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Simple analysis of scattering data with the Ornstein-Zernike equation

E. I. Kats[1] and A. R. Muratov[2,3]
[1]*Landau Institute for Theoretical Physics, RAS, 142432, Chernogolovka, Moscow Region, Russia*
[2]*Oil and Gas Research Institute, RAS, Gubkina St. 3, Moscow, 119333, Russia*
[3]*Gubkin State University of Oil and Gas, Department of Physics, Leninsky Prospekt, 65, Moscow B-296, GSP-1, 119991, Russia*

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In this paper we propose and explore a method of analysis of the scattering experimental data for uniform liquidlike systems. In our pragmatic approach we are not trying to introduce by hands an artificial small parameter to work out a perturbation theory with respect to the known results, e.g., for hard spheres or sticky hard spheres (all the more that in the agreement with the notorious Landau statement, there is no physical small parameter for liquids). Instead of it being guided by the experimental data we are solving the Ornstein-Zernike equation with a trial (variational) form of the interparticle interaction potential. To find all needed correlation functions this variational input is iterated numerically to satisfy the Ornstein-Zernike equation supplemented by a closure relation. Our method is developed for spherically symmetric scattering objects, and our numeric code is written for such a case. However, it can be extended (at the expense of more involved computations and a larger amount of required experimental input information) for nonspherical particles. What is important for our approach is that it is sufficient to know experimental data in a relatively narrow range of the scattering wave vectors (q) to compute the static structure factor in a much broader range of q. We illustrate by a few model and real experimental examples of the x-ray and neutron scattering data how the approach works.

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I. INTRODUCTION

Liquids (and not only so-called complex liquids or colloidal suspensions but also not exotic at all conventional simple organic and inorganic ones) are not structureless at any scale uniform media. The knowledge of their structure is very essential for understanding the underlying physics and chemistry, and it allows a nonblind search of new "smart" materials possessing properties required for various applications. Nowadays the topic is a multidisciplinary area including many basic science problems involving physics, chemistry, biology, and applications. Recently there has been an essential evolution in our understanding of the structures and phase transitions in liquids. It can be illustrated merely by a continuously growing number of exciting new publications (some of those will be cited in what follows in our paper). The progress, as always, is driven not only by developments of new experimental techniques but also theoretical advances, promising potential applications and related interesting fundamental scientific problems.

Experimentally complete and detailed structural information is obtained by various scattering methods (x rays, neutrons, light). Results are summarized in many reviews and monographs, e.g., in multiple editions of the well-known Hansen and McDonald book [1], containing also numerous relevant references. However, liquids as any objects studied in physics have so-to-speak two faces. First, the mentioned above experimental data, and second their theory descriptions. Modern powerful computers and software enable one to perform large-scale simulations of molecular liquids or colloidal dispersions. Thus, there are high precision scattering data and high accuracy simulations, and therefore it is tempting to think that nothing else is needed in the field. Unfortunately this is not completely true. The fact of the matter is that the full set of parameters which determine the experimentally measured scattering intensity I [or related to I the static structure factor $S(q)$], and the parameters needed to perform numeric simulations are not exactly the same, and what is worse only barely known. Readers can find a lot of original publications, reviews, and monographs from the theory and simulation sides (just to mention a few, see [2–5]). One of the main difficulties in comparing the results of the large-scale simulations with specific experimental measurements is the availability of an accurate connection between the experimental control parameters and the theoretical variables needed for the simulations. The actual values of the parameters are determined by the microscopic interactions, which are not well known. It might be not so important because in simulations the level of details is much greater than can be obtained experimentally, but there is another disadvantage of large-scale simulations in that they do not tell us which elements of the interactions are the most essential for a given system behavior. It should be cause for general embarrassment in the field that there are still no answers on even the most basic questions on structural and thermodynamic properties of liquids.

To overcome somehow this mutual uncertainty of the scattering data and simulations, and to relate the data to physical system characteristics we need the theory guideline. And here we face another problem. Theory in the rigoristic meaning of the word (see e.g., [6]) may not be developed for molecular or not very dilute colloidal liquids, since there is no small parameter. To find a way around the impasse we propose a pragmatic approach. The rigoristic theoretical view is certainly correct, however, the heuristic theory approach combined with experimental input and common physical wisdom, provides a useful tool to describe experimental data with a few phenomenological parameters. Moreover, results obtained theoretically also can be used for certain new predictions. We introduce some effective (model) interparticle potentials, which we regard as experimentally determined ones. Along this way to test such a combined (theory-experiment) approach we need a standard reference system. For the colloidal dispersions such a reference system is the dispersion of hard spheres. The fact is that structural and even dynamic properties of liquids are dominated by the molecular repulsive cores. This general deceptively simple Van der Waals observation leads to the idea that hard spheres are a suitable starting model of the liquid state.

