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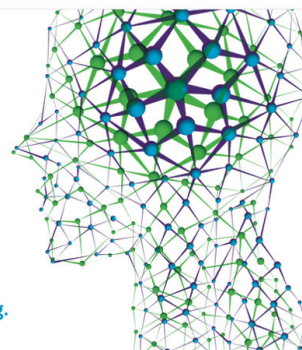
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Practical thermodynamics of Yukawa systems at strong coupling

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Simple practical approach to estimate thermodynamic properties of strongly coupled Yukawa systems, in both fluid and solid phases, is presented. The accuracy of the approach is tested by extensive comparison with direct computer simulation results (for fluids and solids) and the recently proposed shortest-graph method (for solids). Possible applications to other systems of softly repulsive particles are briefly discussed. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921223>]

I. INTRODUCTION

A large class of soft matter systems can be described generically as massive charged particles immersed in a neutralizing medium of lighter particles.¹ Two well-known examples are colloidal suspensions^{2–4} and complex (dusty) plasmas.^{4–8} The interaction between the massive particles is a key issue to adequately understand most of the phenomena in these systems. Although it can be rather complex in real situations, it is often assumed that the electrical interactions between the small particles can be described, in the zero approximation, by the Yukawa (also known as the screened Coulomb or Debye-Hückel) repulsive potential

$$V(r) = (Q^2/r) \exp(-r/\lambda_D), \quad (1)$$

where Q is the particle charge, λ_D is the Debye screening length associated with the neutralizing medium, and r is the distance between a pair of particles. The effect of the neutralizing medium on the effective interactions between the particles can involve more than only screening. This is particularly relevant in complex plasmas, where continuous absorption of plasma electrons and ions on the particle surface result in inverse-power-law asymptotes of interaction at large interparticle separations.^{5,8–11} Plasma production and loss processes can also produce a double-Yukawa interaction potential characterized by two different screening lengths.^{12,13} Nevertheless, many experimentally observed trends can be already reproduced by the simplest model considering point-like particles interacting via repulsive Yukawa potential (1), at least qualitatively. For this reason, this model, which we will refer to as the single component Yukawa system, has received a great deal of interest. Another remarkable property, which makes the model Yukawa interaction particularly important for the soft condensed matter research, is that by varying λ_D an extremely broad range of interaction steepness can be explored. The two limiting cases correspond to extremely soft unscreened Coulomb interaction (one-component-plasma

limit) for $\lambda_D \rightarrow \infty$ and extremely steep hard-sphere-like repulsion for $\lambda_D \rightarrow 0$.

Depending on the strength of the interparticle interaction, Yukawa systems can be regarded as weakly or strongly coupled. Weak coupling corresponds to the situation when the energy of the interaction at a characteristic mean interparticle separation Δ is much smaller than the system temperature T (expressed in energy units), so that $V(\Delta) \ll T$. In this regime, the interaction provides only small corrections to the thermodynamic quantities of an ideal gas. These corrections can be relatively easily evaluated (e.g., by means of the second virial coefficient). In the opposite regime, $V(\Delta) \gg 1$, the interaction produces significant (or dominant) contribution to the thermodynamic quantities. The particles form either the fluid phase or, at even stronger coupling, the solid phase. Evaluation of thermodynamic properties becomes less trivial than in the limit of weak coupling. The focus of the present paper is, therefore, on the strong coupling regime.

Thermodynamic properties and phase diagram of strongly coupled Yukawa systems are relatively well investigated using various computational and analytical techniques. Some relevant examples include Monte Carlo (MC) and molecular dynamics (MD) numerical simulations,^{14–18} as well as integral equation theoretical studies^{19–24} (see also references therein).²⁵ In particular, accurate results for the excess internal energy obtained in MD and MC simulations have been tabulated in Refs. 17 and 18 for a number of state points in the phase diagram of Yukawa systems. However, since the calculation of other thermodynamic functions requires knowledge of certain integrals and derivatives of the excess energy (see examples below), these data are very useful as reference points, but less appropriate as a practical tool for estimating thermodynamic properties. Semi-empirical fitting formulas^{26–28} and simplistic approaches^{29,30} to estimate thermodynamics of Yukawa systems have been also discussed in the literature. These can be useful in certain situations, but are not very helpful when sufficient accuracy is required.

