximation of the PDE the step sizes must go to zero as appropriate inverse powers of $\bar{\varepsilon}$ determined by r, s, and the orders of the local truncation error in ΔQ and $\Delta\varrho$. Unless the divergence of f is very weak, however, the rapid growth of $\bar{\varepsilon}$ certainly renders so fine a grid impractical [12], and below some cutoff $Q_{\Delta Q}(T, \varrho) > 0$ the numerics can no longer follow the evolution in Q of the true solution of the PDE; by the same token, the step sizes $\Delta\varrho$ are only appropriate down to some $Q_{\Delta\varrho}(T, \varrho) > 0$. Except possibly right at ϱ_1 and ϱ_2, the $Q_{\Delta x}$ are actually rather well defined in the scenario under consideration due to the non-zero exponents $s > r > 0$. The basic assumption underlying any FD method is the applicability of Taylor expansions of finite, and usually rather low, order, which is tantamount to smoothness of the solution on the scales set by the discretization grid spacings; below the $Q_{\Delta x}$, however, this is no longer the case, and a discretization derived on the basis of this assumption is used outside the range of its validity. As Q further approaches zero, a chosen implementation of the theory may therefore fail to enter the asymptotic region altogether due to inappropriately large step sizes; in this case no solution is ever obtained at $Q = 0$ below the critical temperature, and neither criticality nor phase separation can be described successfully. Alternatively, judicious choice of the formulation of the theory and of its discretization may allow the numerical scheme to solve the FD equations all the way to vanishing cutoff; as mentioned in section II, it is this very property of eq. (1) that prompted adoption of the quasilinear form of the HRT PDE in the first place. Taylor expansion arguments no longer being applicable, however, *a priori* bounds on the local truncation error are not available, and the global error may well be substantial. Furthermore, as any solution generated in a FD calculation on a given grid is well represented on that same grid by definition, we can use the same arguments as in section III to show that the numerical results obtained with step sizes of order $\mathbf{O}(1)$ in $\bar{\varepsilon}$ are characterized by vanishing effective exponents $r_{\mathrm{eff}} = s_{\mathrm{eff}} = 0$ despite the highly oscillatory nature of the exact solution of the PDE, $s > r > 0$. This reduction of the exponents corresponds to a smoothing of f that presumably weakens the singularity and also suppresses any oscillations on density scales smaller than $\Delta\varrho$. Such smoothing is, of course, very well known in the numerics of PDEs and, in fact, forms the conceptual basis for the highly efficient multi-grid methods for the solution of integral and differential equations [18, 19].

All in all, unless the cancellation requirement of section III is met or the singularity of f is of the logarithmic type discussed in the preceding section, the asymptotic scaling relations (3) through (5) imply the PDE's stiffness in that part of $\mathcal{D}$ where infinite compressibility is built up, with $r > 0$ and $s > 1$. Any results obtained by FD methods then necessarily appear smooth even below the critical temperature and thus realize the simplistic scenario with vanishing effective exponents $r_{\text{eff}} = s_{\text{eff}} = 0$. In this case the artifical smoothing attendant to the reduction of the exponents directly affects the solution for $T \leq T_c$ at any cutoff lower than $Q_{\text{smooth}}(T, \varrho) \equiv \max(Q_{\Delta Q}, Q_{\Delta\varrho})$, and the final results for $\varrho_v \leq \varrho \leq \varrho_l$. Given the d_{02} term of the PDE, however, such drastic qualitative ($r_{\text{eff}} \neq r$) and quantitative ($s_{\text{eff}} \neq s$) changes inside the region of large $\bar{\varepsilon}$ must have an effect outside the binodal, too. Restriction of large f to only a rather well-defined density interval $[\varrho_1, \varrho_2]$, the PDE's parabolic character, and the boundary conditions imposed at $\varrho_{\min}$ and $\varrho_{\max}$, however, inspire some hope that the error incurred outside the binodal might be limited. Indeed, in the "stiff," or only "effectively smooth," scenario just sketched this very hope must underlie any attempt at a numerical solution of the HRT equations and certainly has to be justified at least *a posteriori* by combining related calculations and testing the internal consistency of the results obtained [12–14].