The liquid structure factor which can be determined from the measured scattering intensity is a Fourier transform of the pair density correlation function. The density correlation function satisfies the formally exact Ornstein-Zernike (OZ) equation. Unfortunately the equation is not in a closed form, because it contains two unknown functions, and to solve this equation one has to add a closure relation. It turns out that the structure factor of the hard-sphere liquid can be accurately calculated using the Percus-Yevick (PY) closure relation. Unfortunately the remainder (with respect to hard spheres) interactions may not always be treated as a perturbation. Then one has to rely on different methods (see, e.g., [7–10]). In this work we are solving the OZ equation for a specially selected combination of the correlation functions (see details in the next section) and introduce an effective interparticle interaction potential. This combination, $\gamma(r) \equiv h(r) - c(r)$, where $h(r)$ is called a total correlation function, and $c(r)$ is the so-called direct correlation function [unlike separately taken correlation functions $h(r)$, $c(r)$, and the pair correlation function $g(r)$] turns out to be a smooth function of space variables, what allows one to perform numerically fast and accurate its Fourier transformation. To find the other correlation functions this input is iterated numerically to satisfy the OZ equation supplemented by a closure relation [1].

For the sake of simplicity we study the case of spherically symmetric scatterers. It is simply one example (although an important one which often occurs in practice, e.g., as a solution of micelles or small vesicles for an application of our general results. In principle the formalism could be extended for nonspherical particles (at the expense of more involved computations and a larger amount of required experimental input information). Furthermore the generalization requires more caution. The fact is that depending on a specific scattering technique the data collection time can be about 0.1 s (and up to 10 min for neutrons). Due to rotational diffusion of the particles their nonsphericity effectively generates the results similar to those from the spherical particles polydispersity. Both effects can be taken into consideration via the particle form factor. If the corresponding size variation due to particle nonsphericity is less than several percents, our approach remains valid.

We test the approach investigating a number of model and real experimental examples of the x-ray and neutron scattering data.

Common experience with the experimental data fitting shows that for short-range interactions between the particles, the PY closure relation gives a very reasonable description of the data. For more long-ranged interactions the better description of the data is obtained by the so-called hypernetted-chain (HNC) closure relation [1]. Variation of external conditions and material parameters results in the change of physical properties of the system. The static structure factor $S(q)$ is the main quantity one needs to analyze experimental data and to confront the data with the theory. The OZ equation with PY closure can be solved analytically only for hard spheres [11,12] or hard spheres with a very short-range attraction (sticky hard-sphere model [13], and more recent experimental and theoretical advances and improvements can be found in [14,15]). The first example (hard spheres) is very important but oversimplified to describe the real molecular liquids and colloidal dispersions. As it concerns the second model (sticky hard spheres) its application is strongly limited [16]. In fact this is a general drawback of the standard approach. The interpretation of the scattering data and the obtained values of the parameters are model dependent, and heavily rely on the assumptions used in the data analysis. Although the OZ integral equation can be solved by iterations [1], the method of the solution which provides the convergence and stability for a general case is not proposed (see the documentation to SASFIT software [17]). Stability of the algorithm can be obtained if one can guess in advance the form of the solution with several adjustable parameters, and it is not a trivial and not always realizable task.

Thus, the desire to understand and to get a sort of "express analysis" of the physical system characteristics behind its measured structure factor which is the main aim of this paper, is hardly surprising.

Any experimental data treatment is always concerned with fitting, however, our goal in this work is not a fitting itself. The problem is that in many cases (e.g., in complex fluids) the interaction potential is unknown (even its functional form). Very often many relevant details of the particle internal structure are unknown. In such a case the automatic numeric routine bluntly applied can produce not very reliable results. Our approach and numeric procedure allows one to estimate the correctness of the chosen model and the quality of the description. Our semiempirical and approximate express-analysis method can give a guideline for more elaborate automatic routine numerics and simulations.

The plan of our paper is as follows. In Sec. II we describe the main steps of our approach. We analyze the scattering data in the framework of the OZ equation. Our method can be applied for not too dense colloidal dispersions, if polydispersity is not too high. Sometimes the method as well works for molecular liquids (see below in Sec. III as an example the neutron data and our model analysis for liquid krypton). Then in Sec. III we illustrate how our approach works and present a few models (with known form for the structure factor) and experimental results which we analyze by our method. Finally, in Sec. IV we summarize the main steps of our approach and the results of the work.

II. THEORY

Consider suspension of monodisperse hard spheres of diameter σ. The volume fraction occupied by the spheres is $\phi = \pi\sigma^3\bar{n}/6$, where $\bar{n}$ is its average concentration. The pair correlation function is defined as $g(r) = 1 + \bar{n}h(r) = \langle n(r)n(0)\rangle/\bar{n}^2 - \bar{n}\delta(r)$, and one more correlation function useful to describe the scattering data is the direct correlation function $c(r) = -[\delta^2\mathcal{F}/(T\delta n(r)\delta n(0))]$ (where $\mathcal{F}$ stands for the system free energy). The functions $h(r)$ and $c(r)$ enter to the exact OZ equation,

$$h(\mathbf{x}) = c(\mathbf{x}) + \bar{n}\int d^3y\, h(\mathbf{y})c(\mathbf{x}-\mathbf{y}). \tag{1}$$

Static structure factor $S(q)$ is determined as

$$S(q) = 1 + \frac{4\pi\bar{n}}{q}\int_0^\infty dr\, r\sin(qr)h(r). \tag{2}$$

Then, the OZ equation can be rewritten in the Fourier representation as

$$S(q) = 1 + \bar{n}h(q) = 1/(1 - \bar{n}c(q)), \tag{3}$$

and to solve this equation it is necessary to add a closure relation.

