Nonanalytical equation of state of the hard sphere fluid

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An equation of state of the hard sphere fluid which is not analytical at the freezing density is proposed and tested. The nonanalytical term is based on the classical nucleation theory and is able to capture the observed “anomalous increase” of pressure at high densities. It is combined with the virial expansion at low densities.

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I. INTRODUCTION

It is well known that liquids can be easily superheated or supercooled \[1\]. Equations of state (EOS) describing liquids and gases are constructed as analytical functions for apparent practical and also theoretical reasons (thermodynamic approximations usually lead to classical mean-field type theories). These functions continuously extend to metastable and in most cases also unphysical unstable regions. Phase equilibria are then calculated from these functions. Yet there are arguments casting doubt on this picture.

The first argument is based on the nucleation process, see Review \[2\] and references therein. Pure liquid (any state in general) in a locally stable but globally metastable state undergoes after a certain period of time a spontaneous transition to a more stable state. In three-dimensional systems, liquid/gas and liquid/crystal transitions are of the first order and the process is controlled by homogeneous nucleation: When a nucleus (droplet) of the more stable phase grows above a certain critical limit, it keeps growing until bulk liquid freezes or evaporates. Since thermodynamic quantities are time averages over functions of configurations, we cannot calculate them with arbitrary precision. It does not help to change the size of the system because in a larger system the probability of the critical fluctuation is larger, therefore a value of a thermodynamic quantity in a metastable state is not a function at all because it is a metastable state and therefore the magnetization is not an analytical function of the magnetic field at the phase transition point. This is the first hint that the magnetization below the Curie temperature is not a function at all because it is a metastable state which serves as the simplest model of the first-order phase transition (in the equivalent form of the lattice gas as a model of liquid-vapor equilibrium). It has been proven \[3\] that the magnetization below the Curie temperature cannot be analytically continued to the metastable state. (A function is analytical at a point if its Taylor expansion about this point exists and converges to given function in a neighborhood of the point.) Approximate approaches to this “essential nonanalyticity” problem are based again on the droplet model \[2\].

The second argument is based on the Ising ferromagnet which serves as the simplest model of the first-order phase transition in the equivalent form of the lattice gas as a model of liquid-vapor equilibrium. It has been proven \[5\] that the magnetization below the Curie temperature is not an analytical function of the magnetic field at the phase transition point and therefore the magnetization cannot be analytically continued to the metastable state. These arguments led us to an attempt to use formulas derived from the simplest version of the classical nucleation theory in combination with the virial expansion to develop an equation of state which is not analytical at the freezing point.

II. THEORY

A. Classical nucleation theory

In the classical nucleation theory \[1\] the Gibbs energy of a spherical droplet of solid phase of radius \(r\) emerged in fluid is estimated by

\[
\Delta G(r) = \frac{4}{3}\pi r^3 \rho (\mu_s - \mu_f) + 4\pi r^2 \gamma, \tag{1}
\]

where \(\mu_s\) and \(\mu_f\) are the chemical potentials of the solid and fluid phases, respectively, \(\gamma\) is the s/f interfacial energy (surface tension), \(\rho\) is the reduced number density (sphere diameter is unity).

For metastable fluid (\(\rho > \rho_{fp}\), where \(\rho_{fp}\) is the fluid density at the freezing point) it holds \(\mu_s < \mu_f\) and the Gibbs function \(G(r)\) exhibits a maximum at \(r = r^*\),

\[
r^* = -\frac{2\gamma}{\rho(\mu_s - \mu_f)} \approx \frac{2\gamma}{(\rho - \rho_{fp})A},
\]

where we linearized the difference, \((\mu_s - \mu_f)\rho \approx -(\rho - \rho_{fp})A\), \(A > 0\). As soon as the nucleus happens to reach
radius \( r^* \), it keeps growing. The probability of this spontaneous freezing (per unit time and particle) is proportional to

\[
\exp \left[ -\frac{\Delta G(r^*)}{kT} \right] = \exp \left[ -\frac{\text{const}}{(\rho - \rho_{fp})^2} \right], \tag{2}
\]

where const is a positive constant. This is proportional to the “metastable uncertainty”, the inherent inaccuracy of measurements on the metastable state.