VII. STIFFNESS AND THE SCALING LIMIT OF HRT

So far our considerations have led us to the formulation of three different possibilities for the asymptotic behavior of the HRT PDE for high compressibility states characterized by true smoothness of the solution, by monotonous growth leading to only a logarithmic singularity, and by stiffness giving rise to effective smoothness of f, respectively.

At first sight, however, anything but the genuinely smooth solution corresponding to vanishing exponents r and s seems to be at variance with the detailed analysis of HRT's scaling limit in ref. 6: In section III B of that report we find the prediction that the quantity denoted u_Q there (corresponding to $-f$) should be quadratic in the density-like variable x and scale like $Q^{-(d-2)}$ in d dimensions; in our notation, f should thus grow like $1/Q$ in $d = 3$ dimensions, which corresponds to the simplistic scenario as noted already in section III.

In order to resolve this seeming contradiction let us have a closer look at the reasoning of ref. 6 for $T < T_c$: The pivotal relation is eq. (3.9) there, *viz.*,

$$e^{u_Q} \frac{\partial u_Q}{\partial Q} = 2\,Q - \frac{1}{2} \frac{\partial^2 u_Q}{\partial x^2} Q^{d-1}. \tag{13}$$

For this equation, the direct analogue of our eq. (1), the authors of ref. 6 invoke the validity of "neglecting exponentially small terms" to justify replacing its left hand side by nought; the asymptotic solution proportional to $Q^{-(d-2)}$ then follows immediately by separation of the cutoff and density dependencies. Said replacement is, however, legal only if the slope of u_Q actually remains small in modulus compared to its exponential or, translating to our notation, if $(1/\bar{\varepsilon})\,(\partial f/\partial Q)$ tends to zero as f goes to $+\infty$, *i. e.*, if $s < 1$ as is the case for the solution cited where it actually vanishes. Conversely, eq. (13) can also be read to indicate that its left hand side will be small if and only if the PDE's initial and boundary conditions have caused u_Q at the cutoff considered to almost exactly solve a simple ODE in the density-like variable x, *viz.*,

$$\frac{\partial^2 u_Q}{\partial x^2} = 4\,Q^{2-d},$$

which is completely equivalent to the cancellation requirement of section III, eq. (7) in particular. The above directly shows that $\partial^2 u_Q/\partial x^2$ is proportional to $Q^{2-d} \propto u_Q$ and so of order $\mathbf{O}(1)$ in e^{-u_Q}; in terms of f this means that $\partial^2 f/\partial\varrho^2$ is of order $\mathbf{O}(1)$ in $\bar{\varepsilon}$ and, hence, that $r = 0$.

As the assumptions both of smoothness in the ϱ direction, $r = 0$, and of cancellation of the leading terms on the right hand side of eq. (1), $s < 1$, are thus built right into the derivation of the scaling solution of ref. 6, conformance of the latter with the simplistic scenario is quite obvious and certainly cannot be used to rule out any of the other possibilities considered in the present report. As for the numerical solution, both genuine ($r = s = 0$) and effective ($r_{\text{eff}} = s_{\text{eff}} = 0$) smoothness suggest an f that asymptotically grows like $1/Q$, although in the latter case there is little justification for construing this as a property of the exact solution of the PDE. We are thus led to a reappraisal of the analysis presented in section III B of ref. 6 as certainly applicable to the FDEs solved numerically but not to the true PDE unless $r = s = 0$, *i. e.*, unless the cancellation requirement of the simplistic scenario is met. With this proviso the conclusions of ref. 6 remain largely unaffected and the intuitively appealing picture sketched in section III is effectively salvaged even in the stiff scenario, if only for the numerical process. The properties of the solution derived in ref. 6 also suggest that the form of f at sufficiently small cutoff Q conforms with the sketch of fig. 1 whereas eq. (7) might well be compatible with a more general outline, which certainly supports the stable mechanism of growth proposed in section III. — As far as the possibility of a monotonous solution of the kind of section V is concerned, we defer discussion of this point to section II of part II [15].