Two of the most popular closure relations are the PY and HNC closure equations. It is easy to see that the PY closure relation implies that

$$\begin{gathered} g(r) \propto e^{-\beta\bar{V}}, \quad \text{if } r < \sigma, \\ c(r) = 0, \quad \text{if } R_{\text{int}} < r. \end{gathered} \tag{4}$$

For the HNC closure if $R_{\text{int}} < r$, $c(r) = h(r) - \ln(1 + h(r))$. If we take $|h(r)| < 0.1$, then $|c(r)| < 0.005$. Thus with a sufficient accuracy in our express-analysis method we put $c(r) = 0$, $r > 3.3\sigma$. In fact the cutoff can be chosen more or less arbitrarily in the region where the interparticle potential is small: $V(r) << kT$.

$$c(r) = (1 - e^{\beta V(r)})g(r), \tag{5}$$

where $V(r)$ is the interaction potential between particles and $\beta = (k_BT)^{-1}$. The HNC closure reads as

$$g(r) = e^{\gamma(r) - \beta V(r)}, \tag{6}$$

where $\gamma(r) = h(r) - c(r)$.

If the form of the interparticle potential $V(r)$ is known, the closure relation allows one to solve the OZ equation and then to compute $S(q)$. Unfortunately it is almost never the case, and one has either to guess about $V(r)$, or try to find some insight by fitting the scattering data. It looks like a vicious circle (because to fit the data we need to solve the OZ and the closure equations, what is impossible without knowledge of the potential). Luckily the situation is not so hopeless, and both tasks [namely to compute $S(q)$ and to guess the form of $V(r)$] can be done simultaneously by iterations. We choose first (guided by qualitative physical arguments) a model potential, then compute $S(q)$, compare the results to the experimental data, and repeat the procedure, until the agreement with experimental data becomes satisfactory. What is important for our approach is that it is sufficient to know experimental data in a relatively narrow [around the first peak in $I(q)$] range of the scattering wave vectors to compute the static structure factor in a much broader range of q.

The main object of investigation in this work is colloidal dispersions of spherical particles. The formalism could be extended for nonspherical particles (at the expense of more involved computations and a larger amount of required experimental input information). Since our aim is a theory from an experimental point of view, the generalization requires more caution. The fact is that depending on a specific scattering technique the data collection time can be about 0.1 s (and up to 10 min for neutrons). Therefore due to rotational diffusion of the particles their nonsphericity effectively generates results similar to those from the spherical but polydisperse particles. Both effects can be taken into consideration via the particle form factor. If the corresponding effective polydispersity is less than several percents, our approach remains valid. Thus we believe it was worthwhile to develop a theory which works for spherical particles with short-range interactions and not too large polydispersity.

Usually it is supposed that the interaction potential is very large and repulsive for small interparticle distance $r < \sigma$ (where σ stands for an effective size of the particle hard core), $V(r) = \bar{V} \gg k_BT$, and vanishes outside the interaction region $R_{\text{int}} < r$, $V(r) = 0$. It is easy to see that the PY and HNC closure relations imply that

$$g(r) \propto e^{-\beta\bar{V}}, \quad \text{if } r < \sigma, \tag{7}$$

and in the range $R_{\text{int}} < r$, we can approximate $c(r)$ as

$$c(r) = 0, \quad \text{if } R_{\text{int}} < r. \tag{8}$$

However, what is directly measured in any scattering experiment is not the static structure factor. The measured quantity is the scattering intensity $I(q,\bar{n})$ (where as before q is the scattering wave vector, and $\bar{n}$ is the average particle concentration). For a very dilute dispersion, when $\bar{n} = \bar{n}_{\text{dil}}$ is small $\bar{n}_{\text{dil}}\sigma^3 \ll 1$, $I(q,\bar{n}_{\text{dil}})$ is the scattering intensity from a single particle, termed traditionally as the particle form factor. For molecular liquids, or for colloidal dispersions with relatively small polydispersity (e.g, protein solutions have very narrow particle-size distribution function [18]), the static structure factor can be determined as $S(q) = \bar{n}_{\text{dil}}\, I(q,\bar{n})/(\bar{n}\, I(q,\bar{n}_{\text{dil}}))$.