The purpose of the present paper is to describe simple practical approach to evaluate thermodynamic properties of Yukawa systems at strong coupling, *both in the fluid and solid*

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phases. The approach is based on simple phenomenological arguments, which can be also relevant to a wider class of soft repulsive interactions. The accuracy of the approach is tested by calculating the compressibility factor and comparing this with available as well as new results from direct computer simulations. We also use the recently proposed shortest-graph method,^{31,32} which allows to calculate the radial distribution function and, hence, pressure in crystals. The relative deviations between theoretical and simulation results normally do not exceed one part in 1000 for dense fluids not too far from crystallization and solids not too close to the melting point. The largest deviations are documented for the solid phase near melting transition and superheated solid, but even there they are below 1%. Hence, the proposed approach represents very convenient and accurate tool to estimate thermodynamics of Yukawa and other related systems in a very broad parameter regime.

II. THERMODYNAMIC FUNCTIONS OF YUKAWA SYSTEMS

The main thermodynamic quantities of interest here are the internal energy U , Helmholtz free energy F , and pressure P of the system of N Yukawa particles, occupying volume V and having temperature T . These thermodynamic functions are related via³³

$$U = -T^2 \left(\frac{\partial F}{\partial T} \right)_V, \quad (2)$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (3)$$

We will use conventional reduced units: $u = U/NT$, $f = F/NT$, and $p = PV/NT$. The latter ratio, $Z = PV/NT$, is also known as the compressibility factor.

The single component Yukawa system is conventionally characterized by two dimensionless parameters. The first is the coupling parameter, $\Gamma = Q^2/aT$, where $a = (3V/4\pi N)^{1/3}$ is the Wigner-Seitz radius and the temperature T is expressed in energy units throughout this paper. The second is the screening parameter, $\kappa = a/\lambda_D$. It is useful to express reduced thermodynamic functions in terms of Yukawa system phase state variables, κ and Γ . For a fixed number of particles, we have $\Gamma \propto (aT)^{-1} \propto V^{-1/3}T^{-1}$ and $\kappa \propto a \propto V^{1/3}$. This implies

$$\frac{\partial \Gamma}{\partial T} = -\frac{\Gamma}{T}, \quad \frac{\partial \Gamma}{\partial V} = -\frac{1}{3} \frac{\Gamma}{V}, \quad \frac{\partial \kappa}{\partial T} = 0, \quad \frac{\partial \kappa}{\partial V} = \frac{1}{3} \frac{\kappa}{V}.$$

The following equations for the reduced thermodynamic functions are then obtained:

$$\frac{u}{\Gamma} = \frac{\partial f}{\partial \Gamma} \quad (4)$$

and

$$Z = 1 + \frac{\Gamma}{3} \frac{\partial f}{\partial \Gamma} - \frac{\kappa}{3} \frac{\partial f}{\partial \kappa}. \quad (5)$$

To conclude this section, we remind that in this paper, we consider exclusively the single component Yukawa system, where thermodynamics is completely determined by particle-particle interactions and correlations. In real systems

(e.g., complex plasmas or colloidal suspensions), neutralizing medium is normally present to neutralize and stabilize like-charged particles. In this case, particle-medium interactions also affect thermodynamics. However, the effect of particle-medium interactions is additive to that of particle-particle interactions and can be easily evaluated.³⁴ For example, the excess (free) energy associated with the presence of neutralizing medium (e.g., plasma) is

$$f_{\text{pl}} = u_{\text{pl}} = -\frac{3\Gamma}{2\kappa^2} - \frac{\kappa\Gamma}{2}. \quad (6)$$

Note that the contribution of the neutralizing medium is negative and dominant at strong coupling, implying that the excess energy and pressure of the corresponding system are also negative in this regime. For the single component Yukawa system, these quantities are obviously positive.