In view of this resolution of the seeming contradiction between the earlier analysis of HRT's scaling limit and the possibility of non-zero exponents r and s none of the three scenarios can be excluded from further consideration at this point. On the other hand, the rather summary analytical considerations presented here can only identify the solution types consistent with the asymptotic properties of the PDE for infinite compressibility and explore their preconditions and consequences, which has been the subject matter of the present report. The all-important question of which of them is in fact realized in applications of the theory, however, crucially depends on global aspects of eq. (1) in all of $\mathcal{D}$ and certainly cannot be answered without considering the influence of the initial and boundary conditions that, after all, uniquely determine $f(Q,\varrho)$ throughout the integration domain. To arrive at a decision we therefore need to actually solve a discretized version of the PDE, scrutinize the computational process, and interpret the numerical evidence so gained, a task we will undertake in the second installment of the present series of reports [15].

VIII. ACKNOWLEDGMENTS

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APPENDIX A: NOTATIONAL CONVENTIONS AND FULL EXPRESSIONS FOR THE PDE COEFFICIENTS

A most detailed account of the process of re-writing the PDE for the free energy into the quasilinear eq. (1) can be found, alongside the explicit expressions for the PDE coefficients d_{0i}, in appendix A of ref. 14. Further specializing these to take into account the elimination of the core condition and the purported density-independence of the potential we obtain

$$\begin{aligned} d_{00} = \; & +\frac{\partial\tilde{\phi}}{\partial Q}\left(\frac{\tilde{\phi}_0^2}{\tilde{\mathcal{K}}\,\tilde{\phi}^2}-\frac{\tilde{\mathcal{K}}\,\bar{\varepsilon}^2\,\tilde{\phi}_0^2}{\varepsilon\,\tilde{\phi}^4}-\frac{2\,f}{\tilde{\phi}}\right) \\ & +\frac{\partial\tilde{\mathcal{K}}}{\partial Q}\left(\frac{\bar{\varepsilon}^2\,\tilde{\phi}_0^2}{\varepsilon\,\tilde{\phi}^3}-\frac{\tilde{\phi}_0^2}{\tilde{\mathcal{K}}^2\,\tilde{\phi}}\right) \\ & +\frac{\partial^2(1/\tilde{\mathcal{K}})}{\partial\varrho^2}\,\frac{Q^2}{4\pi^2}\,\frac{\bar{\varepsilon}^2\,\tilde{\phi}_0}{\varepsilon\,\tilde{\phi}}, \\ d_{02} = \; & -\frac{Q^2}{4\pi^2}\,\frac{\bar{\varepsilon}^2}{\varepsilon\tilde{\phi}_0}. \end{aligned} \tag{A1}$$

In the above expressions we have suppressed the obvious function arguments Q and ϱ, and we rely on the notational convention introduced in our earlier work on HRT according to which superscripts indicate the system a quantity refers to and a tilde signals Fourier transformation. We also make use of the following auxiliary quantities:

$$\begin{aligned} u_0(r) &= \phi(r)/\tilde{\phi}_0, \\ \tilde{\phi}_0 &= \tilde{\phi}(0), \\ \tilde{\mathcal{K}}(k,\varrho) &= -\frac{1}{\varrho}+\tilde{c}_2^{\mathrm{ref}}(k,\varrho), \\ \ln\varepsilon(Q,\varrho) &= f(Q,\varrho)\,\tilde{u}_0^2(Q)-\tilde{\phi}(Q)/\tilde{\mathcal{K}}(Q,\varrho), \\ \bar{\varepsilon}(Q,\varrho) &= \varepsilon(Q,\varrho)-1. \end{aligned} \tag{A2}$$

As far as the definition of $\mathcal{K}$ is concerned, it is important to note that the ideal gas term involving $-1/\varrho$ is customarily included in the definition of the hard sphere reference system direct correlation function c_2^{ref} throughout much of the literature on HRT. Furthermore, when explicitly taking into account the core condition $\mathcal{K}$ is typically augmented by a truncated series expansion of the deviation of the direct correlation function of the Q system inside the core from that of the reference system, a scheme designed to allow one to side-step the need for costly numerical Fourier transformations that would otherwise arise from the inversion of the Ornstein-Zernike equation [5, 12].