### B. Anomalous behavior in the stable region

The stable phase \((\rho < \rho_{fp})\) can be viewed as a fluid phase with “virtual” nuclei of solid phase of radius \( r \). The probability of finding a nucleus of radius \( r \) is

\[
\text{Prob}(r) \propto \exp \left[ -\frac{\Delta G(r)}{kT} \right]. \tag{3}
\]

Quantities as the compressibility factor, \( Z = p/(\rho kT) \) (\( p \) denotes pressure, \( T \) temperature, and \( k \) the Boltzmann constant), are sensitive to the volume of the nucleus, \( \frac{4}{3} \pi r^3 \). The anomalous part (caused by “fluctuating nuclei”) is obtained by integrating over all sizes of the nuclei,

\[
Z_{\text{anom}} = \text{const}' \times \int_0^\infty r^3 \exp \left[ -\frac{\Delta G(r)}{kT} \right] \, dr. \tag{4}
\]

Substitution \( r = x/(8\pi\gamma)^{1/2} \) and rearrangement of constants leads to the normalized form

\[
Z_{\text{anom}}(\rho) = \beta \psi_3(\alpha(\rho - \rho_{fp})), \tag{5}
\]

where \( \alpha, \beta > 0 \), and \( \alpha \) are constants and

\[
\psi_n(t) = \int_0^\infty x^n \exp \left( \frac{x^3}{3} - \frac{x^2}{2} \right) \, dx. \tag{6}
\]

This integral converges for all \( t \leq 0 \) (then \( \rho < \rho_{fp} \) in Eq. 4), but function \( \psi_n(t) \) is not analytical at \( t = 0 \) and cannot be analytically continued to \( t > 0 \) \((\rho > \rho_{fp})\). This result is in agreement with similar derivations, e.g., in [2].

It follows immediately from the above statement that the radius of convergence of the virial expansion

\[
Z(\rho) = \sum_{n=1}^\infty B_n \rho^{n-1} \tag{7}
\]

is less than or at most equal to \( \rho_{fp} \). In addition, approximation

\[
B_n/\mathcal{V}^{n-1} = \text{const}_0 + \text{const}_1 n + \text{const}_2 n^2,
\]

\( n > n_0 \), leading to the Carnahan-Starling and other popular equations of state \([3]\) of the form polynomial \((y)/(1-y)^3\), is not valid for sufficiently large \( n \) and therefore such equations cannot describe accurately a vicinity of the freezing point. In the above formulas, \( y = \mathcal{V}\rho \) is the packing fraction and \( \mathcal{V} \) is the sphere volume.

### C. Beyond stability

Integral \([1]\) diverges in the metastable region \( \rho > \rho_{fp} \) \((t > 0)\), but it can be approximately evaluated if the upper bound is identified with the maximum \( r^* \) of \( G(r) \). It means that configurations with droplets larger than the critical size \( r^* \) are omitted. The error of this approximation is estimated by \([4]\). In other words, the nonanalyticity at \( \rho = \rho_{fp} \) does not allow extrapolation of \( Z(\rho) \) to \( \rho > \rho_{fp} \) with precision higher than given by \([2]\).

After normalization we get Eq. 5 with the following extension of 6,

\[
\psi_n(t) = \int_0^{\infty} x^n \exp \left( \frac{x^3}{3} - \frac{x^2}{2} \right) \, dx. \tag{8}
\]

This function for \( n = 3 \) is drawn in Fig. 1. The maximum, appearing also on higher derivatives, matches the third hint of the Introduction.

### D. Nonanalytical equation of state

The equation of state should sew together both the low-density region and the anomalous part valid near the freezing point. We tried a simple sum of a polynomial in \( \rho \) up to order \( \rho^{m-1} \) and the anomalous term,

\[
Z_m(\rho) = \sum_{i=1}^m C_i \rho^{i-1} + \beta \psi_3(\alpha(\rho - \rho_{fp})), \tag{9}
\]

where coefficients \( C_i, i = 1, \ldots, m \), are determined so that the virial coefficients \([3, 7]\) up to \( B_m \) are reproduced. Two adjustable parameters \( \alpha \) and \( \beta \) were fitted to MD data \([3]\) up to density \( \rho_{\text{max}} \). The value of \( y_{fp} = \pi \rho_{fp}/6 = 0.494 \) was taken from \([8]\). The standard deviation \( \sigma \) of
the fit (the objective function) was

\[ \sigma^2 = \frac{1}{N_{\text{data}} - 2} \sum_{i=1}^{N_{\text{data}}} \left[ Z_i - Z_m(\rho_i) \right]^2 / \sigma_i^2, \]  

(10)

where \( \sigma_i \) is the standard error of molecular dynamics (MD) datum \( Z_i \), see below.