III. YUKAWA SOLIDS

The reduced excess energy of a solid in the harmonic approximation is

$$u_s = M_s \Gamma + \frac{3}{2}, \quad (7)$$

where M_s is the corresponding lattice sum (Madelung constant). The reduced Helmholtz free energy of a solid is related to the excess energy by the standard integration [Eq. (4)], which yields

$$f_s = M_s(\Gamma - \Gamma_m) + \frac{3}{2} \ln(\Gamma/\Gamma_m) + f_m, \quad (8)$$

where the integration starts from Γ_m —the coupling parameter at the fluid-solid phase transition, and $f_m = f(\Gamma_m)$. According to the Ross melting criterion,³⁵ which he obtained by reformulating the celebrated Lindemann melting law in terms of the statistical-mechanical partition function

$$f_m \approx M_s \Gamma_m + C, \quad (9)$$

where C is some constant. In other words, the thermal component of the reduced excess free energy remains *approximately* constant at melting. Hoover *et al.*³⁶ observed that $C \approx 6$ for several inverse-power-law (IPL) repulsive potentials. More recently, Agrawal and Kofke³⁷ documented some dependence of C on the potential softness (C somewhat increases for softer potentials) for a wide range of IPL potentials. However, this variation remains relatively weak, with $5.9 \lesssim C \lesssim 6.6$ in a very wide range of softness investigated.

We have calculated the values of C at melting of the bcc and fcc Yukawa solids, in the harmonic lattice approximation, using the data tabulated in Refs. 16 and 17. In addition to neglecting anharmonic corrections, we assumed that fluid-bcc and fluid-fcc transition lines are very close to each other in the parameter regime of present interest (for the confirmation see Fig. 7 of Ref. 19) so that a unique value of Γ_m can be used (this is further justified by the fact that Γ_m appears under the logarithm when calculating C). The results are shown in Fig. 1. Taking into account some scattering in the data points, it is reasonable to apply linear fitting procedure. This yields

$$C(\kappa) = \begin{cases} 6.55 - 0.13\kappa & (\text{bcc lattice}) \\ 6.57 - 0.10\kappa & (\text{fcc lattice}) \end{cases}. \quad (10)$$

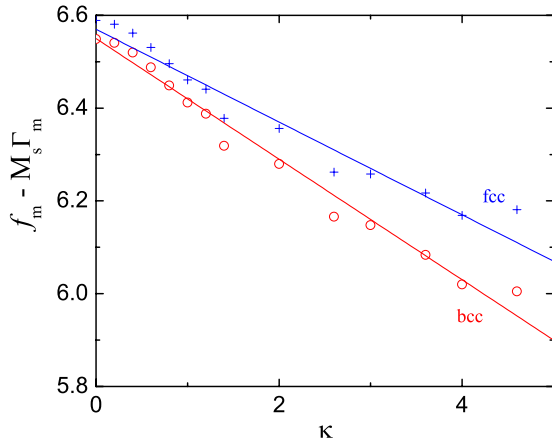


FIG. 1. Thermal component of the reduced excess free energy of Yukawa solids at melting. Red circles correspond to the solid bcc lattice, and blue crosses denote the solid fcc phase. Symbols are calculated from the harmonic lattice approximation using the data tabulated in Refs. 16 and 17. Solid lines are linear fits to these data points.

The resulting expression for the reduced free energy of the solid phase is

$$f_s(\kappa, \Gamma) = M_s(\kappa)\Gamma + \frac{3}{2} \ln [\Gamma/\Gamma_m(\kappa)] + C(\kappa). \quad (11)$$

To use Eq. (11) for practical evaluations, we need to specify the dependence $\Gamma_m(\kappa)$. A simple expression proposed by Vulina *et al.*^{38,39} is suitable for this purpose,⁴⁰

$$\Gamma_m(\kappa) \approx \frac{172 \exp(\alpha\kappa)}{1 + \alpha\kappa + \frac{1}{2}\alpha^2\kappa^2}, \quad (12)$$

where the constant $\alpha = (4\pi/3)^{1/3} \approx 1.612$ is the ratio of the mean interparticle distance $\Delta = (V/N)^{1/3}$ to the Wigner-Seitz radius a .

