



## Web applet for predicting structure and thermodynamics of complex fluids

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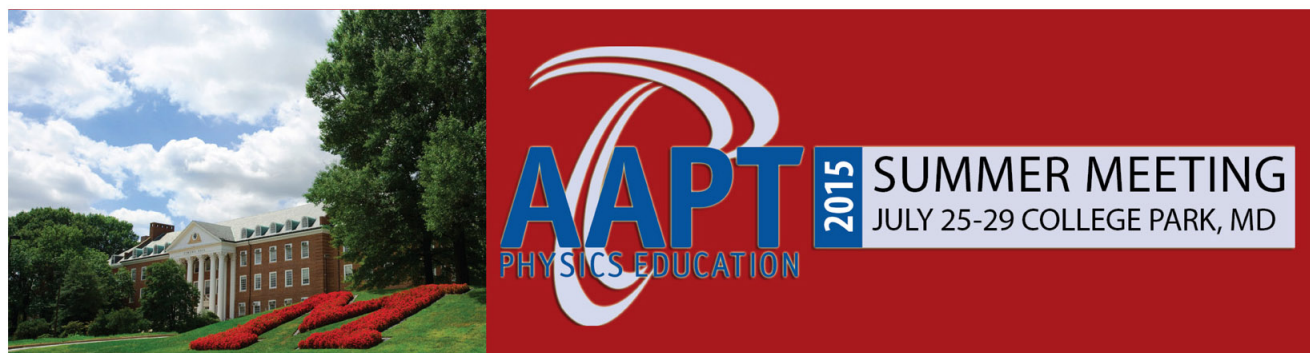
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# Web applet for predicting structure and thermodynamics of complex fluids

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Based on a recently introduced analytical strategy [Hollingshead *et al.*, J. Chem. Phys. **139**, 161102 (2013)], we present a web applet that can quickly and semi-quantitatively estimate the equilibrium radial distribution function and related thermodynamic properties of a fluid from knowledge of its pair interaction. We describe the applet's features and present two (of many possible) examples of how it can be used to illustrate concepts of interest for introductory statistical mechanics courses: the transition from ideal gas-like behavior to correlated-liquid behavior with increasing density, and the tradeoff between dominant length scales with changing temperature in a system with ramp-shaped repulsions. The latter type of interaction qualitatively captures distinctive thermodynamic properties of liquid water, because its energetic bias toward locally open structures mimics that of water's hydrogen-bond network. © 2015 American Association of Physics Teachers.

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## I. INTRODUCTION

Statistical mechanics provides quantitative links between a fluid's interparticle interactions and its resulting equilibrium structure and thermodynamic properties. However, particularly for dense systems or systems with complex interactions, it can be challenging to find ways for students to explore these relationships within the framework of a university course. These challenges may be due to limits on time, expertise (either computational or experimental), and/or resources required to, e.g., numerically solve the Ornstein–Zernike relation with an appropriate closure,<sup>1,2</sup> construct a molecular simulation to extract relevant equilibrium data,<sup>3–5</sup> or carry out relevant measurements in a laboratory.<sup>6,7</sup> As a result, for students to become familiar with the relevant concepts, additional tools are required that help them to overcome these technical hurdles.

Here, we present a web-based applet that helps students develop some familiarity with these systems. The applet uses a new analytic integral equation-based method for equilibrium fluids in three dimensions<sup>8</sup> and provides rapid and semi-quantitative graphical predictions of structural and thermodynamic quantities from knowledge of the pair interaction and parameters that describe the thermodynamic state (i.e., density and temperature). Apart from awareness of a few practical constraints, detailed knowledge of the internal calculations is not required to make productive use of the applet as a pedagogical tool or as an experimental guide. Because of its efficiency and accessible layout, students are empowered to interactively experiment with a fluid's pair potential or its thermodynamic state and extract meaningful relationships and trends.<sup>9–13</sup>

The applet is written in JAVA, which ensures portability across different operating systems and allows the applet to be embedded in a web page. It is freely available for online use or download,<sup>14</sup> and its source code is also freely available under an open-source license.<sup>15</sup>

