Communication: Nonexistence of a critical point within the Kirkwood superposition approximation

Jarosław Piasecki,[1] Piotr Szymczak,[1,a)] and John J. Kozak[2]

[1]*Institute of Theoretical Physics, Faculty of Physics, University of Warsaw, Hoza 69, 00-681 Warsaw, Poland*
[2]*DePaul University, 243 South Wabash Avenue, Chicago, Illinois 60604-2301, USA*

An analytic argument is given to show that the application of the Kirkwood superposition approximation to the description of fluid correlation functions precludes the existence of a critical point. The argument holds irrespective of the dimension of the system and the specific form of the interaction potential and settles a long-standing controversy surrounding the nature of the critical behavior predicted within the approximation. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4824388]

Developing a fundamental understanding of the liquid-vapor phase transition has been the focus of attention of statistical physics for more than a century. The quantity of central importance in this regard is the radial distribution function, $g(r)$. However, an exact, analytic determination of $g(r)$ turned out to be impossible, even for simple fluids. As a result, various approximations have been proposed in order to make the analysis more tractable.

One of the most widely studied approaches is based on the Kirkwood superposition approximation (KSA) which yields a closed integral equation for the radial distribution function.[1–3] However, combined analytic and numerical attempts to derive from the integral equation the existence of a liquid-vapor critical point in three dimensions failed.[4–9] Only a "near-critical" behavior could be revealed, with the correlation functions attaining very long, but finite range. Interestingly, it was hypothesized that the critical behavior under KSA approximation depends on the dimensionality of the system,[7,8] with the true criticality present only for $d \geq 5$. This conclusion was reached, however, by introducing another approximation: the moment expansion was applied to Yvon-Born-Green (YBG) integral equation which yielded a nonlinear differential equation describing the long-range correlations.

By adopting a different approach, we prove here that KSA applied to the exact relation between the derivative with respect to the density of the pair correlation function and the three-particle correlation function leads to a theory incompatible with the existence of a critical point. The result holds irrespective of the dimension of the system and the specific form of the interaction potential and thus settles the long-standing controversy over the existence of a critical point in KSA-based theories and the potential dependence of the critical behavior on the dimensionality of the system.

To proceed, we consider the cluster decomposition of the two - and three-particle number density

$$n_2(r_{12}) = n^2 g(r_{12}) = n^2[h_2(r_{12}) + 1] \tag{1}$$

a)Electronic mail: Piotr.Szymczak@fuw.edu.pl

and

$$n_3(r_{12}, r_{13}, r_{23}) = n^3[h_3(r_{12}, r_{13}, r_{23}) + h_2(r_{12}) + h_2(r_{13}) + h_2(r_{23}) + 1], \tag{2}$$

which defines the two- and three-particle correlation functions h_2 and h_3. In the above equations n is the density of a homogeneous fluid, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ denotes the distance between points $\mathbf{r}_i$ and $\mathbf{r}_j$. We assume here that the potential of interaction is spherically symmetric.

The correlation functions h_2 and h_3 satisfy the nonlinear equation[10,11]

$$\int d\mathbf{r}_3 \, h_3(r_{12}, r_{13}, r_{23})$$
$$= 2\left[\int d\mathbf{r} h_2(r)\right] h_2(r_{12}) + \left[1 + n \int d\mathbf{r} h_2(r)\right] \frac{\partial h_2(r_{12})}{\partial n}, \tag{3}$$

involving the isothermal compressibility $\mathcal{K}(n, T)$ through the so called compressibility equation

$$1 + n \int d\mathbf{r} h_2(r) = k_B T \left(\frac{\partial n}{\partial p}\right)_T = n k_B T \mathcal{K}(n, T), \tag{4}$$

where T and p denote the temperature and the pressure, respectively.

The relation (3) reflects the mechanism of equilibrium density fluctuations and has a very general character. It is valid in any dimension and holds in principle for an arbitrary potential of interaction.

Within the superposition approximation one puts

$$n_3(r_{12}, r_{13}, r_{23}) = n^3[1 + h_2(r_{12})][1 + h_2(r_{23})][1 + h_2(r_{31})], \tag{5}$$

which, when compared with (2), implies an approximate expression for the three-particle correlation function

$$h_3(r_{12}, r_{13}, r_{23}) = h_2(r_{12})h_2(r_{13})h_2(r_{23}) + h_2(r_{12})h_2(r_{13}) + h_2(r_{13})h_2(r_{23}) + h_2(r_{12})h_2(r_{23}). \tag{6}$$

Upon inserting (6) into the integral relation (3) we find

$$\int d\mathbf{r}_3 \left[h_2(r_{12})h_2(r_{13}) + h_2(r_{13})h_2(r_{23}) \right.$$
$$\left. + h_2(r_{12})h_2(r_{23}) + h_2(r_{12})h_2(r_{13})h_2(r_{23}) \right]$$
$$= 2h_2(r_{12}) \int d\mathbf{r}\, h_2(r) + \left[1 + n \int d\mathbf{r}\, h_2(r) \right] \frac{\partial h_2(r_{12})}{\partial n},$$
$$(7)$$

which reduces to

$$[1 + h_2(r_{12})] \int d\mathbf{r}_3\, h_2(r_{13})h_2(r_{23})$$
$$= \left[1 + n \int d\mathbf{r}\, h_2(r) \right] \frac{\partial h_2(r_{12})}{\partial n}. \qquad (8)$$

The relation (8) is a direct consequence of the superposition approximation, valid in any spatial dimension.