Unfortunately it is impossible to calculate accurately the correlation functions $h(r)$, $c(r)$ in the r space by the inverse Fourier transformation of the static structure factor, because $S(q)$ decreases too slow, usually as q^{-1}. Luckily, for the function $\gamma(r)$ the situation is much better. It can be obtained by the Fourier transformation. The reason is that $\gamma(r)$ is a smooth function unlike the total and direct correlation functions, and its Fourier transform decreases fast, e.g., for the hard spheres like $1/q^3$. The required range of the wave vectors in the experimentally measured scattering intensity depends on the interaction potential. For the hard spheres at not too high particle volume fraction [say $\phi \leqslant 0.4$)], it is sufficient to know the scattering intensity for $q < 10/\sigma$. Then the function $\gamma(r)$ can be calculated directly from the static structure factor and the exact OZ equation (without an explicit use of any closure equation):

$$\gamma(r) = \frac{1}{2\pi^2 r\bar{n}}\int_0^\infty dq\, q\sin(qr)(S(q) - 2 + 1/S(q)). \tag{9}$$

Equation (9) allows one to calculate $\gamma(r)$ in the broad range of r needed for sufficiently accurate data analysis. Of course to compute $c(r)$, $g(r)$, and $h(r)$ separately one has to supplement the OZ equation by one or another closure relation.

The equation for the direct correlation function for the PY closure reads as

$$c(r_i) = (1 + \gamma(r_i))(e^{-\beta V(r_i)} - 1), \tag{10}$$

and for the HNC closure it is

$$c(r_i) = e^{\gamma(r_i) - \beta V(r_i)} - 1 - \gamma(r_i). \tag{11}$$

Technically to solve the OZ equation we develop a simple numerical method (see our code and comments in the Supplemental Material to the paper [19]). In its spirit our approach is similar to that proposed by Gillan [20]. The original [20] method is based on the discrete form of the equations and Fourier transform of the correlation functions [instead of direct calculation of the integral in (1)]. By our code we are solving the following discretized equations:

$$\begin{aligned} \tilde{c}_j &= \frac{4\pi h_r}{q_j} \sum_{i=1}^{N} c_i r_i \sin(q_j r_i), \\ S'_i &= \frac{h_q}{2\pi^2 r_i} \sum_{j=1}^{N} \frac{q_j \sin(q_j r_i)}{1 - \bar{n}\tilde{c}_j}, \end{aligned} \tag{12}$$

where $r_i = i\,h_r$, $q_j = j\,h_q$, $h_q = \pi/(N h_r)$, and h_r and h_q are steps in r space and q space, correspondingly. Fitting the results obtained from Eqs. (9)–(12) to the experimentally found static structure factor, we also are able to determine the interaction potential, calculate the density correlation function $g(r)$, and its main characteristic features, and compute as well some thermodynamic properties of the system, e.g., the pressure. (See also discussion of the inverse problem to find the interaction potential from the scattering data in the work [21].)

For the illustrative examples considered below, both closure relations (PY and HNC) lead to comparable accuracy predictions, although it is believed that the PY closure is an adequate approach for short-range interactions and the HNC closure is better for long-range interactions. However, we are not dealing with the ideal scattering data. Usually accurate data are available only for the finite (and not very broad) range of wave vectors. To catch the difference between these two closures, one needs the data in a sufficiently broad range of wave vectors. How broad the range depends on the interaction potential length scale. For the examples considered in our manuscript (with basically short-range interaction) both closures give very similar results. For truly long-range potential, one has to rely on the HNC closure.

III. ANALYSIS OF EXPERIMENT

Before presenting our illustrative examples, one essential comment is in order. Our theory consideration is based on the pairwise approximation. No doubts that in molecular liquids or dense colloidal suspensions many-body interactions are essential. And this is the main problem in any description of a liquid state. For not too dense (i.e., not too close to critical, crystallization, value of the particle volume fraction) colloidal dispersions, the pairwise approximation is a reasonable starting point in the theory analysis of the data. Besides in many cases the properties of the liquid state are dominated by the first peak in the pair-correlation function. This is the spirit of the Landau-Brazovskii weak crystallization theory (see the original Brazovskii [22] publication, or review paper [23], and discussions on so-called Frenkel-like liquid state in [24,25]). For such a situation (when liquidlike short-range order is not dramatically different from solidlike order) the pairwise approach (supplemented by some not too large experimental input) can provide the adequate data description. We illustrate the issue presenting below our analysis of the neutron scattering data in liquid krypton.

As the first test of our approach we treat the hard-sphere model data obtained by the exact solution of the OZ and PY equations. This is our input "experimental" data. The test also will allow us to estimate the accuracy of our computation due to the limited range of the available wave vectors, and finite precision of the discretized Fourier transform. In the test (in dimensionless r measured in units of σ) we take the hard-sphere volume fraction $\phi = 0.17$ and 200 points from the data set of the exact solution for the structure factor $S(r)$ in the range of dimensionless r $r/\sigma = 1 \div 11$. To analyze these "experimental" data by our method, we should first find the effective interaction potential. The suitable choice of the potential is a guarantee of the efficiency, accuracy, and fast convergence of the procedure. For the hard-sphere data, the natural choice is the hard-sphere potential supplemented by the correction terms,

$$\beta V(x) = (-V_a\, e^{-\kappa_a (x-1)} + V_r\, e^{-\kappa_r (x-1)})/x, \tag{13}$$

where x is r/σ. Fitting four adjustable parameters V_a, V_r, κ_a, and κ_r we estimate the corrections to the hard-sphere potential smaller than $\beta V(r) < 0.05$. The calculated structure factor deviates from its "experimental" value less then 0.07%!.