## II. INTERNAL CALCULATIONS

The applet accepts as inputs a pairwise interaction potential  $\phi(r)$  as a function of interparticle separation  $r$ , the temperature  $T$ , and the number density  $\rho$ , and it approximately

calculates the corresponding unique radial distribution function (RDF)<sup>16</sup> as well as other related thermodynamic quantities. The applet requires that the interactions be isotropic, consisting of a hard core of diameter  $\sigma$  plus an arbitrary short-ranged contribution  $\varepsilon\phi(r)$ , where  $\varepsilon$  is a characteristic energy scale, that decays to zero by  $r = 2\sigma$

$$\frac{\phi(r)}{\varepsilon} = \begin{cases} \infty & r < \sigma, \\ \phi(r) & \sigma \leq r \leq 2\sigma, \\ 0 & r > 2\sigma. \end{cases} \quad (1)$$

Through the choice of different functions for  $\phi(r)$ , this generic form encompasses many different types of effective model interactions routinely used to describe the thermodynamics and structure of complex fluids.<sup>8</sup> Two possible choices are discussed explicitly in this article: (1) a bare hard-sphere potential, for which  $\phi(r) = 0$ , that models excluded-volume interactions in fluids, and (2) a repulsive ramp potential, for which  $\phi(r) = 2 - r/\sigma$ , that qualitatively captures some distinctive properties of liquid water.<sup>17–19</sup> Other possible model interactions include, but are not limited to, Yukawa potentials that model screened electrostatic repulsions in colloidal suspensions and dusty plasmas,<sup>7,20,21</sup> and the Asakura–Oosawa potential<sup>22,23</sup> that models polymer-mediated depletion attractions between suspended colloids. Structural predictions for interactions appropriate for modeling dense, simple liquids like argon and nitrogen are also possible.

### A. Radial distribution function

The radial distribution function (RDF) is the average number density of particle centers located at a distance  $r$  from the center of an arbitrarily chosen reference particle, divided by the number density of the fluid.<sup>1</sup> This function, which characterizes the short-range order displayed by a liquid, can be measured in conventional scattering experiments. Knowledge of a fluid's RDF and its pair interaction  $\phi(r)$  allows one to compute many macroscopic thermodynamic properties including the pressure, the isothermal compressibility, and the energy.

In order to predict the RDF from a given  $\phi(r)$ , the applet uses a strategy that builds upon successful analytical

approaches introduced for fluids with piece-wise constant pair interactions. Specifically, it first decomposes the continuous potential interaction into a “terraced” representation of  $M = 100$  equally spaced discrete steps,<sup>8</sup> each with an outer range

$$\frac{\lambda_i}{\sigma} = 1 + \frac{i}{M} \quad (2)$$

and a constant energy

$$\frac{\phi_i}{\epsilon} = (\lambda_i - \lambda_{i-1})^{-1} \int_{\lambda_{i-1}}^{\lambda_i} \phi(r) dr. \quad (3)$$

The integration in Eq. (3), and other integrations for the applet are carried out via the trapezoidal rule.

Unlike the original continuous potential, the terraced potential yields a jagged or “sawtoothed” RDF,  $g_{ST}(r)$ , which can be readily and accurately computed via modern liquid-state theory.<sup>8</sup> Then, to arrive at a continuous RDF prediction that corresponds to the original continuous potential, the “teeth” are smoothed by computing a series of linear corrections to  $g_{ST}(r)$  such that adjacent pieces of the smoothed RDF,  $g(r)$ , have equal values at each intersection, i.e.,  $g(\lambda_i^-) = g(\lambda_i^+)$ , where the superscripts  $-$  and  $+$  indicate limiting values approaching each  $\lambda_i$  from the left and right, respectively (see Ref. 8 for details).