Rewriting (8) as

$$\frac{1}{1 + n \int d\mathbf{r}\, h_2(r)} \int d\mathbf{r}_3\, h_2(r_{13})h_2(r_{23})$$
$$= \frac{1}{1 + h_2(r_{12})} \frac{\partial h_2(r_{12})}{\partial n} \qquad (9)$$

and integrating over the variable $\mathbf{r}_{12}$ we find

$$\int d\mathbf{r}\, \frac{1}{1 + h_2(r)} \frac{\partial h_2(r)}{\partial n} = \frac{\left[\int d\mathbf{r}\, h_2(r) \right]^2}{1 + n \int d\mathbf{r}\, h_2(r)}. \qquad (10)$$

Equation (10) permits to prove that the critical point cannot be attained within the superposition approximation. Indeed, we show below that assuming the existence of a critical isotherm leads to a contradiction.

Let us thus suppose that there exists an isotherm $T = T_c$ such that when the density n approaches some critical value n_c, the isothermal compressibility $\mathcal{K}(n, T_c)$ defined in (4) diverges. This happens because at $n = n_c$ the function $h_2(r)$ becomes non-integrable showing a slow power-like decay at infinity. Naturally, both sides of Eq. (10) should diverge in the same manner. Let us then analyze their asymptotic behavior as $n \to n_c$.

As $h_2(r) \to 0$ when $r \to \infty$, the large distance decay of the integrand on the left-hand side of Eq. (10) coincides with that of the derivative $\partial h_2(r)/\partial n$. So, when $n \to n_c$, the dominant (supposed diverging) contribution to the left-hand side behaves like

$$\frac{\partial}{\partial n} I(n, T_c), \text{ where } I(n, T_c) = \int d\mathbf{r}\, h_2(r) = k_B T_c \mathcal{K}(n, T_c) - \frac{1}{n}. \qquad (11)$$

In other words, the left-hand side of (10) diverges like the derivative of the compressibility.

The right-hand side of Eq. (10) equals

$$[I(n, T_c)]^2 / [1 + nI(n, T_c)],$$

so that the diverging contribution takes here the form $I(n, T_c)/n = [nk_B T\mathcal{K}(n, T_c) - 1]/n^2$. The divergence of the right-hand side of (10) coincides thus (up to a factor) with that of the compressibility. Equation (10) thus requires that the derivative with respect to the density of the compressibility at the approach to the critical density diverges exactly in

the same way as the compressibility itself. That this is impossible can be seen by considering the equation

$$\frac{\partial \mathcal{K}(n, T_c)}{\partial n} = b \frac{\mathcal{K}(n, T_c)}{n}. \qquad (12)$$

For $n \to n_c$, Eq. (12) expresses the fact that the divergent terms in Eq. (10) are proportional (b is a constant), i.e., that they diverge according to the same law. However, the solution of Eq. (12) reads $\mathcal{K}(n, T_c) = a(n)^b$, where a is another constant, giving a finite value to the compressibility at $n = n_c$, which excludes the assumed divergence.

For example, if one assumes the power-law divergence characteristic for the critical behavior, $\mathcal{K}(n, T_c) \sim (n - n_c)^{-\gamma}$, $\gamma > 0$, then the LHS of Eq. (12) diverges as $(n - n_c)^{-(\gamma+1)}$, whereas the RHS as $(n - n_c)^{-\gamma}$, which is clearly incompatible.

We thus find here a contradiction with the assumed divergence of the compressibility, which leads to the conclusion that the existence of a critical isotherm, and thus of a critical point, is ruled out when the Kirkwood superposition approximation is applied to the general relation (3).

