

## Asymptotic density correlations and corrections to scaling for fluids with non-finite-range interactions

R. F. Kayser and H. J. Raveché

*Thermophysics Division, National Bureau of Standards, Washington, D.C. 20234*

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The asymptotic behavior of the pair-correlation function in fluids with realistic long-range pair potentials is shown to give rise to a correction to scaling that has not been previously taken into account.

The current theory of corrections to scaling in fluids<sup>1</sup> is based on renormalization-group theory developed for systems with strictly finite-range interactions, i.e., interactions that vanish identically beyond a certain distance. All real fluids, on the other hand, interact with intermolecular potentials that are long ranged, and it is these which are of concern here. The term long-range potential is used to denote any non-finite-range interaction that is absolutely integrable at large distances. Realistic examples of such interactions in fluids are provided by potentials that decay as inverse powers of the distance at large distances, one familiar case being the induced dipole-induced dipole interaction in  $d=3$  dimensions, for which the potential decays (neglecting retardation effects) as  $\phi(r) = -A/r^6$ , where  $r$  is the interparticle separation and  $A$  is a constant.

It has been known for some time that long-range potentials give rise to an important contribution to the radial distribution function,  $g(r)$ , at distances greater than the correlation length  $\xi$ . The main purpose of this Rapid Communication is to point out that this contribution, when included in the calculation of thermodynamic properties such as the isothermal compressibility  $\chi$ , leads to a correction to scaling that has not been previously taken into account.<sup>2</sup> It is shown that this new correction can have a temperature exponent that is comparable in some cases to that of the first Wegner correction.<sup>1</sup> The amplitude, however, is probably small, and the implications of this for the analysis of fluid equation-of-state data near the critical point are examined. The correlation length here is defined by the usual formula<sup>3</sup>

$$\xi^2 = \rho \int d^d r r^2 [g(r) - 1] / (\rho \chi / \beta),$$

where  $\rho$  is the number density of particles and  $\beta^{-1}$  is Boltzmann's constant  $k_B$  times the absolute temperature  $T$ , and  $\chi$  is related to  $g(r)$  through the compressibility relation

$$\rho \chi / \beta = 1 + \rho \int d^d r [g(r) - 1].$$

In order to assess the effect of a long-range potential on corrections to scaling it is necessary to first consider the long-range asymptotic behavior of  $g(r)$ . This problem has been solved for power-law potentials by Enderby, Gaskell, and March<sup>4</sup> using the Ornstein-Zernike integral equation together with the assumption that the direct correlation function for such potentials satisfies

$$c(r) = -\beta \phi(r) \text{ for } r \rightarrow \infty. \quad (1)$$

One may then show by Fourier transform techniques that

$$g(r) - 1 = -(\rho \chi / \beta)^2 \beta \phi(r), \text{ for } r \rightarrow \infty. \quad (2)$$

The salient feature of this important result is its propor-

tionality to the square of the isothermal compressibility, which diverges strongly as one approaches the critical point. While a rigorous proof of (1) has yet to be given, the result is widely believed to be of general validity: its truth at low densities is evident from the density expansion of  $c(r)$ , and a formal demonstration not restricted to low densities has been given by Stell.<sup>5</sup> With regard to (2), the form of the result suggests only that it might break down near the critical point (where the amplitude diverges), and it is believed that the result holds at arbitrarily large  $r$  for any fluid state of finite compressibility.<sup>5</sup> (See also Ref. 6.) This will be the point of view taken here.

Consider then the issue of corrections to scaling near the critical point, and in particular, the following question: What form should the scaling laws take near the critical point in the case of long-range intermolecular potentials? It should be noted that the asymptotic scaling behavior for such fluids (i.e., the behavior so close to the critical point that corrections to scaling may be neglected) has been analyzed in some detail, first by Stell<sup>7</sup> and later in a renormalization-group context by Fisher, Ma, and Nickel<sup>8</sup> and Sak.<sup>9</sup> These analyses provide some motivation for the scaling behavior presented here, although the present emphasis is on corrections to scaling.

For strictly finite-range potentials the asymptotic behavior of  $h(r) = g(r) - 1$  near the critical point is given by<sup>10</sup>

$$h(r) = F(r/\xi) (\sigma/r)^{d-2+\eta}, \quad (3)$$

where  $\eta$  is the correlation function exponent and  $\sigma$  is a measure of the microscopic fluid particle size. The scaling function  $F(x)$  is known<sup>10</sup> to tend to a constant as  $x \rightarrow 0$  and to decay like  $x^{(d-3)/2+\eta} \exp(-x)$  for  $x \gg 1$ : that is, the correlations differ significantly from zero only inside a sphere of radius equal to the correlation length. In view of the result (2) discussed above, the expression (3) for short-range potentials must therefore be modified in the case of long-range potentials (e.g., those with asymptotic power-law decay), where at arbitrarily large  $r$  the right-hand side of (2) dominates the right-hand side of (3) for any finite  $\xi$ . This is in accord with a statement by Widom<sup>11</sup> that the correlations in the positions of two fluid particles cannot effectively disappear at distances at which the particles are still in mutual interaction.