The connection to the thermodynamics as well as to the original formulation of the theory is afforded by the relations linking f and the auxiliary quantities defined in eq. (A2) to the first derivative with respect to Q of the free energy $A^{(Q)}$ of the system at cutoff Q: From the expressions given in ref. 12 one may easily show that the evolution of $A^{(Q)}$ is given by

$$\begin{aligned} \frac{\partial}{\partial Q}\left(\frac{\beta\,A^{(Q)}}{V}\right) &= \frac{Q^2}{4\,\pi^2}\left(\ln\varepsilon-\tilde{\phi}\,\varrho\right) \qquad \text{for } Q>0, \\ \frac{\beta\,A^{(0)}}{V} &= \lim_{Q\to 0^+}\frac{\beta\,A^{(Q)}}{V}-\frac{\varrho^2\,\tilde{\phi}_0}{2}. \end{aligned} \tag{A3}$$

The structure of the Q system follows from the closure relation that imposes a direct correlation function $c_2^{(Q)}(r,\varrho)$ of the form

$$c_2^{(Q)} = c_2^{\mathrm{ref}}+\phi^{(Q)}+\gamma_0^{(Q)}\,u_0 \tag{A4}$$

parameterized by the single scalar $\gamma_0^{(Q)}(\varrho)$ that is determined throughout $\mathcal{D}$ from thermodynamic consistency in the form of the compressibility sum rule

$$-\frac{1}{\varrho}+\tilde{c}_2^{(Q)}(0) = -\frac{\partial^2}{\partial\varrho^2}\frac{\beta A^{(Q)}}{V}. \tag{A5}$$

In the spirit of LOGA/ORPA, when implementing the core condition eq. (A4) is taken to hold only for $r>\sigma$, and the direct correlation function inside the core is optimized so as to approximately minimize the pair distribution function there. As shown in appendix A.3 of ref. 14, the isothermal compressibility $\kappa_T^{(Q)}$ of the Q system is also readily evaluated and, in the limit $Q\to 0$, found to reduce to

$$\kappa_T = \kappa_T^{(0)} = \frac{\beta\,\bar{\varepsilon}}{\varrho^2\tilde{\phi}_0} = -\frac{\bar{\varepsilon}}{\varrho^2\tilde{w}(0)}. \tag{A6}$$

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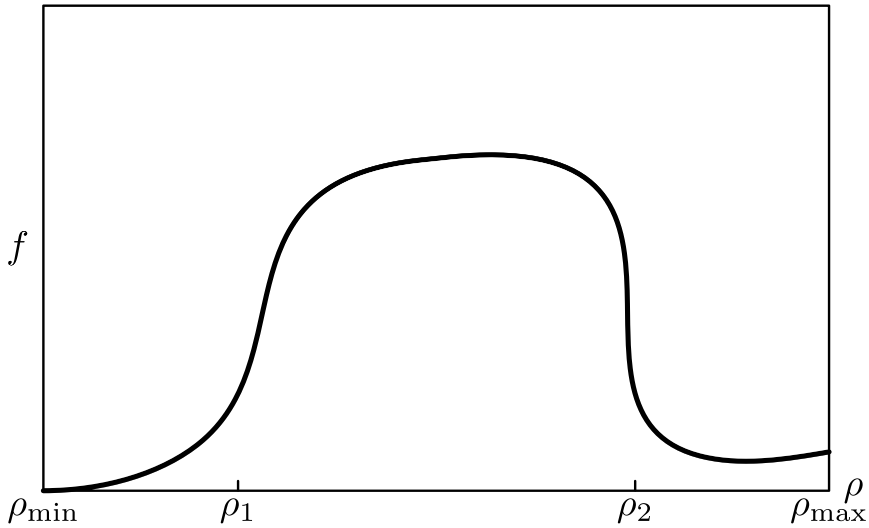

FIG. 1: Sketch of the auxiliary function $f(Q, \varrho)$ for fixed and sufficiently small Q in the simplistic scenario: $\varrho_{\rm min}$ and $\varrho_{\rm max}$ are the densities where boundary conditions must be imposed upon the solution of the PDE; the density range where f is large extends from ϱ_1 to ϱ_2, and there is a single, rather flat maximum of f for $\varrho_1 < \varrho < \varrho_2$.