Equation (5) complemented by Eqs. (10)–(12) allows us to calculate the compressibility of Yukawa solids. We compare our theoretical results with the direct MC simulation of Meijer and Frenkel.¹⁵ In addition, the compressibility has been evaluated using the recently proposed *shortest-graph* method.^{31,32} In this method, the pair distribution function $g(\mathbf{r})$ is calculated by assuming that it can be represented as a sum of the Gaussian peaks which describe the corresponding partial contributions of the particles in the crystal. The radial distribution function is then obtained by angular integration, $g(r) = (1/4\pi) \int d\Omega g(\mathbf{r})$. The shortest-graph method allows to calculate $g(r)$ for a wide range of interaction potentials, crystalline lattices, temperatures, and densities.^{31,32} The compressibility is obtained from the virial equation of state,⁴¹

$$Z = 1 - \frac{2\pi N}{3VT} \int_0^\infty r^3 V'(r) g(r) dr.$$

The details of implementation of the shortest-graph method are described in Ref. 32.

Numerical and theoretical results for the compressibility of the fcc solid phase are summarized in Table I. Our present theoretical results are always below the MC results; the relative difference increases on approaching melting and, in particular, in the superheated regime. However, even in this case the difference is below 1%. The shortest-graph method

TABLE I. The compressibility factor (reduced pressure) for the single component Yukawa fcc solid. The first two columns specify the location of the system state point on the (κ, Γ) plane. The third column lists the values of the reduced coupling strength Γ/Γ_m , as calculated using Eq. (12). (Note that the last three rows may correspond to a superheated solid.) The remaining columns contain the values of Z obtained using MC simulations by Meijer and Frenkel¹⁵ and tabulated in Ref. 19 (Z_{MC}), present theoretical approach (Z_{present}), and the shortest-graph method^{31,32} (Z_{SG}).

κ	Γ	Γ/Γ_m	Z_{MC}	Z_{present}	Z_{SG}
4.034	5764.8	1.44	41.058	40.941	41.197
4.066	5719.1	1.37	38.927	38.809	39.075
4.096	5678.3	1.32	37.115	36.992	37.274
4.128	5634.0	1.26	35.259	35.096	35.399
4.169	5577.8	1.19	32.969	32.820	33.126
4.208	5526.8	1.12	31.005	30.870	31.202
4.251	5470.4	1.05	28.991	28.883	29.196
4.300	5408.0	0.98	26.919	26.729	27.113
4.344	5353.2	0.92	25.211	25.000	25.409
4.406	5277.8	0.84	22.996	22.799	23.268

demonstrates comparable accuracy, but overestimates the compressibility obtained in MC simulations. The documented accuracy is considerably better than (for example) the hard-sphere perturbation theory described in Ref. 19 can provide.

Since the data tabulated previously¹⁹ are limited to a relatively narrow range of κ around $\kappa \approx 4$ and are all for the fcc solid phase, we performed additional comparison for the regime of smaller κ , where Yukawa solid forms a stable bcc lattice. The MD simulations have been performed for $N = 64\,000$ particles in the canonical (NVT) ensemble, using the Langevin thermostat. The numerical time step is set to $10^{-4} \sqrt{m\lambda_D^3/Q^2}$, where m is the particle mass. The cut-off radius for the potential is 15Δ . To obtain the equilibrium state and calculate the compressibility, the simulations have been run for 1.5×10^6 steps.

Comparison between MD simulations, the shortest-graph method, and the present theory is summarized in Table II. The calculations using the shortest-graph method yield values extremely close to the “exact” MD results. The present analytical approach has almost the same accuracy, and the agreement with MD results is very impressive. The relative deviations are well below one part in 1000 for all phase states. Reasons for these deviations can include the approximate character of the

TABLE II. The compressibility factor (reduced pressure) for the single component Yukawa bcc solid. The first three columns are similar to those in Table I. The remaining columns contain the values of Z obtained using our MD simulation (Z_{MD}), the shortest-graph method^{31,32} (Z_{SG}), and the present theoretical approach (Z_{present}).

