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Soluble Model Fluids with Complete Scaling and Yang-Yang Features

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Yang-Yang and singular diameter critical anomalies arise in *exactly soluble compressible cell gas* (CCG) models that obey *complete scaling* with pressure mixing. Thus, on the critical isochore $\rho = \rho_c$, $\widetilde{C}_\mu := -Td^2\mu/dT^2$ diverges as $|t|^{-\alpha}$ when $t \propto T - T_c \to 0^-$ while $\rho_d - \rho_c \sim |t|^{2\beta}$ where $\rho_d(T) = \frac{1}{2}[\rho_{\rm liq} + \rho_{\rm gas}]$. When the discrete local CCG cell volumes fluctuate freely, the Y-Y ratio $\mathfrak{R}_\mu = \widetilde{C}_\mu/C_V$ may take any value $-\infty < \mathfrak{R}_\mu < \frac{1}{2}$ but 'anti-correlated' free volumes are needed for $\mathfrak{R}_\mu > 0$. More general decorated CCGs including 'hydrogen bonding' water models illuminate *energy-volume coupling* as relevant to $\mathfrak{R}_\mu$.

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In 1964 Yang and Yang [1] discovered a serious defect of the standard lattice gas model (say, SLgas), *alias* the Ising model, for studying criticality in fluids. The same defect, furthermore, characterizes Landau-Ginzburg-Wilson or field theory (FT) models. Explicitly, consider an upper critical point at which the isochoric specific heat $C_V(T)$ diverges as $|t|^{-\alpha}$ as $t \equiv (T - T_c)/T_c \to 0^-$ with $\alpha \simeq 0.109$ in $d = 3$ dimensions. Then, if $p_\sigma(T)$ and $\mu_\sigma(T)$ are the pressure and chemical potential on the gas-liquid phase boundary, Yang and Yang proved $C_V = \widetilde{C}_p + \widetilde{C}_\mu$, where $\widetilde{C}_p = Tp''_\sigma v$ and $\widetilde{C}_\mu = -T\mu''_\sigma$ while $v = 1/\rho$ is the specific volume (and $'$ denotes d/dT). On the critical isochore $\rho = \rho_c$ one should thus expect $\widetilde{C}_p = A_p/|t|^\alpha$ and $\widetilde{C}_\mu = A_\mu/|t|^\alpha$.

However, in the SLgas and its usual variants $\mu_\sigma(T)$ is completely analytic. This implies that the Yang-Yang (Y-Y) ratio

$$\mathfrak{R}_\mu = A_\mu/(A_p + A_\mu) \tag{1}$$

vanishes identically with only p''_σ diverging! But is this reasonable? Yang and Yang thought not [1].

This question was finally answered negatively [2, 3] when careful analysis of data for propane yielded $\mathfrak{R}_\mu \simeq 0.56$ whereas CO_2 data indicated a clearly distinct value, $\mathfrak{R}_\mu \simeq -0.3$ [2–5]. Simulations suggest $\mathfrak{R}_\mu \simeq -0.04$ for a hard-core square-well fluid but $\mathfrak{R}_\mu \simeq 0.26$ for the restricted primitive model electrolyte (hard-sphere 1:1) [6].

To accommodate $\mathfrak{R}_\mu \neq 0$ the traditional scaling theories for criticality need modification since, like the SLgas, they entail $\mathfrak{R}_\mu \equiv 0$. This has been accomplished in what is now termed *complete scaling*, an approach that contemplates a comprehensive set of thermodynamic critical anomalies associated with a nonvanishing Y-Y ratio [7]. Thus a remarkable new term is an $A_{2\beta}|t|^{2\beta}$ correction to the diameter of the coexistence curve, $\rho_d = \frac{1}{2}[\rho_{\rm liq} + \rho_{\rm gas}]$. Asymptotically close to criticality this term dominates a long sought [8] but weak $A_{1-\alpha}|t|^{1-\alpha}$ singularity [9, 10] since $2\beta \simeq 0.652 < 1 - \alpha \simeq 0.891$ for $d = 3$ [2, 7].

