# Compressible Cell Gas Models and Yang-Yang Critical Anomalies

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Asymmetry features of liquid-gas criticality in pure fluids are analyzed with the aid of exactly soluble lattice gas models in which individual cell volumes are allowed to fluctuate. Such *compressible cell gases* CCG's obey *complete scaling* theory with pressure mixing,[1,2] and thereby display, in accord with experimental evidence,[1,3] Yang-Yang anomalies. This means that, in the exact thermodynamic relation for the isochoric heat capacity $C_V$[4]

$$C_V = \tilde{C}_p + \tilde{C}_\mu, \tag{1}$$

$$\tilde{C}_p = \frac{T}{\rho}\Big(\frac{\partial^2 p}{\partial T^2}\Big)_V, \tilde{C}_\mu = -T\Big(\frac{\partial^2 \mu}{\partial T^2}\Big)_V, \tag{2}$$

not only $\tilde{C}_p$ diverges at criticality like $|t|^{-\alpha}$ [where $t \equiv (T - T_c)/T_c$, with $T_c$ denoting the critical temperature and $\alpha \simeq 0.109$] but so also $\tilde{C}_\mu$ does, that is,

$$\tilde{C}_p(T) \sim \tilde{A}_p|t|^{-\alpha}, \tilde{C}_\mu(T) \sim \tilde{A}_\mu|t|^{-\alpha}, \tag{3}$$

with $\tilde{A}_p \neq 0$ and $\tilde{A}_\mu \neq 0$. Complete scaling also predicts that the coexistence-curve diameter in the density-temperature plane, $\rho_d \equiv (\rho^{liq} + \rho^{gas})/2$, behaves like

$$\rho_d(T) = \rho_c\{1 + A_{2\beta}|t|^{2\beta} + A_{1-\alpha}|t|^{1-\alpha} + A_1|t| + ...\}, \tag{4}$$

where $\beta \simeq 0.326$. The existence of the $|t|^{2\beta}$ singularity, which is supported by simulations[5] and experiments,[6,7] is intimately related to the Yang-Yang anomaly. Specifically, $\tilde{A}_\mu \neq 0$ and $A_{2\beta} \neq 0$ as long as the *crucial* pressure mixing coefficient $j_2$ is nonzero, and so the Yang-Yang ratio $\mathcal{R}_\mu \equiv \tilde{A}_\mu/(\tilde{A}_p + \tilde{A}_\mu) = -j_2/(1 - j_2)$.

Complete scaling remains a phenomenological theory with no physical insights regarding microscopic origins, signs, or magnitudes. Here we show that for the models under consideration $\mathcal{R}_\mu$ ranges from $-\infty$ to 1/2. When cell volumes fluctuate independently, nonvanishing $\mathcal{R}_\mu$ values emerge as a result of *local free volume fluctuations*. Among the various decorated CCG's explored, simple versions in which energies and cell volumes are coupled reveal *local void volume fluctuations* associated to interactions as another source of Yang-Yang and related anomalies. A previously reported model for hydrogen bonding in water[8] appears as a relevant example.

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