Inasmuch as the asymptotic result (2) holds as  $r \rightarrow \infty$  for any one-phase fluid not exactly at its critical point, it seems reasonable to decompose the correlation function for a long-range potential into two additive contributions,  $h_{SR}(r)$  and  $h_{LR}(r)$ , where  $h_{SR}(r)$  refers to the right-hand side of (3) plus higher-order terms that account for the usual corrections to scaling, and  $h_{LR}(r)$  denotes the long-range

potential term given in (2). It is important to bear in mind, however, that the derivation of (2) is valid only for those values of  $r$  where the long-range behavior of  $h(r)$  is in fact given by  $h_{LR}(r)$ , and this means that  $h_{LR}(r)$  should be included in  $h(r)$  only when  $h_{LR}(r) \gg h_{SR}(r)$ . Assuming that this condition is satisfied for  $r \geq r_c$ , one then has

$$h(r) = h_{SR}(r) - H(r - r_c)(\rho\chi/\beta)^2\beta\phi(r), \quad (4)$$

where  $H(x)$  is a Heaviside step function. The results to be derived from this expression do not depend in a significant way on the choice of the cutoff function  $H(x)$ , nor do they depend on the fact that  $h_{SR}(r)$  has been included in  $h(r)$  for  $r \geq r_c$ . That is,  $h_{SR}(r) \ll h_{LR}(r)$  for  $r \geq r_c$ , and it hence makes a negligible contribution to  $h(r)$  in that regime.

For simplicity, the remainder of the discussion deals with the behavior of the isothermal compressibility along the critical isochore [ $\rho = \rho_c, t = (T - T_c)/T_c > 0$ ], and with power-law potentials of the form  $\phi(r) = -A/r^{d+p}$  for  $r \rightarrow \infty$ , where  $A$  and  $p$  are positive constants. An immediate upper bound on  $r_c$  then follows from the exponential decay of  $F(x)$  in (3) for large  $x$ , the bound being of the form<sup>12</sup>  $\xi^{1+\epsilon}$ , where  $\epsilon > 0$  is arbitrarily small. Evaluation of (3) and (2) (with<sup>3</sup>  $\chi \sim \xi^{2-\eta}$ ) at  $r = \xi$  further shows that

$$h_{LR}(\xi)/h_{SR}(\xi) \sim \xi^{-(p-2+\eta)},$$

and this implies a qualitative distinction between the cases  $p > 2 - \eta$  and  $p \leq 2 - \eta$ . For  $p > 2 - \eta$  one must have  $\xi \ll r_c \ll \xi^{1+\epsilon}$  for  $\xi \rightarrow \infty$ , and if  $r_c$  is taken to be that value of  $r$  at which  $h_{SR}(r) = h_{LR}(r)$  one finds

$$r_c = (p - 2 + \eta)\xi \ln(\xi/\sigma). \quad (5)$$

For  $p \leq 2 - \eta$ , on the other hand,  $h_{LR}(r)$  is not negligible compared to  $h_{SR}(r)$  even for  $r \leq \xi$ . No attempt is made here to analyze this case (see Refs. 7-9), although the limit  $p - 2 + \eta \rightarrow 0+$  is alluded to below and provides some indication of what is to be expected. It is henceforth assumed that  $p > 2 - \eta$ .<sup>13</sup>

Given the decomposition (4) and the result (5), the compressibility integral relating  $\chi^* = (\beta_c P_c / \rho_c) \rho \chi / \beta$  to  $h(r)$  separates naturally into two terms:  $\chi^* = \chi_{SR}^* + \chi_{LR}^*$ , where<sup>14</sup>

$$\chi_{SR}^* = \Gamma^+ t^{-\nu} [1 + a_1 t^{\Delta_1} + a_2 t^{\Delta_2} + a_3 t^{2\Delta_1} + a_4 t^{\gamma-\alpha} + \dots], \quad (6)$$

and

$$\chi_{LR}^* = \Gamma^+ t^{-\nu} [b t^{\nu(p-2+\eta)} (\ln t)^{-p}]. \quad (7)$$