Such features reflect an underlying *gas-liquid asymmetry* that contrasts with the situation for, e.g., the ferromagnetic-paramagnetic phase transition since the spontaneous magnetization curve —the analog of the gas-liquid coexistence curve— displays an obvious symmetry upon magnetic field reversal. Thus, rather than being a technicality, the issue raised by Yang and Yang addresses a most basic question regarding the precise formulation of scaling for *asymmetric fluid criticality* [2, 7].

The predictions of complete scaling have been tested against experiments [4, 5, 9, 10] and simulations [6, 10]. Furthermore, implications for asymmetry at the mean-field level [9, 11], for surface criticality and inhomogeneous systems [12], for criticality in fluid mixtures [13], for the dielectric constant [14], for the refractive index [15], and for the osmotic compressibility [16] have been explored.

Nevertheless, complete scaling remains a phenomenological theory with no obvious limits on the value of $\mathfrak{R}_\mu$ and no physical insight regarding the origin, magnitude, or even the sign of this basic ratio. The extensive class of exactly soluble *compressible cell gas* (CCG) models introduced here, however, shows that Yang-Yang and related critical anomalies arise as soon as *local volume fluctuations* in fluids are recognized [17, 18].

To describe the CCG models one must note that complete scaling entails three basic *scaling fields*, $\tilde{t}$, $\tilde{h}$, and $\tilde{p}$, in which all thermodynamic fields, T, μ, and p, enter (or mix) explicitly [2, 7, 9]. Specifically, if one writes $\check{\mu} \equiv (\mu - \mu_c)/k_BT$ and $\check{p} \equiv (p - p_c)\, v_c/k_BT$, one needs to leading order

$$\tilde{h} = \check{\mu} - k_1 t - j_2\check{p}, \quad \tilde{t} = t - l_1\check{\mu} - j_1\check{p}, \quad \tilde{p} = \check{p} - k_0 t - \check{\mu}, \tag{2}$$

where the *nonuniversal coefficients* k_0, k_1, j_2, etc., satisfy

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the relations $k_B k_1 = \mu'_{\sigma c} - j_2 p'_{\sigma c} v_c$ while $k_B k_0 = S_c v_c$ with S being the entropy [7]. Furthermore one finds [2, 7]

$$j_2 = -A_\mu / A_p \quad \text{and} \quad \mathfrak{R}_\mu = -j_2 / (1 - j_2) , \tag{3}$$

which implies that the presence of pressure in the *ordering field*, $\tilde{h}$, plays the crucial role in generating a nonzero Yang-Yang ratio. Indeed, one also obtains $A_{2\beta} = \mathfrak{R}_\mu B^2$, where the coexistence curve is described by $[\rho_{\rm liq} - \rho_{\rm gas}]\, v_c \approx 2B|t|^\beta$ [7]. But pressure mixing also leads to $A_{1-\alpha} \sim (l_1 + j_1)$.

It transpires (although not apparently noted previously) that the Second Law implies the restrictions

$$-\infty < j_2 \,,\, \mathfrak{R}_\mu < 1 \quad \text{and} \quad A_p > 0 \,. \tag{4}$$

Explicitly, these follow from (1), (3), and Eq. (3.23) of [7] stating $B = Q_B (1 - j_2)$, while thermodynamics demands $C_V > 0$, $B > 0$, and $Q_B > 0$ [7].

To continue, consider the SLgas interpreted as a continuum cell model: at each of the $\mathcal{N}$ sites of a d-dimensional lattice of coordination number c there is a cell of volume v_0 that may be empty or occupied by one particle that moves freely throughout space; but instead of a normal pair potential, $\varphi(\mathbf{r}_i - \mathbf{r}_j)$, particles in adjacent cells interact only via a discrete energy $\varphi_{\rm min} = -\varepsilon_0$ [19]. Repulsive or excluded volume effects may be taken into account by supposing that a particle in a cell can explore only a 'free volume', say, $\dot{v}_0 < v_0$.

