The Yang-Yang Anomaly in Fluid Criticality: An Exactly Soluble Model

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The traditionally accepted scaling formulation of the thermodynamics of a pure fluid near criticality invokes two 'scaling fields', say $\tilde{t}$ and $\tilde{\mu}$, that are algebraic combinations of the temperature, T, and the chemical potential, μ. But is that adequate? Recent work answers 'No!' Specifically, in response to the original suggestion by Yang and Yang[1] that the chemical potential at vapor-liquid coexistence, $\mu_\sigma(T)$, might become singular when $t = (T - T_c)/T_c \to 0^-$ —with $\mu''_\sigma \equiv d^2\mu_\sigma/dT^2$ diverging, in general, like the isochoric specific heat, $C_V \sim |t|^{-\alpha}$ (with, in fact, $\alpha \simeq 0.11$)— an analysis[2–4] of detailed observations for propane and CO_2 demonstrates the presence of a *nonvanishing* Yang-Yang ratio, R_μ, defined as $R_\mu \sim \mu''_\sigma/C_V$ ($T \to T_c$). This violates the traditional scaling predictions *and* those of simple lattice gas models; but it was shown[2,5] in a *complete scaling theory* that the pressure, p, can *also* mix into $\tilde{t}$ and $\tilde{\mu}$, and thereby generate a nonzero R_μ. Furthermore, careful simulations[6–8] of both a hard-core square-well fluid and the restricted primitive model electrolyte yield Yang-Yang anomalies, *i.e.*, $R_\mu \neq 0$.

It is natural to ask if there are statistical mechanical models that exhibit a Yang-Yang anomaly and pressure mixing. And, if so, what might they teach us? Here we describe a general compressible cell gas (or CCG), a version of the usual lattice gas in which, however, the individual cell volumes are allowed to fluctuate[2,9]. A flexible class of such models can be solved exactly[9] via the *decoration transformation*[10] so yielding insight into the microscopic origins of the Yang-Yang and related anomalies: *e.g.*, provided volume fluctuations are coupled to interaction energies, R_μ may be positive *or* negative and, likewise, it may vary greatly in magnitude[9]. A particular example[9,11] turns out to be of previous interest in connection with hydrogen-bonding in water.

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1 C. N. Yang and C. P. Yang, Phys. Rev. Lett. **13**, 303 (1964).
2 M. E. Fisher and G. Orkoulas, Phys. Rev. Lett. **85**, 696 (2000).
3 G. Orkoulas, M. E. Fisher, and C. Üstün, J. Chem. Phys. **113**, 7530, (2000).
4 A. Kostrowicka Wyczalkowska, M. A. Anisimov, J. V. Sengers, and Y. C. Kim, J. Chem. Phys. **116**, 4202 (2002).
5 Y. C. Kim, M. E. Fisher, and G. Orkoulas, Phys. Rev. E **67**, 061506 (2003).
6 Y. C. Kim and M. E. Fisher, J. Phys. Chem. B **108** 6750 (2004).
7 Y. C. Kim and M. E. Fisher, Comp. Phys. Commun. **169**, 295 (2005).
8 Y. C. Kim, Phys. Rev. E **71**, 051501 (2005).
9 R. T. Willis and M. E. Fisher, *Poster* presented at the Conference *Thermo 2005*, University of Maryland, College Park (April, 2005).
10 M. E. Fisher, Phys. Rev. **113**, 969 (1959).
11 S. Sastry, P. G. Debenedetti, F. Sciortino, and H. E. Stanley, Phys. Rev. E **53**53, 6144 (1996).