κ	Γ	Γ/Γ_m	Z_{MD}	Z_{SG}	Z_{present}
0.6	280.6	1.51	1090.711	1090.889	1090.340
1.0	326.1	1.48	404.169	404.297	403.916
1.4	403.2	1.42	213.525	213.637	213.410
2.0	660.1	1.44	119.450	119.447	119.401
2.7	1266.4	1.41	73.253	73.263	73.290
4.0	5755.5	1.50	43.258	43.272	43.245

dependence $\Gamma_m(\kappa)$ and the neglect of anharmonic corrections to the free energy. These are not easy to estimate. Given the simplicity of the present theoretical approach, the agreement should be considered as excellent. Thus, it can serve as a simple practical tool to evaluate thermodynamic functions of Yukawa fluids when extreme accuracy is not required.

IV. YUKAWA FLUIDS NEAR FREEZING

The reduced excess energy of the fluid phase can be conveniently divided into static and thermal components,^{40,42,43}

$$u_{fl} = M_{fl}\Gamma + u_{th}. \quad (13)$$

The first term corresponds to the static contribution and the coefficient M_{fl} is referred to as the fluid Madelung constant.⁴³ It can be obtained with the Percus-Yevick (PY) radial distribution function of hard spheres in the limit $\eta = 1$, where η is the hard sphere packing fraction.^{42,43} Alternatively, it can be evaluated using the ion sphere model (ISM), where each particle is placed in the center of the charge neutral Wigner-Seitz spherical cell, and the energy is then calculated from simple electrostatic consideration.³⁰ The result is

$$M_{fl}(\kappa) = \frac{\kappa(\kappa + 1)}{(\kappa + 1) + (\kappa - 1)e^{2\kappa}}. \quad (14)$$

The thermal component of the internal energy exhibits quasi-universal scaling for a wide class of soft repulsive potentials, as first pointed out by Rosenfeld and Tarazona (RT scaling).^{42,43} The accuracy of this scaling for various model systems has been recently investigated in extensive numerical simulations.⁴⁴ Previously, a variant of the RT scaling has been successively used to obtain practical expressions for the internal energy and pressure of Yukawa fluids across coupling regimes.⁴⁰ Here, we modify this approach with the main emphasis on the near-freezing regime.

For strongly coupled Yukawa fluids near freezing, the RT scaling is illustrated in Fig. 2, where the dependence of u_{th} on

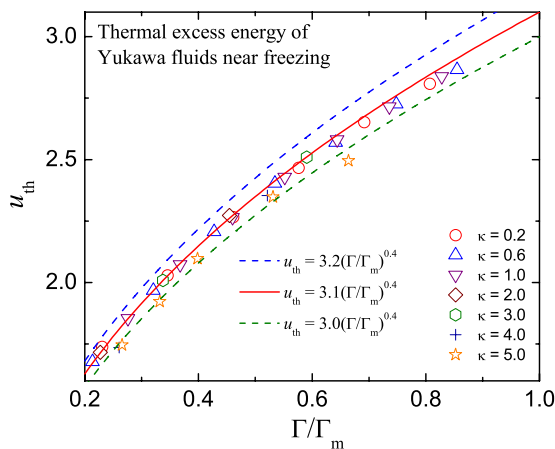


FIG. 2. Thermal component of the reduced excess energy of Yukawa fluids near freezing versus the reduced coupling parameter Γ/Γ_m . Symbols correspond to the numerical simulations for different values of the screening parameter κ .^{17,45} The curves correspond to the functional form $u_{th} = \delta(\Gamma/\Gamma_m)^{2/5}$ with different values of δ . The value $\delta \approx 3.1$ is the most appropriate in the considered near-freezing regime.

Γ/Γ_m is plotted for a number of screening parameters $\kappa < 5$. Except the strong screening regime with $\kappa = 5$, all other data points have a tendency to group around a single quasi-universal curve. Reasonably, accurate fits (shown by the curves) can be obtained using the functional form

$$u_{th} = \delta(\Gamma/\Gamma_m)^{2/5}. \quad (15)$$

Originally, Rosenfeld suggested⁴³ to use $\delta = 3.0$, while in our previous paper,⁴⁰ we used a modified expression, $u_{th} = 3.2(\Gamma/\Gamma_m)^{2/5} - 0.1$, in a wider range of coupling. Figure 2 demonstrates that simple form (15) with $\delta = 3.1$ is more appropriate near freezing and we use this value in calculations.