If we take the Lenard-Jones potential without the hard core part,

$$\beta V(r) = -V_a\, r^{-6} + V_r\, r^{-12}, \tag{14}$$

then the fitting to the "experimental" data (the exact OZ and PY equation solution for the hard spheres) gives $V_a = 0.4$, $V_r = 1.26$, and the deviation of the calculated structure factor from the "experimental" data is about 0.7%, i.e., 10 times worse than for the potential (13). A bit larger (but still not too bad) differences between both potentials take place if we compare the computed and "experimental" pair-correlation functions (see Fig. 1.). In turn with the pair-correlation function in hand, we can find such physically relevant quantity as the average coordination number N,

$$N = 4\pi\bar{n} \int_{\sigma}^{1.2\,\sigma} dr\, r^2 g(r). \tag{15}$$

Here the integral has taken over the relatively narrow region of r (around the main peak of the correlation function at $r = \sigma$). For the potential (13) $N \simeq 3.97$, whereas for the Lenard-Jones potential $N \simeq 3.89$. For the Lenard-Jones potential the correlation function is nonzero at $r < \sigma$. Then, the main peak of the pair-correlation function for this potential is more broad and has a smaller height, however, the coordination number is approximately the same. We conclude from these two pure methodical (but instructive) examples, that both model effective potentials provide fairly good (although not ideal) data descriptions. The accuracy of the computed integral characteristics (like the average coordination number N) is

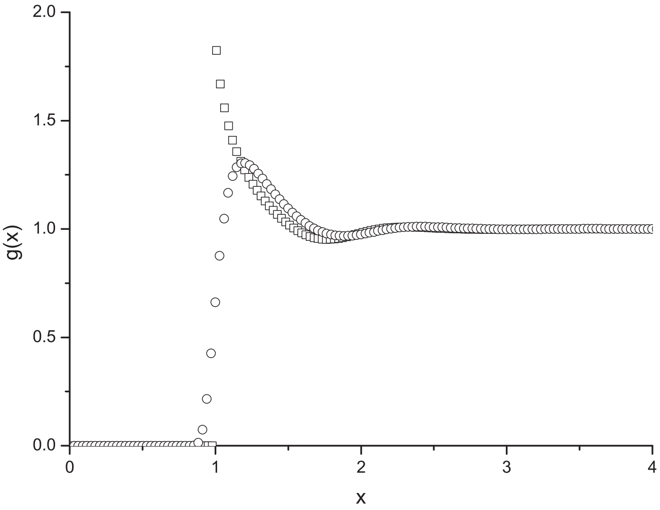

FIG. 1. Pair correlation function for hard-sphere (squares) and LJ (circles) potentials ($x \equiv r/\sigma$ is dimensionless distance in the particle diameter σ units.)

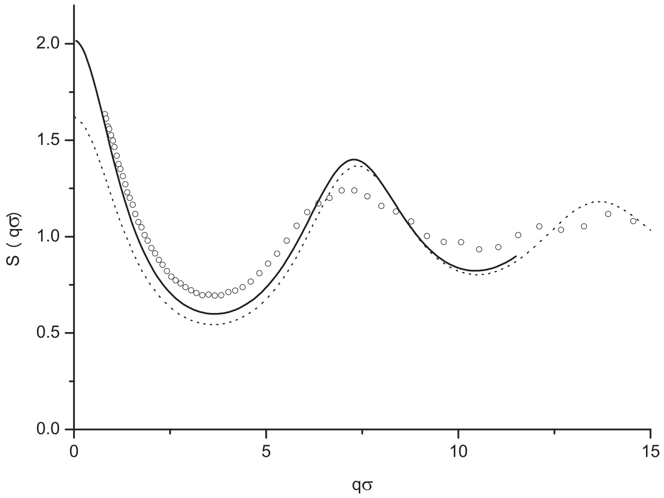

FIG. 2. Static structure factor for PMMA spheres with attraction caused by the depletion potential. Circles present the experimental data obtained in [28]; dotted line are the results of calculation in [28]; solid line present the results of the current approach.

less impressive; it is about 2%. Nevertheless, if we are dealing with real experimental data (with finite systematic errors and noise), the accuracy of our method can be considered a very satisfactory one.

The fact that at low concentrations and short-ranged potentials $S(q)$ has only very weak dependence on the potential shape (we illustrate above for entropic hard spheres with short-ranged energetic corrections or LJ potentials) is known in the literature: See, e.g., [26] with an extended corresponding state principle which enables one to formulate a few relevant characteristics of the effective potential, or [27] with so-called isosbestic points [q values for which $S(q)$ is invariant under changes of the effective potential well depth] introduced instead. The identification of the effective potential with the physical "microscopic" interaction energy is possible only in the very low concentration limit. At higher density the physically relevant quantity is just the effective potential related to the pair-correlation function. Another problem with such approaches is that the effective potential that reproduces the structure factor, may not be the same as the potential to reproduce thermodynamic properties. In this work we bypass the problem: First we are not trying to find the potential from the scattering data [we calculate the static structure factor solving the OZ equation with a trial effective potential found from the fitting experimental data in a relatively narrow range of the scattering wave vectors (q)], and then we can compute the static structure factor in a much broader range of q. Second, we determine the value of $S(q=0)$ from the independently computed thermodynamic characteristics of the system under consideration.