Now to generate a *compressible cell gas* suppose that each cell can, individually, assume n discrete values, $0 < v_k \leqslant v_0$, but with distinct free volumes $\dot{v}_k > 0$ if occupied (or, more generally, $\ddot{v}_k$ if doubly occupied, etc.). To analyze such a model one must, in place of a standard canonical or $(N,\, V,\, T)$ ensemble, employ a great grand canonical or $(\mu,\, p,\, T)$ ensemble [20]. The partition function then embodies sums over particle numbers, energy levels, and volume fluctuations with corresponding Boltzmann factors $e^{\bar{\mu} N}$, $e^{-\bar{\beta} E}$, and $e^{-\bar{p} V}$, where $\bar{\beta} = 1/k_B T$, $\bar{p} = \bar{\beta} p$ and $\bar{\mu} = \bar{\beta}\mu - \ln(\Lambda_T^d / v_0)$ with $\Lambda_T = \hbar\sqrt{2\pi / m k_B T}$ for N particles of mass m and overall energy E.

In the simplest models, say, CCG_0, the free volumes $\dot{v}_k \leqslant v_k$ fluctuate *independently*. One then easily finds [21] an exact analytic mapping into the corresponding SLgas. Specifically, in terms of the isobaric volume-fluctuation sums

$$S_{lm}(\bar{p}) = n^{-1} \sum_{k=1}^{n} v_k^l \dot{v}_k^m \exp(-\bar{p} v_k) \,, \tag{5}$$

and the standard Ising variables [22] $h = H/k_B T$, $K = J/k_B T$, and $\bar{f} = -F/k_B T$, one has

$$2h = \bar{\mu} + \tfrac{1}{2} c \bar{\beta} \varepsilon_0 + \ln\left[S_{01}(\bar{p}) / v_0 S_{00}(\bar{p})\right] , \tag{6}$$

$$4K = \bar{\beta}\varepsilon_0 \,, \qquad \bar{f} = -\ln\left[S_{00}(\bar{p})\right] + \tfrac{1}{8} c \bar{\beta} \varepsilon_0 - h \,, \tag{7}$$

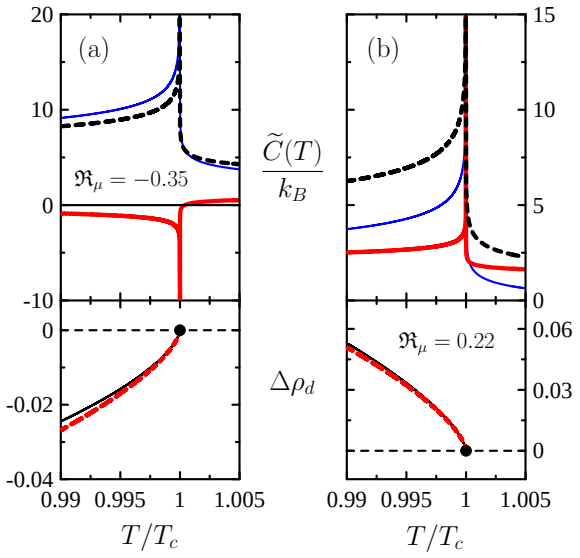


FIG. 1: (Color online) Yang-Yang ratios $\mathfrak{R}_\mu$ and anomalies for simple compressible cell gas models (CCG_0) showing C_V (bold dashed), $\widetilde{C}_\mu$ (bold solid, red), and $\widetilde{C}_p$ (thin solid, blue) for $\rho = \rho_c$, and the reduced diameters, $\Delta\rho_d = (\rho_d - \rho_c)/\rho_c$ (thin solid), and their $|t|^{2\beta}$ components (bold dashed, red) with (a) $n = 3$, $v_2 = \theta v_1$, $v_3 = v_1$, $w = 0$ (point particles) and $\theta = 5$ [while $\theta = 50$ gives $\mathfrak{R}_\mu = -1.23$] and (b) $n = 2$, $v_2 = \theta v_1$ and, for highly compressible particles, $\dot{v}_2 = \dot{v}_1/\theta$ and $\theta = 1/5$ [while $\theta = 1/50$ yields $\mathfrak{R}_\mu = 0.46$].

which relations effectively parallel (2).

