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On the Yang-Lee theory of condensation and phase transitions

M. Apostol
Department of Theoretical Physics, Institute of Atomic Physics,
Magurele-Bucharest MG-6, POBox MG-35, Romania
email: apoma@theory.nipne.ro

While progress has been made in second-order phase transitions through Landau-Ginsburg theory and Wilson's renormalization group, the first-order phase transitions enjoyed comparatively less advance.[1] However, it seems that a certain trend has been developed recently for the first-order phase transitions,[1] which can be traced back, in my opinion, to a pair of well-known papers by Yang and Lee on the subject.[2] This trend consists in associating the horizontal platteau and the corresponding jump in the volume in the van der Waals isotherms to the jump in an order parameter across a second-order phase transition.

Actually, this is an improper association, because the first-order transitions are discontinuous across the van der Waals platteux (unphysically, the van der Waals equation replace these platteaux with continuous regions of metastable states), while the thermodynamic functions across the second-order phase transitions are in fact continuous in the order parameter, and the order parameter itself is in fact continuous through the transition point. It is true that the van der Waals equation indicates a critical point where the isotherms are continuous and the metastable states disappear, which indeed may be viewed as a second-order transition, but this point is in fact the point *terminus* for a first-order phase transition.

Yang and Lee start their classical analysis by writing the grand-partition function for an interacting gas like

$$Z = \sum y^N Q_N/N! \ , \tag{1}$$

where, with usual notations,

$$y = (2\pi mT/\hbar^2)^{3/2} e^{\beta\mu} \tag{2}$$

is related to the fugacity $\exp(\beta\mu)$ and

$$Q_N = \int d\mathbf{r_1}...d\mathbf{r_N} \cdot \exp(-\beta U) \ , \tag{3}$$

is the configurational part of the canonical function, where U is the interaction. The grand-partition function given by (1) is quite a regular function, and there is no apparent reason for it to produce discontinuities or singularities. For instance, for a free gas it is given by $Z = \exp(yV)$, and the thermodynamic potential is given by $\Omega = -pV = -TyV$. The number of particles is given by $N = yV\partial(-\beta\Omega)/\partial(yV) = yV$, so we get the well-known equation of state $\Omega = -pV = -NT$.

For a weakly interacting gas the canonical partition function can be approximated by $Z_N = (2\pi mT/\hbar^2)^{3N/2} \langle \exp(-\beta U)\rangle (V - bN)^N/N! \simeq (2\pi mT/\hbar^2)^{3N/2} \exp(-\beta \langle U\rangle) e^N (V/N - b)^N$, with

[1] A more detailed discussion and references are given in M. Apostol, J. Theor. Phys. **147** (2007).

$\langle U \rangle = (N^2/2V) \int dr \cdot U = -N^2 a/V$, where b is an excluded volume and a denotes a parameter accounting for the interaction. The free energy is given by $-\beta F = \ln Z_N$, and we get straightforwardly the van der Waals equation $p = -\partial F/\partial V = NT/(V - Nb) - aN^2/V^2$.

This suggests that the grand-canonical function given by (1) may vanish for some values of y, as for instance for V approaching Nb for a dense number of N-terms (*i.e.* in the thermodynamic limit), which would lead to non-analytical thermodynamic functions like the van der Waals free energy. This observation was made by Gibbs, and led Yang and Lee to assume that Z may have zeroes for some y's, in general complex. For such zeroes closing unto, or pinching, the real axis, one may have non-analytic thermodynamic functions, and phase transitions. Indeed, assume for instance the roots of the equation $y^N = 1$, given by $y = \exp(2\pi k/N)$ for $k = 0, 1, ...N - 1$. There is a dense distribution of such zeroes cutting the real axis at $y = 1$ in the thermodynamic limit $N \rightarrow\rightharpoonup \infty$. Assuming that the grand-partition function may have such zeroes, we can represent the relevant part of the thermodynamic potential Ω as

$$-\beta\Omega \sim \int_{\sim 0} d\theta \cdot \ln(y - e^{i\theta}) \sim \int_0 d\theta \cdot \ln(y^2 - 2y\cos\theta + 1) \sim \int_0 d\theta \cdot \ln(\varepsilon^2 + \theta^2) \ , \qquad (4)$$

where, without loss of generality, we assumed the zeroes cutting the real axis at $y = 1$, and $\varepsilon = y - 1$ (the integral in (4) gives also the electrostatic potential of an electric charge distributed on a circular cilinder). The relevant part of the integral in (4) is $-\beta\Omega \sim \pi\,|y - 1|$. When y passes through 1 the thermodynamic potential Ω is continuous, but its derivative with respect to y, which is related to the number of particles, is discontinuous. This is not a first-order phase transition, like the gas-liquid transition, but it may viewed as representing the condensation of the gas near the critical point. The jump in the number of particles may be associated with the particles "lost" in the liquid phase. Actually, the number of particles may be viewed as an order parameter, which is continuous in fact, but its derivative is discontinuous, so the transition may be a second-order one, as for the critical point of the van der Waals equation. It is worth noting that the zeroes cut the real axis only in the thermodynamic limit, so the jump in the order parameter is related to the continuous distribution of such zeroes. Actually, nothing definite can be said about such a mechanism representing a phase transition, because, in fact, there is no proof that real zeroes of the grand-partition function (1) exist. Yang and Lee found an analogy of the two-dimesnional Ising ferromagnet in an external magnetic field with a lattice gas, where it is known that there exists real zeroes of the grand-partition function. Then, the transition in an external field is a smoothed second-order phase transition indeed. The lattice gas, however, has little relevance for the real interacting gas. In addition, it is worth noting that the Yang and Lee's "condensation" theory does not produce the transition, or critical, temperature.

References

[1] F. Zhong and Q. Chen, Phys. Rev. Lett. **95** 175701 (2005).

[2] C. N. Yang and T. D. Lee, Phys. Rev. **87** 404 (1952); T. D. Lee and C. N. Yang, *ibid*, **87** 410 (1952).