Integrating the excess energy from Γ to Γ_m and subtracting this from the known value of $f_m(\kappa)$, we get the free energy of Yukawa fluids in the form

$$f_{fl}(\kappa, \Gamma) = M_{fl}(\kappa)\Gamma + \Gamma_m(\kappa) [M_s(\kappa) - M_{fl}(\kappa)] + \frac{5\delta}{2} \left[\left(\frac{\Gamma}{\Gamma_m(\kappa)} \right)^{2/5} - 1 \right] + C(\kappa). \quad (16)$$

Note that the RT scaling in the form of Eq. (15) with constant δ only holds for $\kappa \lesssim 4$ while the fcc-bcc-fluid triple point is located near $\kappa \approx 4.5$ ^{17,46,47} (bcc lattice being thermodynamically favorable at weak screening). Therefore, $M_{bcc}(\kappa)$ and $C_{bcc}(\kappa)$ should be substituted into Eq. (16) in the domain of its applicability.

We calculated the compressibility factors of the Yukawa fluid for several strongly coupled state points and compared these with the data from Monte Carlo simulations¹⁵ and with our previous approximation.⁴⁰ The results are summarized in Table III. Both theoretical approaches demonstrate excellent agreement with MC simulations, especially in the vicinity of the fluid-solid phase transition. Some advantage of the present construction is that the explicit expression for the free energy is available. The validity of the present approach is merely

TABLE III. The compressibility factor (reduced pressure) of the single component Yukawa fluid (note, however, that the first row may correspond to supercooled liquid) at strong coupling. The first three columns are similar to those in Table I. The remaining columns contain the values of Z obtained using MC simulations by Meijer and Frenkel¹⁵ and tabulated in Ref. 19 (Z_{MC}), present theoretical approach ($Z_{present}$), and our previous approximation (Z_{prev}) from Ref. 40.

κ	Γ	Γ/Γ_m	Z_{MC}	$Z_{present}$	Z_{prev}
1.800	396.9	1.03	102.492	102.498	102.526
1.860	383.9	0.95	89.606	89.542	89.567
1.923	371.4	0.87	78.148	78.123	78.145
1.984	360.0	0.80	68.640	68.618	68.637
2.049	348.6	0.73	59.889	59.880	59.895
2.117	337.5	0.66	52.133	52.138	52.150
2.182	327.3	0.60	45.711	45.699	45.707
2.238	319.2	0.56	41.041	40.998	41.002
2.306	309.7	0.51	35.954	35.904	35.903
2.348	304.2	0.48	33.204	33.189	33.184
2.398	297.9	0.45	30.294	30.258	30.249
2.532	282.1	0.37	23.780	23.760	23.741
2.631	271.5	0.32	20.016	20.017	19.989
2.778	257.1	0.26	15.705	15.724	15.682

limited by the validity of RT scaling, i.e., to the regime of strong coupling and weak screening.

V. DISCUSSION AND CONCLUSION

A simple practical approach to estimate thermodynamic properties of strongly coupled Yukawa systems, both in the fluid and solid phases, is presented. The excess free energy is obtained by a standard integration of the expressions for the excess internal energy using the RT scaling in the dense fluid phase and harmonic lattice approximation in the solid phase. The integration starts from the freezing/melting point (where the fluid and solid free energies are equal by the conventional definition of this phase transition in Yukawa systems) and requires the knowledge about the location of this point and excess free energy at this point. This information is available from earlier numerical simulations. The accuracy of the approach is verified by calculating the compressibility factors in a wide parameter regime and comparing the results with those from direct MD and MC computer simulations. The relative deviations are documented to be less than 1% for solids in the near-melting and superheated regimes and more than one order of magnitude smaller in other regimes investigated. Given the simplicity and accuracy of the approach, it represents very convenient practical tools to estimate thermodynamic properties of Yukawa systems in a very broad range of parameters.

