1 The droplet evaporation/condensation transition in a finite volume

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A fluid in the $NVT$ ensemble at $T$ less than the critical temperature $T_c$ and $\rho = N/V$ somewhat in excess of $\rho_{\text{COEX}}^{(1)}$ (density of the saturated gas in the gas-liquid transition) is considered. For $V \to \infty$, a macroscopic liquid droplet coexists with surrounding saturated gas according to the lever rule. For finite $V$, droplets can only exist if they exceed a minimum size. A (rounded) first order transition of the system occurs when the droplet evaporates into the supersaturated gas. Simulation evidence for this transition is given for a Lennard-Jones model and interpreted by a phenomenological theory. At the transition, the chemical potential difference $\mu_t - \mu_{\text{COEX}}$ scales like $L^{-d/(d+1)}$ for a cubic volume $V = L^d$ in $d$ dimensions, as $L \to \infty$.

1.1 Introduction

There is much interest in the pathway of first order phase transitions, where a droplet of the new phase is formed on the background of the old phase [1–4] by applying computer simulations [4–9]. For the liquid-gas transition, simulating $N$ particles interacting with a Lennard-Jones (LJ) potential in a finite volume $V$ and applying periodic boundary conditions in all directions, one finds a liquid droplet coexisting with surrounding supersaturated gas for an appropriate range of $T$ and $\rho$. From such data the excess free energy of the droplet and the associated nucleation barrier can be inferred.

However, for all simulations [10, 11] one must be aware of systematic errors due to finite size effects. Nucleation theory considers the (hypothetical) unstable equilibrium of one liquid droplet coexisting with an infinite amount of surrounding supersaturated gas. This saddle point in configuration space is not accessible to a straightforward simulation, though. For a finite amount of surrounding supersaturated gas, the droplet is stable in a suitable parameter range [6, 12, 13]. If we increase the total volume (at fixed droplet volume), we encounter a size where the droplet is no longer stable but rather evaporating (with an increase in supersaturation of the surrounding gas) [6, 12, 13].

Some aspects of this transition have recently been proven rigorously [13]. Implications are manyfold. The transition is e.g. crucial for the efficiency of multicanonical sampling [14] in large systems. It can also help to understand
related phenomena such as the melting of islands adsorbed on surfaces in the submonolayer range [15,16] or microcanonical simulations close to two-phase coexistence [17].

1.2 Simulation evidence for the Lennard–Jones fluid

Grand canonical Monte Carlo simulations were carried out in $d = 3$ dimensions using a truncated and shifted LJ potential:

$$U_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 + \frac{127}{16384} \right], \text{ if } r \leq r_c = 2(2^{1/6}\sigma) \text{ and } 0 \text{ else.} \quad (1.1)$$

A multicanonical weighting scheme [18] was applied to simulate states below $T_c$. Weighting functions were generated by adopting Wang-Landau sampling [19] to our off-lattice $(\mu V T)$ ensemble [20]. From the resultant probability distribution $P_{\mu V T}(N)$ one can obtain the chemical potential

$$\mu_{NVT} = -kT \left( \frac{\partial \ln P_{\mu V T}(N)}{\partial N} \right) + \text{const} \quad (1.2)$$

and $\Delta \mu = \mu_{NVT} - \mu_{\text{coex}}$ with $\mu_{\text{coex}} = 0$ being an estimate for $\mu$ at the coexisting curve [21]. Inside the two-phase region and for finite $V$, $\Delta \mu$ jumps to a lower value at an effective “spinodal point”, which moves towards the coexistence curve as $V$ increases [21] (Fig. 1.1).

