
The two versions of the above potential are considered here:

\[ V_{\text{potential}} = \begin{cases} \frac{\alpha}{r} & \text{for } r > \alpha \text{ (repulsive)} \\ \frac{\beta}{r^2} & \text{for } r < \alpha \text{ (attractive)} \end{cases} \]

where \( \alpha > 0 \) and \( \beta < 0 \).

The potential of this form is used to study the liquid-gas coexistence curve.

\[ V(r) = \begin{cases} \frac{\alpha}{r} & \text{for } r > \alpha \\ \frac{\beta}{r^2} & \text{for } r < \alpha \end{cases} \]
with $\Delta r$ and $-\Delta r$ such that the system's c.m. remains fixed ($\Delta r$ being a variation randomly chosen in the volume interval $\Delta V$). Then, the move is considered according to the same acceptance.

The present study is started by considering the case of a system at fixed temperature $T$, composed of $A$ particles interacting via TS LJ potential, contained into a spherical recipient of volume $V$, having the c.m. constrained to coincide with the center of the recipient. The corresponding canonical ensemble is simulated as described earlier. Then, isothermal $P(V)$ curves can be evaluated by means of eq. 4 adapted to the considered conservation laws. Subsequently, the borders of the liquid-gas coexistence region are evaluated by performing Maxwell constructions on all $P(V)|_T$ curves bending backwards. The resulting phase diagrams (in temperature vs. density representation) corresponding to two systems of different sizes $A = 20$ and $A = 50$ are represented in the upper part of Fig. 1. The increase of the critical temperature with the system's size can be observed. A striking feature of these phase diagrams is the small densities corresponding to the borders of the liquid-gas coexistence regions. In this respect, note that the liquid border is situated at densities smaller than $0.2\ \sigma^{-3}$ which differs a lot from the LJ phase diagrams corresponding to infinite homogeneous systems 11, where the liquid border goes up $0.8\ \sigma^{-3}$. The reason for this discrepancy can be easily understood from the lower part of Fig. 1. There, the radial density profiles corresponding to three sample points chosen from the coexistence line of the $A=50$ system are represented. In all three cases the system appears to be inhomogeneous, its density varying from higher values (towards the center of the recipient) to very small ones (towards the recipient’s walls). The low density tails of these radial profiles are therefore inducing the above mentioned effect on the global density of the system (calculated as $A/V$). In particular, note that at small values of the distance from the recipient’s center the densities of the considered sample points tend to be consistent with the ones from Ref. 11. Obviously, this inhomogeneity effect is dictated by the c.m. conservation constraint which forces the larger clusters to stay towards the center of the recipient and the smaller ones towards the borders. This example is particularly important in the context of multifragmentation where the system’s c.m. is naturally conserved from event to event and similar density profiles are expected to occur.

Therefore, in order to meaningfully compare the phase diagram calculated for finite systems with the ones corresponding to infinite systems an extra constraint has to be imposed: the homogeneity. The infinite and homogeneous system can be simply approached within the (above-described) Metropolis simulation by implementing a cubic recipient with periodic boundary conditions (PBC). (No c.m. conservation constraint has to be imposed.) A number of 200 particles interacting via TLRC or TS LJ potentials are placed in a cubic box with PBC. The very good agreement between our calculated phase diagram corresponding to the TLRC case (see Fig. 3, the “∞” curve) and the one from Ref. 11 is confirming the accuracy of the method here employed. The PBC simulations are used for evaluating the bulk “virial energy” per particle, defined as:

$$V = \frac{1}{3A} \sum_{i<j} A \frac{\partial^2 V(r_{ij})}{\partial r_{ij}^2}$$

(4)

Eq. 4 can be now translated into:

$$P = \rho \left( T - \frac{\partial V}{\partial \rho} \right),$$

(5)

where $\rho$ is the system’s density. Therefore, in an infinite and homogeneous system, the virial energy per unity of volume can be written as: $V = \rho \nu$. Given the above definitions one may perform surface corrections for evaluating the $\nu$ term corresponding to finite systems. Since the system is supposed to be homogeneous, its total virial energy can be expressed as the difference between a bulk term and a surface one:

$$V_s = V_b(A - A_s f) = V_b(V - V_s f),$$

(6)

where the index $b$ specifies that the respective term is a bulk one, $A_s$ and $V_s$ are respectively the number of par-
FIG. 2: Pressure versus density curves corresponding to systems of various sizes ($A$) at fixed temperature, $T = 1.05\epsilon$, evaluated with eq. (4). The corresponding size of the system is specified on each curve.