The important reason behind the success of the present approximation is that the static component of the internal energy dominates over the thermal component for soft repulsive interactions. This ensures that some deviations from the quasi-universal behavior of u_{th} for Yukawa fluids lead only to very minor corrections of the total internal energy. This also guarantees that anharmonic corrections to u_{th} in the solid phase do not play very important role. To get an idea how soft the repulsion should be, we plot in Fig. 3 the static component of the internal energy at freezing, $M_f \Gamma_m$, along with the rough estimate of the thermal energy at freezing, $u_{th} \approx 3.0$, as functions of the screening parameter κ . The two curves intersect around $\kappa \approx 5.5$. Thus, the absolute upper boundary of the approach applicability can be estimated as $\kappa_{max} \approx 5$. For larger κ , the thermal energy plays significant or dominant role, the

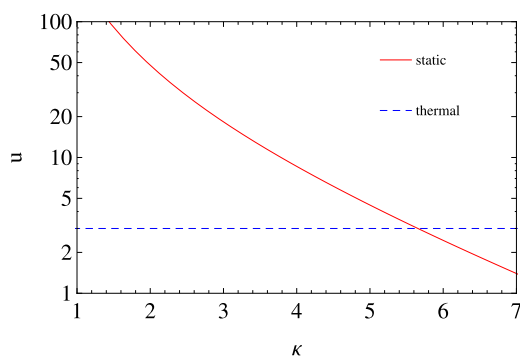


FIG. 3. Approximate static (red solid curve) and thermal (blue dashed curve) components of the reduced excess energy at freezing of Yukawa fluids. The static contribution dominates for $\kappa \lesssim 5$.

RT scaling in its simple form used here is no more applicable (see Fig. 2), and anharmonic corrections can play certain role.

Taking into account certain universal scalings in the behavior of simple condensed matter systems,^{48–51} we can suggest a more general criteria of the applicability of the approach described in this paper. We conjecture that it should (possibly with some minor modifications) be applicable to soft repulsive systems with the generalized softness parameter s above certain threshold. The generalized softness parameter introduced in Ref. 51 reads as

$$s = [-1 - V''(\Delta)\Delta/V'(\Delta)]^{-1}, \quad (17)$$

where Δ characterizes the mean interparticle distance, and $V(r)$ is the pairwise interaction potential. For example, for the IPL interactions $V(r) \propto r^{-n}$, we get the conventional definition $s = 1/n$. Using the Yukawa potential and adopting $\kappa_{max} \approx 5$, we obtain the threshold $s_* \approx 0.19$. This implies, for instance, that thermodynamics of the IPL systems with $n \lesssim 5$ can be treated in a manner similar to that applied here to Yukawa systems. Indeed, the RT scaling [Eq. (15) with constant δ] works well for IPL with $n = 4$, is slightly less appropriate for $n = 6$, and significant deviations are observed for $n = 9$ and $n = 12$ (see Fig. 1 of Ref. 43). We expect that the present approach can also be helpful in connection with the thermodynamics of systems exhibiting water-like anomalies (Gaussian core, exp-6, Hertz and related model potentials) in the regime of sufficiently soft interaction (high density), but this requires proper verification. Another interesting question is to which extent the shortest-graph method is applicable for these model systems taking into account their rich solid polymorphism. This is also left for future studies.

The last remark concerns the relevance of the single component Yukawa model to real systems, like complex (dusty) plasmas or colloidal suspensions. First of all, the effect of neutralizing medium has to be properly taken into account. This should not constitute a major problem as we briefly discussed in Sec. II. Second, the idealized model considered here does not account for some important properties of real systems. For example, the openness of complex plasma systems is known to be responsible for some deviations from the model Yukawa interaction (as was pointed out in the Introduction) and variability of the particle charge. These complications have been repeatedly discussed in recent publications and we refer the reader to Refs. 29, 30, and 52. It is not clear at the moment how large the related modifications to thermodynamic properties can be and whether they can be evaluated using conventional methods. Nevertheless, the present approach can be an important element in constructing more realistic and accurate models for the thermodynamics of real systems.

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