## B. Thermodynamic properties

The applet calculates several thermodynamic properties that are directly accessible via the pair potential and the RDF. The internal energy per particle  $u$  is<sup>1</sup>

$$u = \frac{3k_B T}{2} + 2\pi\rho \int_0^\infty \phi(r) g(r) r^2 dr, \quad (4)$$

where  $k_B$  is the Boltzmann constant,  $T$  is temperature,  $\rho = N/V$ ,  $N$  is the total number of particles, and  $V$  is the volume. The compressibility factor  $Z$  is<sup>24</sup>

$$Z = \frac{\beta P}{\rho} = 1 + \frac{2\pi\rho}{3} \sum_{i=0}^M \lambda_i^3 [g_{ST}(\lambda_i^+) - g_{ST}(\lambda_i^-)], \quad (5)$$

where  $\beta = (k_B T)^{-1}$ ,  $P$  is the pressure, and  $\lambda_i$  is given by Eq. (2). Note that the excess Helmholtz free energy of the fluid (and other properties of interest through standard thermodynamic relations) can subsequently be obtained from knowledge of the density and temperature dependence of  $Z$ , i.e., the equation of state.<sup>1</sup> The two-body contribution to molar excess entropy  $s^{(2)}$  is also directly computable from the RDF<sup>25–27</sup>

$$\frac{s^{(2)}}{k_B} = -2\pi\rho \int_0^\infty [g(r) \ln g(r) - g(r) + 1] r^2 dr. \quad (6)$$

This last quantity—the entropy cost of pair correlations (relative to a structure-free ideal gas)—is of interest because it is known to correlate with dynamic properties (e.g., self diffusivity) in a wide class of fluid systems.<sup>25–30</sup>

Similar to most theories of simple liquids,<sup>1</sup> this theoretical approach loses accuracy near a critical point or in systems with very high density (e.g.,  $\rho\sigma^3 \gtrsim 1$ ) or very low

temperature (e.g.,  $k_B/\epsilon \lesssim 0.05$ ), with the details depending on the chosen interaction.

## III. APPLLET FEATURES

Full instructions for using the applet are included in the electronic supplement to this article.<sup>14</sup>

The applet organizes all information under one or more “systems,” each comprising a name, a short-ranged addition to the pair potential  $\phi(r)$ , a thermodynamic state ( $k_B T/\epsilon$  and  $\rho\sigma^3$ ), and a maximum calculation range  $r^{\max}/\sigma$ . Systems can be imported from a file on the user’s computer, or defined interactively through text boxes. Multiple systems can be present simultaneously, and all numerical data can be exported as tab-separated value files for further processing in, e.g., a spreadsheet program.

Once a terraced potential has been generated, the continuous and terraced pair potentials are presented graphically for easy inspection. By default, the full data sets are plotted, but the user can adjust the plot axes to focus on a region of interest.

After a system’s RDF has been calculated, both  $g_{ST}(r)$  and  $g(r)$  data are available for plotting. Multiple data series can be plotted simultaneously so the user can compare different systems and analyze, e.g., the impact of the smoothing algorithm or the differences in RDF structure between two systems. Care should be taken to ensure that oscillations in the RDF have decayed before  $r^{\max}/\sigma$ ; for most state points away from the critical point of the fluid, the default choice of  $r^{\max}/\sigma = 10$  is conservative.

The thermodynamic properties described in Sec. II B—average configurational energy, average internal energy, compressibility factor, and two-body excess entropy—are also calculated for each system and tabulated.

## IV. TEACHING EXAMPLES

This applet offers many pedagogical opportunities to teachers and students of classical statistical mechanics. Most simply, it can illustrate the effects of changing temperature, density, or interactions on the fly, e.g., during a lecture. The applet can also be used to prepare example figures through the use of the plot saving functionality, or by exporting the calculated data and plotting in a preferred environment. Because of its ability to save and load states, an example “initial state” could be prepared for further manipulation during a lecture, or distributed as part of a homework assignment. Students are also able to experiment freely by modifying the attractions or repulsions, changing the density or temperature, etc., to develop an intuition for complex fluid phenomena, without needing a simulation suite or coding knowledge.

Here, we provide examples of how our applet might be used to illustrate two fundamental ideas.