The quantity  $P_c$  is the critical pressure,  $\Gamma^+$ ,  $a$ ,  $a_1$ ,  $a_2$ ,  $a_3$ , and  $b$  are constants,  $\gamma = \nu(2 - \eta)$  is the compressibility index (in the usual notation<sup>10</sup>),  $\Delta_1$  and  $\Delta_2$  are gap exponents,  $\alpha$  is the specific-heat exponent, and  $\nu$  is the correlation length exponent, defined by  $\xi = \xi_0 t^{-\nu}$  and characterizing the divergence of  $\xi$  as  $t \rightarrow 0+$  along the critical isochore. Thus, in addition to the usual corrections to scaling given in (6) and involving the exponents  $\Delta_1$ ,  $\Delta_2$ , and  $\gamma - \alpha$ , long-range potentials give rise to a new correction involving an exponent  $q = \nu(p - 2 + \eta)$ . This correction depends, through  $p$ , on the explicit form of the intermolecular potential at large distances. Note that for  $p > 2 - \eta$ ,  $\chi_{LR}^*$  is in fact merely a correction to  $\chi_{SR}^*$ , but that as  $p - 2 + \eta \rightarrow 0$  these two contributions become codominant. Since<sup>15</sup>  $\eta \approx 0.03$  for

$d = 3$ , this would happen for a potential with asymptotic form  $\phi(r) = -A/r^{4.97}$ , the important point being that for more slowly decaying potentials one must be prepared to find critical exponents somewhat different from those usually associated with fluids, as was first emphasized by Stell.<sup>7</sup>

There is no reason to believe that the usual critical exponents are affected when  $p > 2 - \eta$ , and it is therefore assumed that they are not. A definite illustration of the term  $t^q$  is then provided by the induced dipole-induced dipole potential ( $p = 3$ ) for  $d = 3$ . Using accepted numerical values for the exponents,<sup>15</sup> one then finds  $\Delta_1 \approx 0.50$ ,  $\Delta_2 \approx 0.90$ ,  $2\Delta_1 \approx 1.00$ ,  $\gamma \approx 1.24$ ,  $\alpha \approx 0.11$ ,  $\gamma - \alpha \approx 1.13$ ,  $\nu \approx 0.63$ ,  $\eta \approx 0.03$ , and  $q \approx 0.65$ , so that the new correction is characterized by a correction-to-scaling exponent that is only slightly larger than that of the dominant Wegner term ( $at^{\Delta_1}$ ). The amplitude  $b$  in (7) may in turn be estimated by replacing the potential parameter  $A$  by  $4\epsilon\sigma^6$ , where  $\epsilon$  and  $\sigma$  are the well-depth and length-scale parameters of a Lennard-Jones potential. One then obtains

$$b = (16\pi/3)(1 + \eta)^{-3}(\rho_c\sigma^3)(\beta_c\epsilon)(\rho_c/\beta_c P_c)(\sigma/\xi_0)^3\Gamma^+.$$

This quantity is generally of order unity and is readily calculable in particular instances.<sup>16</sup>

A final point concerns the significance of the new correction to scaling for the analysis of fluid equation-of-state data.<sup>17</sup> It is important to realize that experimental measurements typically have  $t \geq 10^{-4}$ , and in this regime the corrections to scaling given in (6) are of the order of at least a few percent. The first three or more terms are in fact often needed to obtain adequate data fits.<sup>18</sup> Ordinarily one then either assumes that the correction-to-scaling exponents are known and adjusts  $\gamma$  and the amplitudes, or one assumes that  $\gamma$  is known and adjusts  $\Delta_1$  (with  $\Delta_2 = 2\Delta_1$ ) and the amplitudes. Given this, consider again the case of the attractive  $1/r^6$  potential, which describes reasonably well the interactions in a wide variety of fluid systems.<sup>19</sup> Consider for definiteness the specific case of xenon, as this provides some indication of what can be generally expected. Compressibility data in the range  $10^{-2} \geq t \geq 10^{-4}$  are given in Ref. 18 together with critical constants and related parameters, and the potential parameters  $\epsilon$  and  $\sigma$  are given approximately by<sup>20</sup>  $\epsilon/k_B \approx 220$  K,  $\sigma \approx 4$  Å. Reduced temperatures  $t \geq 10^{-4}$  turn out to be too large for the expression (5) to accurately represent the solution to  $h_{SR}(r_c) = h_{LR}(r_c)$ , and it is therefore necessary to recompute both  $r_c$  and the long-range contribution  $\chi_{LR}^*$  given in (7). That is, both (5) and (7) are valid only for  $t \rightarrow 0+$  and represent poor approximations for  $t \geq 10^{-4}$ . The function  $r_c(t)$  is nevertheless easily determined numerically, and when this is done for Xe one finds that  $\chi_{LR}^*/\chi_{SR}^*$  decreases from the value  $3 \times 10^{-4}$  at  $t = 10^{-2}$  to the value  $6 \times 10^{-6}$  at  $t = 10^{-4}$ . This implies that the new correction to scaling is negligible compared to the corrections in (6) in the temperature interval  $10^{-2} \geq t \geq 10^{-4}$ , i.e., in the regime where experimental data exist and has been analyzed on the basis of (6). While the new correction must of course eventually become the second most important contribution, this will not happen (for Xe) until one reaches reduced temperatures considerably smaller than  $10^{-4}$ .