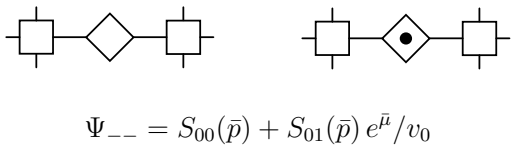
If, as we may surely accept, Ising models for $d = 2$ and 3 obey simple scaling, the associated CCG models must exhibit *complete scaling* in *all* its aspects [2, 7]. But may all the values allowed by (4) be realized in reasonable models? And might the singularity in μ''_σ dominate so that $|A_\mu| > A_p$ and can one have $\mathfrak{R}_\mu > \frac{1}{2}$? For CCG_0 models (6) and (7) lead to

$$j_2 = \rho_c \big(S_{11}/S_{01} - S_{10}/S_{00}\big)_c = \langle \Delta v \Delta \dot{v} \rangle_c / v_c \langle \dot{v} \rangle_c \,, \tag{8}$$

where $\Delta v = v - \langle v \rangle$, etc., while $\langle v^l \dot{v}^m \rangle = S_{lm}/S_{00}$ [21].

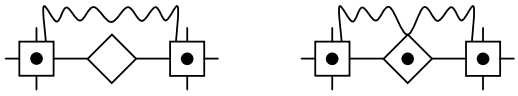
Now, suppose the free volumes are fixed, $\dot{v}_k = v_0$ (all k), so that $\Delta\dot{v} \equiv 0$. This recaptures $j_2 = \mathfrak{R}_\mu = 0$, the usual SLgas or FT result, and so demonstrates clearly that the *origin* of the Y-Y anomaly lies in the *fluctuating free volumes* available to fluid particles.

More realistically, suppose that the particles have a fixed "core volume" $w \geqslant 0$ so that $\dot{v}_k = v_k - w > 0$. Via (8) this yields $j_2 \propto \langle \Delta v^2 \rangle > 0$ and hence, using (3) and (4), $\mathfrak{R}_\mu$ is always negative: see Fig. 1(a) computed with 3D Ising data [22]. Note that large core volumes w relative to $v_{\rm min}$ (or broad $\langle \dot{v}_k \rangle$ distributions) yield arbitrarily large values of $-\mathfrak{R}_\mu$. For all such models, the diameters $\rho_d(T)$ close to T_c must curve up to higher densities: see Fig. 1(a). This is contrary to typical observations [10] which, however, may be dominated numerically by



$$\Psi_{--} = S_{00}(\bar{p}) + S_{01}(\bar{p})\, e^{\bar{\mu}}/v_0$$

$$\Psi_{+-} = S_{00}(\bar{p}) + S_{01}(\bar{p})\, e^{\bar{\beta}\varepsilon_0+\bar{\mu}}/v_0$$



$$\Psi_{++} = S_{00}(\bar{p}) + S_{01}(\bar{p})\, e^{2\bar{\beta}\varepsilon_0+\bar{\mu}}/v_0$$

FIG. 2: States of a CCG for a lattice of primary cells (squares) decorated by secondary cells (diamonds) with, as indicated, decorating factors, expressed using the notation (5), that depend on the occupancy of the primary cells [25].