Particles from the surface and the "volume" of the surface, and finally, $1 - f$ is the ratio between the virial energy of a particle from the surface and the virial energy of a bulk particle. While for very large values of the recipient’s radius $(R)$ $1 - f$ is rigorously equal to $1/2$ (i.e. the particles on the surface have half the number of nearest neighbors they have in bulk), for small values of $R$ (the case of small systems) curvature corrections have to be applied to this factor. In the spirit of the previous definition, $f$ can be fairly approached by the ratio between the surface of spherical cap situated outside the recipient, corresponding to a sphere of radius $\sigma$ having the center on the surface of the recipient and $4\pi\sigma^2$. After some algebraic manipulation one gets:

$$f = \frac{1}{2} \left(1 + \frac{\sigma}{2R}\right).$$

Note that when $R \to \infty$ then $f \to 1/2$. Considering the surface “width” equal to $\sigma$ (i.e. no two particles from that region, situated on the same radius, attract each other) one can re-express eq. (4) as:

$$V_h = V_0 A \left(1 - \frac{V_s}{V} f\right),$$

so that:

$$V = \frac{V_h}{A} = V_0 \left\{1 - \frac{1}{2} \left(1 + \frac{\sigma}{2R}\right) \left[1 - \left(1 - \frac{\sigma}{R}\right)^2\right]\right\}.$$  

Eq. (4) can be further expressed in terms of $\rho$ using the identity $\sigma/R \equiv 4\pi \rho \sigma^3/(3A)^{1/3}$. Subsequently, eq. (8) [with $V$ given by eq. (4)] can be applied for calculating the pressure of a finite system of size $A$ at various values of $\rho$.

An illustration of the results of the method is given in Fig. 2 where $P(V)/T$ curves, corresponding to the temperature $T = 1.05\epsilon$ are represented for various sizes of the system. One can observe that the depth of the backbending of the curve is diminishing as the size of the system is increasing and as $A = 20$ the backbending completely disappears.

Maxwell constructions have been further performed on the $P(V)/T$ curves corresponding to various values of $T$ and $A$ allowing thus the construction of phase diagrams for various sizes of the system. The results corresponding to the TLR and TS LJ forms of potential are given in Figs. 3 and 4 respectively. The points from the coexistence region borders obtained via Maxwell constructions can be further interpolated in order to get an estimation of the critical point and a clearer view on the systems’ phase diagrams by means of the Guggenheime scaling relations for the coexistence curve:

$$\rho_\pm = \rho_0 (1 + a \varepsilon \pm b \varepsilon^\beta),$$

where $\rho_\pm$ corresponds to the liquid branch, $\rho_\to$ to the vapor branch of the coexistence curve, $\rho_0$ is the critical density, $\varepsilon \equiv (T_e - T)/T_e$ ($T_e$ being the critical temperature) and $\beta$ is the critical exponent of the coexistence curve. Eq. (9) is fitted on the points obtained via the Maxwell construction method by adjusting the parameters: $T_e$, $\rho_0$, $\beta$, $a$ and $b$. As observed in Figs. 3 and 4 the quality of the obtained fits is very good. (It is worth mentioning that for the TS potential, infinite system case, $\beta = 0.34$ which sharply corresponds to the liquid-gas universality class.) For both considered potentials the critical temperature is drastically decreasing and the critical density
This method makes possible the deduction of the $P(V)\rho_T$ curves corresponding to any size of the system, $A$, by using the information embedded in the bulk $P(V)\rho_T$ curves. The resulting phase diagrams corresponding to homogeneous systems of various sizes show a strong dependence on the size of the system. In this respect, the critical temperature is drastically decreasing when the size of the system is reduced. For example, important deviations from the bulk phase diagram can be noticed even for systems as large as $A = 10^4$. This means that the largest equilibrated systems formed in nuclear multifragmentation experiments are not even close to the bulk limit. To this effect one should, of course, couple the inhomogeneity (discussed earlier) and the Coulomb ones. And as shown in Ref. 1, Coulomb is independently bringing a very important contribution towards lowering the system’s critical point.

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References:

[12] Contributions from the neglected tail to the system's potential energy and virial energy term (see eq. 1) are taken respectively as:

\[
\Delta V = \frac{1}{\rho A} \int_0^\infty \rho A \, \rho A \, \frac{\sigma}{\sigma^2} \, d(\sigma / \rho A) = 8 \pi \rho A \left[ \sigma^2 / (2 \rho A) - \sigma^2 / (3 \rho A) \right];
\]

\[
\Delta \psi = \frac{1}{\rho A} \int_0^\infty \rho A \, \rho A \, \rho A \, \frac{\sigma}{\sigma^2} \, d(\sigma / \rho A) = 8 \pi \rho A \left[ 4 \sigma^2 / (6 \rho A) - 2 \sigma^2 / (3 \rho A) \right].
\]