Let us move now to the real experimental data. We take the scattering intensity data from the work [28] for the polymethylmetacrylate (PMMA) spheres. Using our methodology and depletion interaction potential induced by the polystyrene globules dispersed in the solution [29] (see also more recent results and advances on the depletion interaction [30]), we fitted all the experimental data presented in the work [28] with our new method described above and the corresponding numerical procedure (which is simpler and faster than that used in [28]). One more advantage of the new approach is that it is flexible and can be adapted for a rather wide range of interaction potentials. Just as illustrated in Fig. 2, we plot the static structure factor calculated by the method of [28] (black squares) and by our new method (red circles). Presented data correspond to the volume fraction of the PMMA particles $\phi = 0.2$ and the polyethylene glycol concentration $c_p = 23$ mg/L. The radius of particles was fixed at the experimental value, and the interaction potential is the depletion potential. Note to the point that the method of [28] gives the value for the potential amplitude $V_{a1} = -3.3kT$, and our new method leads to $V_{a2} = -2.97kT$ and the coordination number is about 5.8.

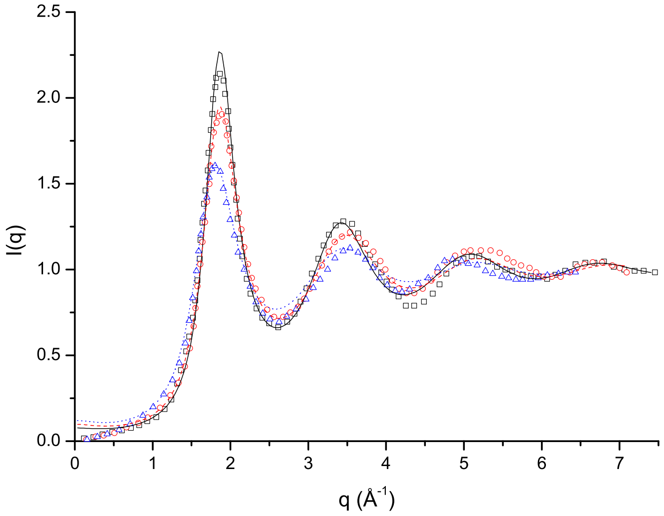

FIG. 3. Structure factor of liquid krypton at liquid-gas coexistence. The squares present the data for the temperature 133 K; circles, 153 K; and triangles, 183 K. Our calculations are presented by the solid black line (133 K), dashed red line (153 K), and dotted blue line (183 K), correspondingly.

TABLE I. Values of the parameters determined from the fitting for the Lenard-Jones potential to the experimental data for krypton.

T	σ	$\bar{n}$	V_a	V_r	Coordination number
133	3.91	0.72	2.56	1.91	7.3
153	3.55	0.68	3.11	3.77	6.5
183	3.55	0.68	2.64	3.6	4.7

Our next example is related to the neutron scattering data on liquid krypton [31]. We reproduce the data borrowed from the work [31] on scattering intensity in Fig. 3. The data cover the large interval of the scattering wave vectors $q\sigma \sim 1 \div 40$ (where σ is estimated by the position of the main peak in the static structure factor). Results of the fitting for the Lenard-Jones potential to the experimental data are presented in Fig. 3 by solid lines. The values of parameters determined from the same fitting are presented in Table I. Four parameters were used as adjustable: scaling factor for the wave vector σ, density $\bar{n}$, and the amplitudes of the Lenard-Jones potential V_a and V_r.

By the common physical wisdom for the krypton (noble gas) one should expect the Lenard-Jones interaction potential provides an adequate description of the system. Surprisingly enough (see Fig. 3) this is not the case (as was mentioned in [31] and as we confirmed by our own computation). Something is evidently wrong. In our opinion, the catch is in a small q region. As is known (see, e.g., [1]) there is the exact thermodynamic relation,

$$S(0) = k_B T \left(\frac{\partial \bar{n}}{\partial P} \right)_T . \tag{16}$$

We take the values entering (16) parameters from [31] and the handbook [32] and calculate the structure factor at $q = 0$ for a few temperature points along the liquid-gas coexistence line: $S(q = 0, T = 133\ \text{K}) \approx 0.076$, $S(q = 0, T = 153\ \text{K}) \approx 0.13$, $S(q = 0, T = 183\ \text{K}) \approx 0.459$.

