Reply to the Comment by M. Biskup, L. Chayes and R. Kotecky

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Abstract

In their comment to the paper “Theory of the evaporation/condensation transition of equilibrium droplets in finite volumes” [Physica A319, 99 (2003)], Biskup et al. claim that in finite systems at fixed density “the physical significance of the conjugate thermodynamic variable is of dubious value”. This claim is critically discussed.

Key words: phase coexistence, phase transitions, Ising model, finite-size effects, droplets.

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While in the thermodynamic limit the various ensembles of statistical thermodynamics are trivially related to each other by Legendre transformations, in finite systems nontrivial differences of the physical properties in different ensembles appear. This fact, emphasized in the preceding comment [1], of course, is very well known [2], and it is emphasized in the literature on computer simulations [3, 4, 5] in particular, since computer simulations always have to deal with systems of finite size only.

For instance, considering an Ising ferromagnet for temperatures below the critical temperature $T_c$, as a function of magnetic field $H$, the conjugate variable, the magnetization $m$, is a quantity that exhibits nontrivial fluctuations, but its average $\langle m \rangle$ increases monotonically from negative to positive values as $H$ is increased from negative to positive values. Thus $\langle m \rangle = -\partial f(T, H, L)/\partial H$ is a smooth regular function for all finite linear dimensions $L$, in the d-dimensional $L^d$ geometry with periodic boundary conditions, and its derivative $\chi = \partial \langle m \rangle / \partial H$ is everywhere nonnegative and finite. When $L \to \infty$, $M(H)$ develops the jump singularity at $H = 0$ from $-m_{\text{coex}}$ to $+m_{\text{coex}}$, $m_{\text{coex}}$ being the value of the spontaneous magnetization. The details of this behavior have been elucidated in the literature and are well understood [6, 7, 8].

The behavior of the finite Ising magnet where the magnetization $m$ is held fixed as an independent variable is very different [2]. Then the conjugate intensive variable $H$ is a quantity that exhibits nontrivial fluctuations, and its average $\langle H \rangle = \partial g(T, m, L)/\partial m$ is a smooth regular function
for all finite $L$, but for $T < T_c$ exhibits a loop as function of $m$, rather than increasing monotonically with increasing $m$. The singular behavior that occurs in the thermodynamic limit due to the presence of this loop was discussed in [9]. Of course, if one keeps $m$ fixed and takes $L \to \infty$, then the isotherm develops a constant horizontal part $H = 0$ from $-m_{\text{coex}}$ to $+m_{\text{coex}}$ (This is trivially related to the corresponding result in the $(H, T)$ ensemble via the Legendre transformation, of course). The different singular behavior of $H$ vs. $m$ discussed in [4] only follows in a special limit where one takes the limits $L \to \infty$ and $m \to -m_{\text{coex}}$ (from the side where $m > -m_{\text{coex}}$) together, such that $\delta m = (m + m_{\text{coex}})L^{d/(d+1)} = \text{const}$. Since at finite $L$ for $m$ near $-m_{\text{coex}}$ some (rounded) remnants of the transition present in this limit are still observed in simulations (the first observation was actually made in [10]), this transition and its various signatures are of interest for simulations, motivating the discussion presented in [9]. In fact, in the equivalent lattice gas interpretation of the Ising model this transition gets the meaning of an evaporation transition of a droplet in a finite volume when it reaches a certain minimum size. The existence of this transition, first suggested in [11] (Eqs. 26, 27), of that reference) was recently established rigorously [12].

Of course, there is nothing wrong to consider the intensive variable conjugate to a fixed density (magnetization density or particle number density, etc.) in a finite system. Considering the fluctuations of the temperature in a finite system in the microcanonical NVE-ensemble is standard textbook wisdom [13]. Similarly, the chemical potential $\mu$ in the NVT ensemble for finite volumes has always been of great interest in the context of computer simulations [14] and the Widom particle insertion method [14] has been especially devised for the sampling of the chemical potential in the NVT ensemble. If the statement of Biskup et al. [1] that “in such systems the meaning of a conjugate variable is rather murky” were correct a large body of well-established work would become obsolete. Even if the chemical potential in a finite system has an “at best secondary meaning” [1] in the context of the rigorous derivations, it is a well accessible and useful quantity for the simulations, and it gives useful information for the phenomenon at hand. As an example, Fig. 1 presents recent data [15] on the distribution of the chemical potential in a three-dimensional Lennard-Jones fluid for $T \approx 0.68 T_c$ in a box of size $L = 22.5\sigma$ ($\sigma$ being the range of the Lennard-Jones potential) for several values of the particle number $N$ near the droplet evaporation/condensation transition. One can see that the distribution of $\mu$ changes from a single peak distribution for $N = 355$ representing the strongly super-saturated gas without a droplet to a two peak distribution near $N \approx 370$, where part of the time a droplet is present in the system, and part of the time of the sampling it is not present, while for $N = 380$ only the second peak remains, describing the state where the droplet always coexists with the surrounding, less strongly supersaturated, gas. This is exactly the behavior suggested on the basis of the considerations described in [9].

In conclusion, we do not agree with the basic claim of the preceding comment, namely that in finite systems at fixed density “the physical significance of the conjugate thermodynamic variable is of dubious value”, but we also would like to emphasize that in science the question whether
something is “valuable” or not is basically subjective, and the real question
about scientific results is whether they are right or wrong. Thus, we invite
the reader to form his own opinion about this subject.

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Figure 1: Distribution $p(\mu)$ of the chemical potential $\mu$ for a Lennard-Jones fluid at $T = 0.68\varepsilon/k_B$ and several choices of $N$ as indicated, for a cubic box of volume $(22.5\sigma)^3$, $\sigma$ being the range parameter of the Lennard-Jones potential and $\varepsilon$ its strength. From MacDowell et al. [15].
References

[1] M. Biskup, L. Chayes and R. Kotecky, preceding comment.
[2] T. L. Hill, *Thermodynamics of small systems* (Benjamin, New York, 1963)
[3] K. Binder (ed.) *Monte Carlo Methods in Condensed Matter Physics*, Springer, Berlin (1992).
[4] D. Frenkel and B. Smit: *Understanding Molecular Simulation: From Algorithms to Applications*. Academic, San Diego (1996)
[5] D. P. Landau and K. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics*, Cambridge University Press, Cambridge (2000)
[6] V. Privman and M. E. Fisher, J. Stat. Phys. *33*, 285 (1983)
[7] K. Binder and D. P. Landau, Phys. Rev. *B30*, 1477 (1984)
[8] C. Borgs and R. Kotecky, J. Stat. Phys. *64*, 79 (1990)
[9] K. Binder, Physica *A313*, 99 (2003)
[10] H. Furukawa and K. Binder, Phys. Rev. *A26*, 556 (1982)
[11] K. Binder and M. H. Kalos, J. Stat. Phys. *22*, 363 (1980)
[12] M. Biskup, L. Chayes and R. Kotecky, Europhys. Lett. *60*, 21 (2002)
[13] L. D. Landau and M. E. Lifshitz, *Statistical Physics*, Pergamon Press, Oxford (1958)
[14] B. Widom, J. Chem. Phys. *39*, 2808 (1963)
[15] L. G. MacDowell, P. Virnau, M. Müller, and K. Binder (unpublished)