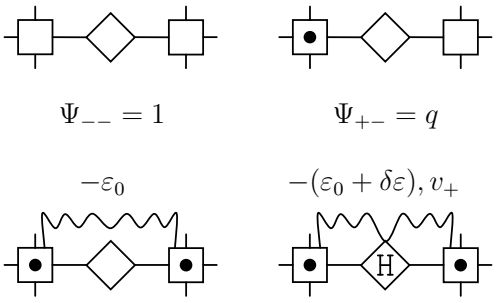


FIG. 3: Decorating factors for the S^3D water model [27], with 'H' indicating the formation of a hydrogen bond with a lower energy but a free volume increase of v_+.

the $|t|^{1-\alpha}$ singularity; but that vanishes in CCG_0 models since $4K = \bar{\beta}\varepsilon_0$ in (7) implies $j_1 = l_1 = 0$, i.e., no mixing of p and μ into the T-scaling field $\tilde{t}$. This feature remains in *augmented models* in which a particle in cell k acquires a potential energy ε_k requiring a further factor $\exp(-\bar{\beta}\varepsilon_k)$ in (5).

To realize positive $\mathfrak{R}_\mu$ in CCG_0 models, requires $j_2 < 0$ and so, by (8), free volumes $\dot{v}_k$ that are *anti*-correlated with the v_k. This may be realized for 'highly compressible' particles that, e.g., when a cell volume v_1 decreases by a factor $\theta < 1$, the core volume decreases *more rapidly* so that the new free volume $\dot{v}_2 = v_2 - w_2$ *exceeds* $\dot{v}_1$ by, say, the inverse $\theta^{-1} > 1$ [23]. Even for $n = 2$ this yields $\mathfrak{R}_\mu > 0$ while $\mathfrak{R}_\mu = \frac{1}{2} - O(\theta)$ when $\theta \to 0$, implying $\widetilde{C}_p \gtrsim \widetilde{C}_\mu$ as $T \to T_c$: see also Fig. 1(b).

A natural extension of the CCGs is to follow Naya [24] and "decorate" each bond of a given lattice with an extra site; indeed, as established long ago [25], this approach can be greatly extended. Then the bond sites or, more generally, *secondary cells* of such a decorated CCG may entail an *arbitrary* number of particles, cell volumes, energy levels, external fields, etc., while exact solubility is retained [25]. Likewise, the secondary parameters may vary independently or, more generally, be coupled to the occupancy of the primary cells. All the needed information is then contained in appropriate *decorating factors*, Ψ_{++}, Ψ_{+-}, and Ψ_{--}, which embody sums over the Boltzmann factors of the secondary cells [25]. See Fig. 2 for the simplest case in which the free volumes, etc., are the same for primary and secondary cells while attractive interactions of magnitude ε_0 are assumed.

In general, for simple occupancy, the transformation in terms of the decorating factors yields [21]

$$2h = \bar{\mu} + \tfrac{1}{2}c\bar{\beta}\varepsilon_0 + \ln\big[S_{01}\Psi_{++}^{c/2}/v_0 S_{00}\Psi_{--}^{c/2}\big], \qquad (9)$$

$$4K = \bar{\beta}\varepsilon_0 + \ln\big[\Psi_{++}\Psi_{--}/\Psi_{+-}^2\big], \qquad (10)$$

$$\bar{f} = -\ln\big[S_{00}\Psi_{--}^{3c/8}\Psi_{+-}^{c/4}/\Psi_{++}^{c/8}\big] + \tfrac{1}{8}c\bar{\beta}\varepsilon_0 - h\,, \qquad (11)$$

which indicates that extra contributions arise from Ψ_{++}, Ψ_{+-}, and Ψ_{--}; from these relations, in addition to "pressure mixing", i.e., $j_2 \neq 0$, one can derive nonvanishing expressions for j_1 and l_1 in (2).

Naturally it is not necessary to decorate *every* bond or to decorate each one in the *same* way! Thus one may readily construct layered or anisotropic models. Furthermore, the various decorating factors entering a given primary cell can be chosen to couple in special ways: e.g., as used for Ising antiferromagnets exactly soluble in an arbitrary magnetic field [26].