![Fig. 1.1. Plot of $\beta \Delta \mu$ vs. $N$, for a LJ fluid in a box of $L = 22.5$ at $T = 0.68$ ($\Delta \mu = \mu_{NVT} - \mu_{\text{coex}}$). Note that lengths are measured in units of $\sigma$, temperature in units of $\epsilon/k_B$, and $\beta = 1/k_B T$. $\circ$ denotes densities at which configurations were stored for analysis (compare with Fig. 1.2)
While in principle this has been known for a long time [22], we now present direct evidence from simulation. During the multicanonical run, we saved configurations for typical densities (compare with Fig. 1.1). After simulation, the cluster size distribution $p(N_c)$ and the distribution $p(\mu)$ of the chemical potential $\mu$ in the gas region outside of the cluster was determined. (Fig. 1.2). Any ensemble of atoms whose distance is smaller than $1.5\sigma$ is assumed to belong to the same cluster [23]. The chemical potential was measured by the Widom particle insertion method [24]. For $N \leq 350$, i.e. on the ascending branch of the $\Delta \mu$ vs. $N$ curve in Fig. 1.1, $p(N_c)$ is monotonically decreasing with $N_c$. For $N \approx 355$ a peak near $N_c \approx 120$ appears. It becomes more pronounced and moves to larger $N_c$ as $N$ increases. This peak represents a single large liquid droplet, present in the descending part of the $\Delta \mu$ vs. $N$ curve. However, the liquid droplet cannot be found in all sampled configurations: when we sample the distribution of the largest cluster $N_c^{\text{max}}$ in the system [21], we find a bimodal distribution with one peak near $N_c^{\text{max}} \approx 20$ in the whole range of $N$ studied in Fig. 1.2a. This peak corresponds to configurations which consist of supersaturated gas with small clusters but no single large droplet. The second peak is identical to the peak of the single droplet as shown in Fig. 1.2a. This clear cut evidence for the “evaporation” of the liquid
droplet also appears in double peak - distributions of the chemical potential (Fig. 1.2b) and the internal energy [21].

1.3 Phenomenological theory using the Ising lattice gas model and concluding remarks

The discussion is simplest for the lattice gas, due to its perfect symmetry between liquid and gas, brought out in the magnetic interpretation: the two coexisting phases have spontaneous magnetization $\pm m_{\text{coex}}$, and $\Delta \mu$ corresponds to the magnetic field. The thermodynamic potential $g_{\text{s.g}}(m)$ of the supersaturated gas is simply expanded at the coexistence curve, for magnetization $m$ near $-m_{\text{coex}}$:

$$g_{\text{s.g}}(m) = g_0(T) + \frac{1}{2\chi_{\text{coex}}}(m + m_{\text{coex}})^2,$$  \hspace{1cm} (1.3)  

$\chi_{\text{coex}}$ being the susceptibility (per lattice site) at the coexistence curve. Similarly, the state containing a droplet is described by

$$g_{\text{drop}}(m) = g_0(T) + \frac{1}{2\chi_{\text{coex}}}(m' + m_{\text{coex}})^2 + \frac{S_d\gamma(R^*)^{d-1}}{L^d},$$  \hspace{1cm} (1.4)  

where the last term describes the surface free energy of a droplet (per lattice site) in the capillarity approximation, $S_d$ being the surface area of a $d$-dimensional unit sphere, $\gamma$ the interfacial tension, and $R^*$ the critical droplet radius (satisfying $R^* = (d-1)S_d\gamma/[2dm_{\text{coex}}V_dH]$ $V_d$ being the volume of the unit sphere), and $m' + m_{\text{coex}} = \chi_{\text{coex}}H$ for $H \to 0$.

The transition occurs for $g_{\text{s.g}}(m) = g_{\text{drop}}(m)$ [12]. Rescaling variables $\tilde{m} = m/m_{\text{coex}}, \tilde{H} = H\chi_{\text{coex}}/m_{\text{coex}}$ one finds [13] a first order transition at $\tilde{m}_t = -1 + (d+1)(S_d/2d)^{(d-1)/(d+1)}V_d^{(d-1)/(d+1)}L^{-d/(d+1)}$, where the field exhibits a jump between $\tilde{H}_t^{(1)} = 1 + \tilde{m}_t$ and $\tilde{H}_t^{(2)} = (d-1)\tilde{H}_t^{(1)}/(d+1)$, $\tilde{L} = L/\xi_{\text{coex}}, \xi_{\text{coex}}$ being the correlation length, and $c$ is a constant that is universal near $T_c$ [$c = \gamma\chi_{\text{coex}}/m_{\text{coex}}^2\xi_{\text{coex}}$] [12]. The variation with $L^{-d/(d+1)}$ was first noted in [6] and recently proven rigorously [13]. Of course, for finite $L$ this anomalous first order transition is rounded, but it becomes sharp as $L \to \infty$ [13].

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