Effects similar to those considered here may be expected to arise in thermodynamic properties other than the isothermal compressibility as well as in systems such as binary liquid mixtures. In addition, it is conceivable that long-

range potentials alter the behavior of  $h(r)$  for  $r < r_c$  to a greater extent than has been assumed here. A renormalization-group calculation of the corrections to scaling could resolve this question.

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- <sup>1</sup>For reviews of corrections to scaling, see J. M. H. Levelt Sengers and J. V. Sengers, in *Perspectives in Statistical Physics*, edited by H. J. Raveché (North-Holland, Amsterdam, 1981), p. 239; *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley, New York, 1978), p. 103.
- <sup>2</sup>J. V. Sengers (private communication).
- <sup>3</sup>When  $M_2 = \rho \int d^d r r^2 [g(r) - 1]$  does not exist,  $\xi$  may be defined by  $(\xi/\sigma)^{2-\eta} = \rho\chi/\beta$ , where  $\sigma$  and  $\eta$  are defined in (3). This is equivalent to the usual definition when (3) holds and  $M_2$  exists.
- <sup>4</sup>J. E. Enderby, T. Gaskell, and N. H. March, *Proc. Phys. Soc. London* **85**, 217 (1965). See also F. M. Kuni, *Dokl. Phys. Chem.* **179**, 153 (1968).
- <sup>5</sup>G. Stell, in *Statistical Mechanics, Part A: Equilibrium Techniques*, edited by B. J. Berne (Plenum, New York, 1977), p. 47.
- <sup>6</sup>G. Benfatto, Ch. Gruber, and Ph. A. Martin (unpublished). These authors claim a rigorous proof of (2) for any state for which  $\rho\chi/\beta$  is finite.
- <sup>7</sup>G. Stell, *Phys. Rev. B* **1**, 2265 (1970); **5**, 981 (1972); **8**, 1271 (1973); *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1975), p. 205.
- <sup>8</sup>M. E. Fisher, S.-K. Ma, and B. G. Nickel, *Phys. Rev. Lett.* **29**, 917 (1972).
- <sup>9</sup>J. Sak, *Phys. Rev. B* **8**, 281 (1973).
- <sup>10</sup>M. E. Fisher, *J. Math. Phys.* **5**, 944 (1964); *Rep. Prog. Phys.* **30**, (II), 615 (1976).
- <sup>11</sup>B. Widom, *J. Chem. Phys.* **41**, 74 (1964).
- <sup>12</sup>Parameters required only for dimensional consistency are sometimes omitted.
- <sup>13</sup>It should be noted that corrections to (2) involving the long-range potential have been assumed negligible in (4) for  $r \geq r_c$ . It can be shown by the methods of Ref. 4 that this is indeed the case for  $p > 2 - \eta$  where the correction terms are of order  $\xi^2/r^2$  and  $\xi^{2-\eta}/r^p$  relative to the right-hand side of (2).
- <sup>14</sup>M. Ley-Koo and M. S. Green, *Phys. Rev. A* **23**, 2650 (1981).
- <sup>15</sup>J. V. Sengers, in *Phase Transitions*, edited by M. Levy, J.-C. Le Guillou, and J. Zinn-Justin, NATO Advanced Study Institute Series B, Vol. 72 (Plenum, New York, 1982), p. 95.
- <sup>16</sup>In contrast to  $q$ , the estimate for  $b$  depends on the form of the crossover to the long-range part of  $h(r)$ . The result given in the text should therefore be regarded as suggestive rather than definitive.
- <sup>17</sup>For a review of experiment, see M. R. Moldover, in *Phase Transitions*, edited by M. Levy, J.-C. Le Guillou, and J. Zinn-Justin, NATO Advanced Study Institute Series B, Vol. 72 (Plenum, New York, 1982), p. 63. See also Ref. 15.
- <sup>18</sup>A nice example of this is provided by the case of xenon. See H. Güttinger and D. S. Cannell, *Phys. Rev. A* **24**, 3188 (1981).
- <sup>19</sup>In actual fact, retardation effects become important at distances greater than several hundred angstroms and cause the potential to decay as  $\phi(r) = -B/r^7$  at large distances, where  $B$  is a constant. The calculations based on the potential  $\phi(r) = -A/r^6$  should therefore be regarded as providing only an upper bound on the magnitude of the new correction to scaling. For a discussion of retardation effects, see E.M. Lifshitz and L. P. Pitaevskii, *Statistical Physics* (Pergamon, Oxford, 1980), Part 2, p. 347.
- <sup>20</sup>J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 1110.