The argument presented above is very general, valid in any dimension, and for arbitrary potential. In order to illustrate it on a specific example we consider below the extensively studied case of a three-dimensional square-well fluid. It has been shown that the integral equation corresponding to the superposition approximation leads in this case to the long-range decay of correlations via exponential modes of the form[9]

$$h_2(r) \xrightarrow[r \to \infty]{} A \frac{\exp(-\kappa r)}{r}, \qquad (13)$$

where $\kappa = \kappa(T, n)$ is a function of temperature and density and A is a constant. The divergence of compressibility would correspond thus to the disappearance of exponential damping at $n = n_c$. On a critical isotherm we should thus expect

$$\lim_{n \to n_c} \kappa(T_c, n) = \kappa(T_c, n_c) = 0. \qquad (14)$$

When $\kappa \to 0$, the integral of the correlation function diverges as

$$\int d\mathbf{r}\, A \frac{\exp(-\kappa r)}{r} = \frac{4\pi A}{\kappa^2}. \qquad (15)$$

The asymptotic behavior of the right-hand side of Eq. (10) reads thus $(4\pi A/n\kappa^2)$. On the other hand, inserting into the left-hand side of (10) the large distance formula (13) we find

$$\int d\mathbf{r}\, \frac{1}{1 + h(r)} \frac{\partial}{\partial n} h(r)$$
$$= \frac{\partial}{\partial n} \int d\mathbf{r}\, h(r) - \frac{1}{2} \int d\mathbf{r}\, \frac{1}{1 + h(r)} \frac{\partial}{\partial n} [h(r)]^2$$
$$= 4\pi A \left[1 - \frac{A\kappa}{2} \int_0^\infty dx\, \frac{x \exp(-2x)}{1 + A\kappa \exp(-x)/x} \right] \frac{\partial}{\partial n} \left(\frac{1}{\kappa^2} \right).$$

Assuming that $\kappa \to 0$ along the critical isotherm leads to the asymptotic formula for the left-hand side of (10) of the form

$$4\pi A \frac{\partial}{\partial n} \left(\frac{1}{\kappa^2} \right). \qquad (16)$$

In the $n \to n_c$ limit, Eq. (10) imposes thus the asymptotic relation

$$\frac{1}{n \kappa^2} = \frac{\partial}{\partial n} \left(\frac{1}{\kappa^2} \right). \tag{17}$$

The general solution $\kappa^{-2} = a\, n$, where a is a constant, is in contradiction with the assumed divergence of the correlation length κ^{-1} at $n = n_c$. Equation (17) is a particular case of the general asymptotic condition (12) implying contradiction with the assumed existence of a critical point.

The analysis presented above has been based on relation (3) between the two- and three-particle correlation functions involving compressibility. This relation generalizes the compressibility equation (4) to higher order correlations, and is particularly well adapted to study the possibility of attaining a critical point where the compressibility becomes infinite. As we have already stressed, the relation is general, valid in any dimension. It does not depend on any specific form of interaction. Rather, relation (3) follows directly from the structure of the equilibrium Gibbs ensemble.

In the present study the Kirkwood superposition approximation has been applied directly to the integrated three-particle correlation function. We did not refer to the YBG hierarchy equations. As it turned out, the application of KSA ruled out the possibility of reaching the critical point.

This result sheds light on the studies of three-dimensional square-well fluids based on the YBG hierarchy equations whose authors concluded that within the superposition approximation no true criticality could be attained.[7–9] However, our purely analytic result is much more general. It shows in particular that the predictions of the mean-field criticality in the dimensions $d > 4$ obtained in Ref. 7 must be a consequence of combining KSA with an additional approximation

leading to a nonlinear differential equation. Intriguingly, the presence of a critical point in 5 and 6 dimensions seems to be implied also by the numerical work of Jones *et al.*[8] However, as the authors themselves comment, a numerical proof of the *existence* of the critical point can never be rigorous, as one cannot construct solutions arbitrarily close to the critical point, and must rely on the extrapolation procedures instead. In this context, it should also be remarked that the integral equation derived from the equilibrium YBG hierarchy under KSA closure was shown to magnify the errors introduced by this approximation.[12]

In summary, we have shown that the Kirkwood superposition approximation applied directly to the spatial integral of the three-particle correlation function leads to a result incompatible with the existence of a critical point.

[1] T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).
[2] I. Z. Fisher, *Statistical Theory of Liquids* (University of Chicago Press, Chicago, 1964).
[3] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience, New York, 1965).
[4] K. D. Luks and J. J. Kozak, Adv. Chem. Phys. **37**, 139 (1978).
[5] G. L. Jones, J. J. Kozak, E. K. Lee, S. Fishman, and M. E. Fisher, Phys. Rev. Lett. **46**, 795 (1981).
[6] M. E. Fisher and S. Fishman, Phys. Rev. Lett. **47**, 421 (1981)
[7] M. E. Fisher and S. Fishman, J. Chem. Phys. **78**, 4227 (1983).
[8] G. L. Jones, E. K. Lee, and J. J. Kozak, J. Chem. Phys. **79**, 459 (1983).
[9] J. Piasecki, P. Szymczak, and J. J. Kozak, J. Chem. Phys. **138**, 164506 (2013)
[10] R. J. Baxter, J. Chem. Phys. **41**, 553 (1964).
[11] P. C. Hemmer, Phys. Norv. **3**, 9 (1968)
[12] B. J. Alder, Phys. Rev. Lett. **12**, 317 (1964).