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Critique of the Paper "On the Gas-Liquid Phase Transition"[1]

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The proof of a recently enunciated theorem on the occurrence of a gas-liquid phase transition is shown to be defective in several respects. Also, it is argued that the theorem itself very probably does not hold.

KEY WORDS: Partition function; cluster expansion; grand partition function; fugacity expansion; analyticity; isotherms; phase transitions.

In his recent paper Biswas[1] claims to have proved the following theorem concerning a classical many-particle system with pairwise additive potential with a hard core: "The necessary and sufficient condition for phase transition to occur is that there exist a temperature $T = T_c > 0$ at and below which all $\bar{b}_l$ (excepting perhaps a finite number of them) are positive." In addition, Biswas derives a series expansion for the equation of state in inverse powers of the fugacity, supposedly valid in the liquid phase.

These results, if reliable, would constitute a valuable and welcome addition to the theory of phase transitions as it exists today. However, as we shall indicate, we have found several errors in the derivation, invalidating the entire proof of the theorem and of the related series expansion.

1. Biswas' argument that the condition is necessary fails for two reasons: The first is his implicit assumption that the two functions

[1] The paper, "On the Gas-Liquid Phase Transition" by A. C. Biswas appeared in *Journal of Statistical Physics* 7:131 (1973).

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$\sum_{l=1}^{\infty} \bar{b}_l(T)\zeta^l \equiv B(\zeta, T)$ and $\chi(\zeta, T)$ are necessarily equal for all positive values of ζ up to the first singularity of $B(\zeta, T)$ on the real positive ζ axis. No such a thing is known to be true in general,[3] and in fact it can be shown to be not true in the case of the Van der Waals equation of state (with Maxwell construction): In this case (if $T < T_c$) $\chi(\zeta, T)$ and $B(\zeta, T)$ have their first singularity on the positive real ζ axis at two different points ζ_1 and ζ_1', respectively, where $0 < \zeta_1 < \zeta_1'$.

The second reason is an incorrect quote from the theory of complex variables: For, while it is sufficient (Ref. 4, Theorem 7.21) for a function $f(\zeta) = \sum_{l=1}^{\infty} \bar{b}_l \zeta^l$ to have a singularity on the positive real ζ axis that (a) the series have a finite radius of convergence and (b) all $\bar{b}_l$, excepting perhaps a finite number of them, are positive, this second condition is by no means necessary, as is demonstrated by the example $f(\zeta) = (1 - \zeta^2)^{-1} - \mathrm{Sh}\, \zeta = 1 - \zeta + \zeta^2 - \cdots$.

2. Biswas' argument that the condition is sufficient is, in an essential way, based on the inequality (A.9) of his paper, which is derived from Eq. (A.8) by an incorrect treatment of the integral. In fact, the step from (A.8) to (A.9) would be justified if the contour in (17) had been chosen such that $\theta = 0$ would correspond to a saddle point of the integrand in (17), but it is not.

To see this more clearly, we may take all g_l equal to zero. (This is permitted here since in this part of the proof no assumption is made about the g_l other than that they are nonnegative). Then $I(\bar{N}) = 1$ and the left-hand side of (A.9) can be evaluated, at least asymptotically for large $\bar{N}$, leading to the result that, for fixed $\bar{z} > 1$ and all sufficiently large $\bar{N}$,

$$\bar{z}^{2\bar{N}+2}/(\bar{z}^2 - 1)(1/4\bar{N}) \leqslant 1$$

which is clearly absurd.

Another way of showing the incorrectness of the derivation of (A.9) is to choose, in case 2, for the contour C a circle with radius R, where $R < 1$ but is otherwise arbitrary. Following Biswas' reasoning we would obtain that

$$\chi(\bar{z}, T) - \log \bar{z} = \sum_{l=1}^{\infty} g_l R^l - \log R$$

for all $\bar{z} > 1$ and all $R < 1$, which is self-contradictory, since the left-hand side is independent of R and the right-hand side is independent of $\bar{z}$.

We add a few remarks concerning the theorem itself. First of all, we have been unable to modify Biswas' proof so as to make it rigorous, nor did we find any indication that it can be done. Second, it seems unlikely that

[3] For a discussion of this point see, e.g., Fisher[(2)] or Lebowitz,[(3)] especially pp. 399 and 406–407.

the part of the theorem stating that the condition is necessary is correct. A good candidate for a counterexample is the Van der Waals model for a fluid.[5] Very probably this model exhibits a phase transition,[5] although a completely rigorous proof still seems to be lacking. However, in the so-called "Van der Waals limit"[6] a rigorous proof exists,[6] whereas in this same limit and in one dimension (the case of the Van der Waals equation of state) it can be shown without much difficulty that the $\bar{b}_l$ change sign infinitely often.

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