III. MOLECULAR DYNAMICS DATA

The values of the compressibility factors at reduced densities \( \rho \leq 1.02 \) are taken from [8] where also details of the molecular dynamics algorithm and finite-size corrections are explained. The \( \rho = 1.03 \) value was recalculated and higher densities newly calculated. We combine runs of \( N = 1000, 2000, 4000, \) and 13500 particles, but at lower densities we disregard \( N = 1000 \) results because of too large finite-size errors (according to Eq. (6) in [9], the influence of periodic boundary conditions is about 0.02 in \( Z \) for the \( \rho = 1.04, N = 1000 \) system).

The time in MD calculations can be expressed either as real time \( t \) in reduced time units (mass and sphere diameter are unity) or the number of collisions \( N_{\text{col}} \) in the system. Without finite size corrections they are related by

\[ t = \frac{N_{\text{col}}}{N(3/\pi)^{1/2}(Z - 1)}. \]

Two algorithms for obtaining the initial configuration were used. In the first one [8] a periodic cube with 500 spheres, obtained by Monte Carlo simulation while shrinking to the desired density, was replicated. The second algorithm was based on soft spheres simulated again by Monte Carlo method from random start with decreasing temperature until all overlaps disappeared. Then during a period of 60–100 time units (about 1000 collisions per particle) the system was “partially equilibrated”, i.e., a plateau on the \( Z(t) \) convergence profile was reached. The second algorithm gave better results because in some cases the first one lead to a partly crystallized cube.

The metastable MD results need comment because the principle inaccuracy limit is reached and data interpretation is not straightforward.

At \( \rho = 1.02 \) the system stays at the metastable state for \( 2(1) \times 10^{10} \) collisions and then it “suddenly” freezes. The metastable chunks with approximately constant values of \( Z \) are long enough to be unambiguously extracted and the main source of error is still the statistical uncertainty of the data; the accuracy could be increased by a longer simulation.

The averaged freezing time for \( \rho = 1.03 \) is 3.3(7) \( \times 10^8 \) collisions \( (t = 1500) \) for \( N = 13500 \) and consistently 3.8(9) \( \times 10^8 \) \( (t = 5000) \) for \( N = 4000 \) in agreement with the mechanism of spontaneous homogeneous nucleation—the larger system, the higher probability of nucleation. However, the \( N = 1000 \) system freezes unexpectedly faster, in 6(2) \( \times 10^8 \) collisions \( (t = 1250) \), which we attribute to the influence of the periodic boundary conditions. The chunks of data corresponding to the metastable fluid are clearly visible, but the points when a partly equilibrated metastable state starts and where the first nucleus of the solid phase appears are not exactly defined. Our analysis of the data using a plot therefore contains a subjective factor \( 12 \) leading to scattering of the \( Z \) values by not more than 0.001 if the same procedure is repeated, exemplifying the principle metastable uncertainty. The formally calculated error 0.0014 was therefore increased to 0.002.

For \( \rho > 1.04 \) and partly also for \( \rho = 1.04, N > 4000 \), it becomes difficult to determine the metastable parts as well as the onset of freezing. There is no plateau on the \( Z(t) \) curve but rather a shoulder [9]. Apparent freezing appears within time of roughly \( t = 200 \) (4000 collisions per particle). The main source of error in the estimated \( Z \) is the metastable uncertainty which is inevitably rather guessed than calculated. Our guesses are more pessimistic than those by [8]; in addition, our \( Z \) data are systematically by about 0.001 lower. Our \( \rho < 1.04 \) data also match recent results [11] except the \( \rho = 1.04 \) point which is lower, \( Z = 17.76(2) \); there are no data in range \( \rho \in [1.05, 1.09] \) in [8].

IV. RESULTS AND DISCUSSION

In spite of an obscure nature of error estimates in Table IV we tried to fit them to formula (2), assuming uniform relative inaccuracies of these errors. The resulting estimate of the freezing density, \( \rho_0 = 0.966(12) \), is surprisingly close to the correct value 0.943 [8].

Results for the nonanalytical EOS [3] with \( \rho_{\text{max}} = 0.95 \) (only stable data except the last only slightly metastable point) and \( \rho_{\text{max}} = 1.09 \) (all available data) are collected in Table IV. It is seen that the fitting is stable and the resulting values of \( \alpha \) and \( \beta \) are in a physically sensible range, especially if we do not consider \( m \leq 4 \) (not enough

| \( \rho \) | \( Z \) |
|---|---|
| 1.02 | 16.55873(30) |
| 1.03 | 17.2007(20) |
| 1.04 | 17.847(20) |
| 1.05 | 18.59(4) |
| 1.06 | 19.41(8) |
| 1.07 | 20.32(10) |
| 1.08 | 21.30(15) |
| 1.09 | 22.15(30) |