### A. Emerging coordination shell structure with density

The hard-sphere (HS) fluid—whose particles have no interaction other than a volume exclusion to prevent interparticle overlap, i.e.,  $\phi(r) = 0$  in Eq. (1)—is a canonical reference model for the structure of dense liquid and colloidal systems, and it is one of the simplest models of a non-ideal gas. Because the interaction potential is either infinite or zero, its structure is independent of temperature (as are its

energies and dynamics, apart from a trivial scaling related to particle velocities).<sup>1</sup> Despite their simplicity, hard-sphere fluids (like atomic liquids and particle suspensions) develop nontrivial structure (e.g., interparticle correlations) as density increases. At  $\eta \approx 0.494$ , the HS fluid experiences a purely entropy-driven freezing transition to form an FCC crystal.<sup>1</sup>

In Fig. 1, we have used the applet to plot the radial distribution functions of HS fluid systems at  $\eta = 0.01, 0.15, 0.30$ , and  $0.45$ . As the packing fraction is increased, several trends become evident. First, the range of the correlation increases from slightly beyond  $r/\sigma = 1$  to nearly  $r/\sigma = 5$  as coordination shells of nearest neighbors, next-nearest neighbors, and so on, develop. Second, the magnitude of the first peak in the radial distribution function increases from  $g(r) \approx 1$  to  $g(r) \approx 5$ , indicating that particles are contacting one another with greater and greater frequency. And third, the period of the oscillations (once they are present) shrinks as the coordination shells become more condensed. These structural trends with increasing density, also commonly seen in simple liquids, result in an increased pressure and reduced excess entropy—both of which are readily verifiable in the applet.

## B. Temperature effects in a two-length-scale fluid

In liquids more complex than hard spheres, multiple length scales can be present within the pair potential. For example, in a repulsive ramp system where

$$\phi(r) = 2 - \frac{r}{\sigma}, \quad (7)$$

there are relevant length scales at  $r/\sigma = 1$ , at the edge of the hard core, and at  $r/\sigma = 2$ , at the outer limit of the interaction (see Fig. 2). For an interaction of this form, one would expect that at high temperatures ( $k_B T \gg \varepsilon$ ), the energy associated with the finite repulsion outside  $r = \sigma$  would be negligible compared to the thermal energy of the system; therefore, the hard core length scale might be most relevant (i.e., the system

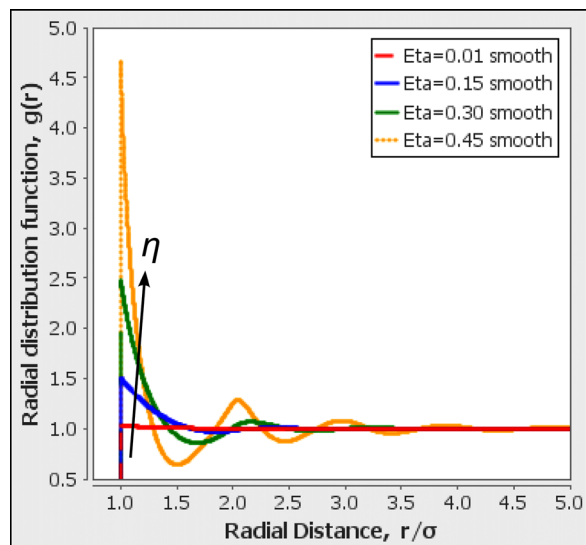


Fig. 1. (Color online) Increasing structure with increasing packing fraction in a hard-sphere fluid. The arrow indicates the direction of increasing packing fraction  $\eta$ . For  $\eta = 0.01$  (tail of the arrow) there are almost no correlations beyond the hard core, while for  $\eta = 0.45$  (head of the arrow) the correlations extend to nearly six particle diameters and a large population of particles are in contact.