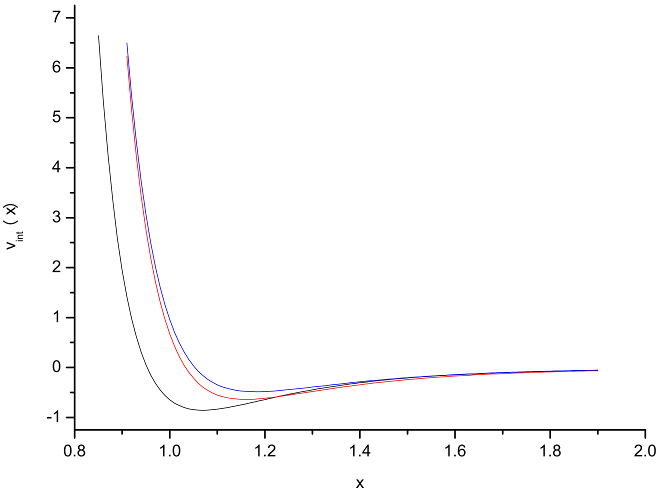

FIG. 4. Lenard-Jones interaction potential for liquid krypton. Solid black line corresponds to 133 K, dashed red line, 153 K; and dotted blue line, 183 K ($x \equiv r/\sigma$, and $v_{\text{int}} \equiv V/k_B T$ is the dimensionless interaction potential in $k_B T$ units).

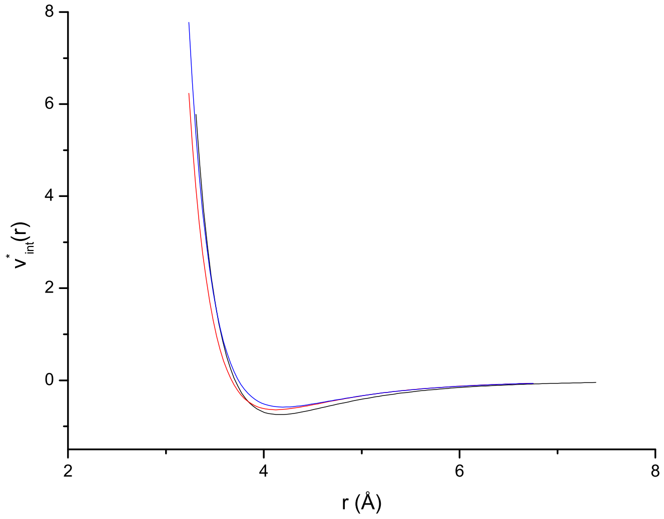

FIG. 5. Interaction potential for liquid krypton, rescaled to the temperature $T^* = 153$K ($v^*_{\text{int}} \equiv V/k_B T^*$, and $x \equiv r/\sigma$). Lines are the same as in Fig. 4.

With these thermodynamic correct values for the $S(q = 0)$, we perform the fitting of the scattering data in the broad range of the wave vectors. We present the results of our approach for the Lenard-Jones effective interparticle potential. The magnitudes of all computed parameters are presented in Table I. To find all three correlation functions we utilize the PY closure relation, but a similar-quality fitting also can be obtained with the HNC closure relation.

As we said already the separate important task is to find (estimate) the interaction potential. We plot the result obtained by our method in Fig. 4.

The curves in Fig. 4 present the potential divided by $k_B T$. All three curves can be rescaled and collapsed into a single universal (master) curve. The result of such a procedure is presented in Fig. 5.

In principle our method also can be extended to study a gas-liquid critical point (e.g., to find the critical exponent for the correlation length). However, in practice it is hardly feasible, since it requires very large (in a broad range of wave vectors and temperatures) and very accurate the scattering data. Note to the point that although the OZ equation is exact, the closure relations needed to calculate the critical behavior of the pair-correlation function are mean field in their nature. Furthermore approaching the critical point long-range forces becomes more and more relevant; therefore one has to utilize the HNC closure relation.

IV. CONCLUSION AND PERSPECTIVES

In recent years there has been an upsurge in interest in structural investigations of various colloidal suspensions and molecular liquids (see, e.g., [33,34] and references therein), although the problem itself is anything but new. The van der Waals theory is the cornerstone of the current understanding of fluid structures and phase behavior. Although modern experimental and numeric methods of structure investigations can provide very detailed information about many structural features and physical properties of the liquid state, no simple way allows one to relate both.

For simple liquids the intermolecular interactions are well known and summarized in textbooks. However, this is not the case for colloidal systems, the main object of our work. For the colloidal systems very often even a functional form of the potential is unknown. In the realm of nonideal experimental data, to analyze the data one can use a sort of iteration procedure starting with a variational form of the potential. For our method (and the relatively short-range interaction potential), the choice of the closure relation is not very important. We checked an approach with the so-called bridge function $b(r)$, often used in the literature (see, e.g., [35]) which is believed to provide thermodynamic consistency. In the approach the pair-correlation function is represented as

$$g(r) \equiv h(r) + 1 = \exp[-\beta V(r) + \gamma(r) + b(r)].$$

With the Rogers and Young (RY) closure, the bridge function is

$$b(r) = -\gamma(r) + \ln\left(1 + \frac{\exp(\gamma(r)f(r)) - 1}{f(r)}\right),$$

with $f(r) = 1 - \exp(-\alpha r)$ and α is an adjustable parameter. For $\alpha = 0$ the RY closure is reduced to the PY, while for $\alpha > 0$ and upon increase of r it approaches the HNC closure. In this limit, we have checked that a theory with the reference bridge function gives the same results as our method (up to a nonessential numerical prefactor).