TABLE I: MD data on the compressibility factor \( Z \) at deeply metastable states. The error bars are estimated standard deviations in units of the last significant digit, for \( \rho \geq 1.04 \) combined with estimated metastable uncertainty.
TABLE II: Parameters $\alpha$ and $\beta$ of the nonanalytical EOS, Eq. (9), its residual standard deviation $\sigma$, Eq. (10), and the residual standard deviation $\sigma_{an}$ of the expansion in $x = y/(1 - y)$ with two adjustable parameters, in dependence on the maximum virial coefficient $B_m$ included.

| $\rho_{\text{max}}$ | $\alpha$  | $\beta$  | $\sigma$ | $\sigma_{an}$ | $\alpha$  | $\beta$  | $\sigma$ | $\sigma_{an}$ |
|---------------------|------------|------------|---------|---------------|------------|------------|---------|---------------|
| 0.95                | 0.6594     | 12.81      | 347     | 381           | 0.6441     | 13.22      | 381     | 85            |
| 1.09                | 0.5453     | 17.20      | 106     | 106           | 0.5337     | 17.69      | 96      | 33            |
| 2.00                | 0.4740     | 23.02      | 34      | 28            | 0.4735     | 23.06      | 28      | 53            |
| 3.00                | 0.4239     | 30.76      | 11      | 4.5           | 0.4371     | 28.66      | 26      | 18            |
| 4.00                | 0.3877     | 40.56      | 5.1     | 8.4           | 0.4212     | 32.31      | 31      | 25            |
| 5.00                | 0.3602     | 52.86      | 6.2     | 8.6           | 0.4266     | 31.06      | 30      | 22            |
| 6.00                | 0.3407     | 66.40      | 6.2     | 8.6           | 0.4619     | 23.10      | 28      | 23            |
| 7.00                | 0.3353     | 71.69      | 6.3     | 21            | 0.5473     | 11.93      | 23      | 47            |

virials to describe low density) and $m \geq 9$ ("too stiff" virial part). It is also seen that the equation is not able to fit the data within their standard deviations—we would need more adjustable parameters. Consequently, using $\sigma_i$ in Eq. (10) may be considered inappropriate. Therefore we tried also $\sigma_1 = 1$ (uniform absolute error) and $\sigma_i = Z_i$, (uniform relative error), but the results were qualitatively the same.

A “standard” approach to the HS EOS is a polynomial in $x = y/(1 - y)$. The coefficients up to power $x^m$ can be determined from the known virial coefficients while higher coefficients are fitted to the MD data. Column $\sigma_{an}$ of Table II contains the residual standard deviation of this analytical function with two adjustable parameters. It is seen that both the analytical and nonanalytical EOSs are for $m \geq 5$ comparable. However, the result of the nonanalytical EOS are, for $m \geq 7$ for $\rho_{\text{max}} = 0.95$ or $m \geq 5$ for $\rho_{\text{max}} = 1.09$, uniformly good (or bad) while adding one virial coefficient to the $x$-expansion may worsen the result considerably.

Similar picture can be obtained from the ability of the EOSs fitted in an (almost) stable range, $\rho_{\text{max}} = 0.95$, to extrapolate to higher densities. The analytical equation, Fig. 2, is better at low densities, but gives nonuniform extrapolation to the deeply metastable region, especially if many virial coefficients are taken into account. In contrast, the nonanalytical equation, Fig. 3, though worse at low densities, gives (for $m \geq 5$) uniformly lower values. The difference is only a few times larger than the inherent metastable error and suggests that there is a systematic inaccuracy in the model, in other words, the nonanalytical term captures most but not all of the “anomalous behavior”.

Both the analytical and nonanalytical equations exhibit a “bump” or irregular behavior at $\rho = 1.04$. This is the density where the well-defined plateaus on the $Z(t)$ curves cease to exist and data interpretation contains a subjective factor. From the microscopic point of view the critical droplet size $r^*$ is comparable with the molecule size and the nucleation model fails.

V. CONCLUDING REMARKS

In spite of many approximations used (surface energy independent on the droplet size, spherical droplets comparable to the atom size, simple combination of the low-density expansion and high-density region) the model of fluctuating droplets of solid state in fluid is able to provide stable results on the equation of state near freezing density and enables extrapolation to higher densities.

Unfortunately, integral is probably too complicated for practical application.
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[12] Using subjective criteria in data analysis may affect the results by unconscious bias. One way to avoid this bias would be a blind analysis by an independent researcher similar to a blind experiment in drug testing.