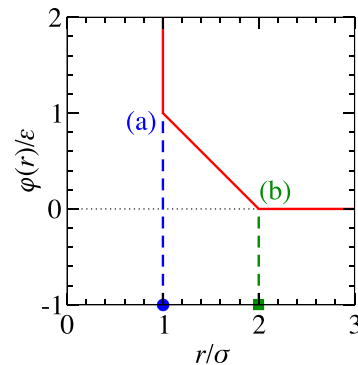


Fig. 2. (Color online) The repulsive ramp potential (solid curve) has two length scales: the hard core diameter (a) and the outer edge of the ramp (b). The former is favored at high temperature, while the latter is favored at low temperature.

approaches hard-sphere-like structure). Conversely, at low temperatures ( $k_B T \ll \varepsilon$ ), contributions from the finite repulsion would be more significant, causing the  $r = 2\sigma$  (more open, low density) length scale to dominate.

The applet can be used to demonstrate this phenomenon, by simulating the same ramp potential at a series of different temperatures (see Fig. 3). Over the range of temperatures from  $k_B T/\varepsilon = 0.2$  to  $1.0$ , peaks corresponding to the two length scales are clearly present at  $r/\sigma = 1$  and  $r/\sigma = 2$ . However, as the temperature decreases, so too does the significance of the inner peak; below  $k_B T/\varepsilon = 0.4$ , the outer peak is taller.

These temperature-dependent trends are analogous to those seen in network-forming fluids like liquid water, where the hydrogen-bond network energetically favors low-coordinated, open structures. Due to analogous physics along isobars, at moderate pressures, such structures dominate in water, leading the fluid to exhibit negative thermal expansivity (expansion upon cooling) at low temperature—a thermodynamic property also exhibited by the ramp model.<sup>17–19</sup> Similar features occur in other network-forming fluids like silica, whose interactions energetically also favor locally open structures.

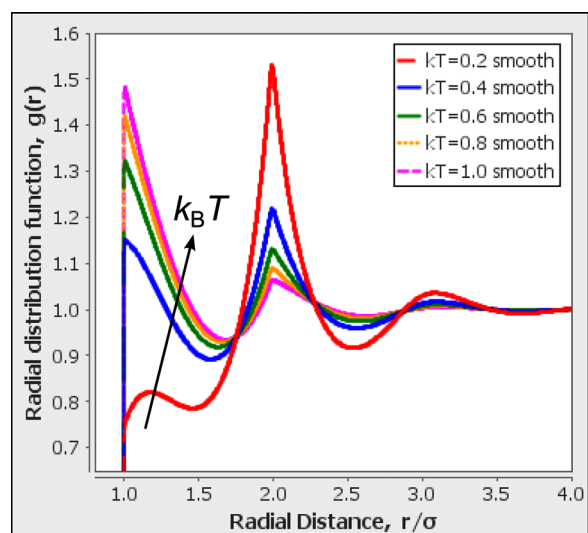


Fig. 3. (Color online) Smoothed radial distribution functions of the ramp system [Eq. (7)] at several temperatures and  $\eta = 0.2$ . The arrow indicates increasing temperature, with  $k_B T/\varepsilon = 0.2$  at the tail of the arrow and  $k_B T/\varepsilon = 1.0$  at the head of the arrow.

## V. CONCLUSION

This applet provides new opportunities for students and teachers of statistical mechanics to explore and develop a deeper conceptual understanding of the relationships between interparticle interactions and the equilibrium properties in a fluid system.

The authors encourage any interested parties to modify or expand the applet in useful ways.<sup>15</sup> We hope to expand its functionality in the future, most immediately by adding options for the use of additional integral equation theory closures in order to treat an even broader variety of possible pair interactions. We also intend to implement a calculation of the structure factor

$$S(k) = 1 + 4\pi\rho \int_0^\infty \frac{\sin(kr)}{kr} [g(r) - 1] r^2 dr, \quad (8)$$

which is an experimentally accessible quantity that can offer insight into, e.g., freezing transitions via the Hansen–Verlet freezing criterion.<sup>31</sup>

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<sup>14</sup>The applet and instructions are available as an electronic supplement to this article at <http://dx.doi.org/10.1119/1.4898626>. The latest version of the applet can also be found at <http://www.truskettgroup.com/fluidapp/>. The applet requires Java version 6 or newer.

<sup>15</sup>The applet source code is available on the GitHub repository at <https://github.com/TRP3/FluidRDFApp>.

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