Another valuable extension of the decoration approach is to introduce *energy-volume coupling*. As illustrated in Fig. 3, this may not need "occupiable" secondary cells! Rather, by introducing appropriate decorating factors, one can solve in the critical region (and in general) what may be called "S^3D" models [27], devised specifically to handle the anomalous thermodynamic properties of water (and D_2O) [28] by recognizing the role of hydrogen bonds in generating expanded *and* lower energy, transient ice-like structures in the fluid. To formulate the model one envisages [27] that each H_2O molecule may take q distinct "orientations", or "configurations", or, less specifically, *microstates*. When adjacent primary

cells — squares in Fig. 3 — are both occupied, one postulates that q of the q^2 joint orientations (or microstates) form a hydrogen bond. Further, such a bond will be awarded an energy lower by $\delta\varepsilon$ *and* gain a free volume greater by v_+. Despite their depiction in Fig. 3, it is also clear that the "secondary cells" serve only to identify the bond!

From the decorating factors in Fig. 3 one finds, using (9)-(11) with $n = 1$ and $v_1 = \dot{v}_1 = v_0$ in (5),

$$j_2 = \tfrac{1}{2} c\rho_c v_+ \, e^{\bar{\beta}_c \delta\epsilon - \bar{p}_c v_+} / \, (q - 1 + e^{\bar{\beta}_c \delta\epsilon - \bar{p}_c v_+}), \qquad (12)$$

while $j_1 \propto v_+$ but l_1 vanishes [21]. Evidently, then, Yang-Yang anomalies and nonzero $\mathfrak{R}_\mu$ can arise even when single particles may explore only a *fixed* free volume, v_0, *provided* the interaction energy of particles is sensitive to free-volume changes. Since $q \geq 1$ the result (12) means $j_2 > 0$ so that, by (3), only *negative* values of $\mathfrak{R}_\mu$ can appear. One may conclude that correlation of lower energy with increased free volume will yield $\mathfrak{R}_\mu < 0$.

Conversely, to generate positive values of $\mathfrak{R}_\mu$ one may simply change the sign of v_+ (which also serves to *correlate* energy with volume). However, to maintain *positive* free volumes for all particles — and thus a proper ideal-gas limit at low densities — one may argue that each primary cell receives inputs from c bonds while each bond can, in essence, share its reduced free volume between its two (neighboring) primary cells. Thus one must require $|v_+| < 2v_0/c$; nevertheless, (12) remains valid for j_2. However, the same bound, $\mathfrak{R}_\mu < \frac{1}{2}$, as found for CCG_0 models, is still valid. To generate simple models that allow larger values of $\mathfrak{R}_\mu$ — as found experimentally for propane [2, 3]— remains an open task.

A natural further question is: "How about 'Compressible Cell Models' with *continuously compressible cells*?" Such models may be constructed along the lines set out following Eq. (4); but rather than introducing n discrete 'compressed cells' one may contemplate a *distribution*. Then the sum in Eq. (5) is replaced by an integral, say, over a normalized Gaussian distribution; the width of the Gaussian sets the scale of allowed local volume fluctuations. Recall, again, that it is these *fluctuations* in *local volume* that — as now clear from the CCG models — lie at the root of Yang-Yang anomalies.

On the other hand, when it comes to off-lattice or *continuum* systems one must rely on careful simulations [6, 10]. These have taught us that decreasing the width of the attractive well (e.g., in a hard-core square-well fluid) increases the *asymmetry of coexistence curves* to which the Y-Y anomalies contribute. Coulombic interactions (in studies of the RPM, i.e., "restrictive primitive model," electrolyte) have a similar effect. But a concrete benefit of our (in effect) exactly soluble (even if somewhat artificial) CCG models is that such trends can be tested individually, analitically, *and* quantitatively — as we sketched above for the S^3D model [27]. Thus one may contemplate studies of anisotropic interactions, particular many-body forces, etc., and hope to gauge explicitly the degree to which the Y-Y anomalies respond.

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