In our work we follow a pragmatic approach and our method allows one to get at least qualitative insight into which form of the interaction potential can provide a reasonable accuracy description of the data. The quality of our fitting (the so-called χ^2 value) depends essentially on the normalization of the static structure factor $S(q)$. For neutron scattering data typically it can be determined accurately and directly from the data. However, for x-ray scattering data the fitting requires more caution, because the density fluctuations of the solution modify the effective shape of the individual scatterers. Then there is no simple way to determine the normalization of the structure factor directly from the experiment, and it should be considered as one additional fitting parameter.

All mentioned above difficulties are equally relevant for the direct simulation methods. The methods are more powerful and effective, but there is a price to pay; more input data are needed. Besides using only the simulation methods in practice one cannot solve all problems (there are limitations to performing effective simulations). For example, sometimes the system relaxation time can be so large that the only practical way to overcome this difficulty is to rely on some ansatz for the correlation functions. For such a case our approach can provide a certain useful hint.

To get such insight one has to rely on the traditional methods of the statistical physics; namely, having in mind the fluid state structure, it is necessary to solve the exact OZ equation. Unfortunately, here we face a problem because the equation is not in a closed form: It contains two unknown functions. In a general case (molecular liquids, or not very dilute colloidal dispersions) it is not possible to derive by a regular theoretical method the needed closure relations. The most popular closure relations (PY and HNC) are basically sort of self-consistent extrapolations from the very dilute dispersion limit. The PY closure allows one to find the exact analytical solution of the OZ equation for the dispersion of hard spheres. Moreover, the PY closure leads to a reasonably good description of the experimental data for the dispersions somehow similar to the hard-sphere ones. Then it is tempting to try to describe experimental data for a more broad class of dispersions using the trial PY or HNC ansatz for the correlation functions and computing perturbatively corrections to the ansatz to fit the data. Unfortunately such a perturbative approach does not always work, and besides this leads to not very efficient and fast computations. To find how to overcome the difficulty, there is no way to improve the theory (it is impossible for a system without any small parameter). As one can expect this intermediate range of parameters is the most difficult one to treat theoretically, all the more, analytically.

Instead, we propose a simple and working instrument, combining the theory solution to the OZ equation for the function $\gamma(r)$ and experimentally measured scattering intensity. It is based on the observation that it is possible to determine the smooth function $\gamma(r) \equiv h(r) - c(r)$ directly from the experimental data for the structure factor (scattering intensity data for the system under consideration and from its diluted state). Then our method enables one to compute the correlation functions and the interparticle potential by using the OZ equation with a closure relation. The procedure is robust and simple, and does not use any ansatz for the correlation functions.

The delicate issue in the procedure is the choice of the functional form for the interaction potential. The accuracy of the resulting description (especially as it concerns the integral characteristics) depends essentially on the choice. An equally delicate issue concerns the input experimental data needed to perform our procedure. First, we need to know the accurate values of the value of the static structure factor at relatively large wave vectors. Second, if the data at small wave vectors are not available (which is often the case), the corresponding values should be found (e.g., by separate thermodynamic computations) and added to the set of fitting data. Last, one note of caution concerns the x-ray form factor of the particle. In a dense solution it can be different from the form factor in the dilute solution. The important conclusion drawn from the aforesaid notes is the need for raw input data tuning. Luckily the tuning concerns the physically measurable quantities and therefore can be well controlled, and besides the tuning never modifies the data in the intermediate wave-vector region which is essential for the solution of the OZ equation.

Our main justification in this work for adding one more approach (numerically very simple and fast) to perform an approximate express analysis of the data is based on our finding that many relevant features of the experimentally measured scattering intensity can be found theoretically with a minimal input from the experiment. Moreover, these features can be computed directly from the exact OZ equation, without an explicit use of the semiempirical closure relations. Our work explicitly separates the aspect of a scattering data fitting independent of the particle interaction potential (provided the latter one is not a long range). The results can be obtained by simply plugging a few input parameters into our numeric code (see Supplemental Material [19]).

We illustrate by a hard-sphere model and real experimental examples how the method works. For a relatively small number of fitting parameters, namely the parameters entering the interaction potential and the scaling factor σ for the wave vectors, the results are very satisfactory. In this sense our approach and the model can be considered as the minimal model, which is just at the border between those that are too primitive to fit even qualitatively the data, and those that fit the data too well by using too many parameters.

It is worth noting that all experimental data are not perfect and always have certain limitations. Neutrons or x rays do not study the same physical quantities and characteristics. For example, very often a position of the so-called base line is only approximately known (neither are many relevant details of the particle internal structure known). In this respect our express-analysis method is more robust (but of course less accurate) than the automatic fitting routine, or more involved Monte Carlo or molecular dynamics simulations. Our method can be considered as a sort of guiding line to get some hints as to what can be expected from these more powerful approaches.

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