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Dear Prof. Hansen,

Thank you very much for your message regarding reviewer comments on our manuscript "Application of phenomenological freezing and melting indicators to the exp-6 and Gaussian core potentials" (TMPH-2011-0225) submitted to Molecular Physics. We studied carefully the reviewer report and agreed with most of the reviewer suggestions. The paper has been therefore revised taking all of the reviewer comments into account. Details of changes are summarized below in the response to the reviewer.

Response: First, we would like to thank the Referees for his/her careful examination of our work, expert comments, and useful suggestions. We took into account all the criticism and recommendation made and revised the manuscript accordingly. The following changes were made:

1. The introductory part has been rewritten. The Lindemann, Hansen-Verlet and a couple of other well known criterion for melting/freezing have been properly acknowledged (Refs. 1-5).

2. We added a reference related to the analytical freezing criterion for cluster-forming liquids proposed by Likos et al. (Ref. 12).

3. When pointing out relevance of GCM for describing polymer solutions (beginning of p. 3) we have added references to papers suggested by the referee (Refs. 18-22).

4. We have rewritten the beginning of the paragraph describing GCM phase diagram. The first sentence now reads "After the first approximate calculation of the GCM phase diagram by Stillinger (Stillinger1997) a detailed analysis was performed by Lang *et al.* (Lang) and subsequently by others (PrestipinoJCP2005,Mausbach)." The reference to the paper by Lang et al. has been added (Ref. 35); reference order has been rearranged.

5. Finally, we made necessary revisions at the end of p. 3 and p. 4 of the manuscript regarding the description of parameters δ and L. Now it is stated explicitly that the parameter δ is expected to be a quasiuniversal constant with the value $\delta = 0.10 \pm 0.01$, based on experience with other systems (LJ and IPL). The parameter L is not a true constant, but can be thought of as quasiuniversal in a broader sense: L is quasiuniversal function of potential steepness. However, for relatively soft interactions we are dealing with in this paper, the value of the parameter L is expected to lie in a relative narrow range around $L \sim 200$. We verify this towards the end of the manuscript (end of p. 5, beginning of p. 6) and find reasonable agreement between these expectation and actual values of δ and L, determined by fitting eqs. (3) and (4) to known simulation results. Our main conclusion that although there is certain level of agreement with the simulation results, this agreement is merely qualitative, is of course not affected by these revisions.

Application of phenomenological freezing and melting indicators to the exp-6 and Gaussian core potentials

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We apply two simple analytical melting and freezing indicators proposed earlier to the two exemplary systems exhibiting anomalous melting behavior, $\exp-6$ and Gaussian core models. It is shown that the main anomalous feature – reentrant melting regime – is well reproduced. Detailed comparison with the available data from numerical simulations demonstrates, however, that the agreement is merely qualitative. This implies that in general these indicators should be used with some care for purposes other than rough estimates of the location of the fluid-solid phase change.

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Investigating phase behavior of different substances is an outstanding physical problem with significant impact on basic and applied research. In general, thermodynamic equilibria can be estimated by means of the knowledge of the Gibbs free energy of the competing phases. However, calculating the free energy of either a dense fluid or a hot solid still remains a demanding computational task. Moreover, there exist various systems in which the effective interaction potential between the constituent particles depends on a number of system parameters, which can vary from one situation to another. In this case even modern computational methods are not very feasible in obtaining the complete phase portrait of the system, since multidimensional parameter space should be scanned. For such reasons other approaches, such as well known criteria for freezing and melting like e.g. Lindemann melting law,[1] Hansen-Verlet freezing rule[2], Raveché-Mountain-Streett criterion for freezing[3] and some other[4,5] can be often quite useful. These criteria typically predict quasiuniversal values of certain structural or dynamical measures of one of the two coexisting phases at the

phase transition. Another possibility is associated with approximate analytical expressions relating the location of phase boundaries to the shape of the interaction potential between the particles or other special parameters of the substance. Although expressions of this kind cannot be completely universal and their applicability is typically limited to a certain class of interactions, they can be very useful in approximately predicting the location of phase changes without any computational cost.

To give a few relevant examples of such expressions we mention the empirical formulae for liquid-vapor coexistence densities proposed by Guggenheim[6] and a number of different approximate methods to estimate the parameters of the liquid-vapor critical point.[7–9] In the context of the fluid-solid phase transition we point out semi-empirical melting equations describing additivity of melting curves,[10] an approximate melting equation derived using the simplest harmonic cell model consideration,[11] an accurate analytical freezing criterion for cluster-forming liquids,[12] a universal freezing equation applicable to a certain class of diverging repulsive potentials,[13] and the freezing indicator in the form of the properly normalized second derivative of the interaction potential.[14,15] The purpose of this research note is to check the applicability of some of these approximate melting and freezing equations to systems exhibiting anomalous reentrant melting behavior. We consider two special examples of such systems: particles interacting via $\exp{-6}$ or Buckingham potential[16] and Gaussian core model (GCM).[17]

The exp-6 potential is defined as

$$
U(r) = \begin{cases} +\infty, & r < r_0, \\ \frac{\epsilon}{\alpha-6}\left\{6\exp\left[\alpha\left(1-\frac{r}{\sigma}\right)\right] - \alpha\left(\frac{\sigma}{r}\right)^6\right\}, & r \geq r_0, \end{cases} \tag{1}
$$

where ϵ is the energy scale, the parameter α controls the softness of the repulsive part of the potential, σ is the distance at which the potential has a minimum, and r_0 is the hard-core diameter, corresponding to the maximum of the function appearing in the second line of Eq. (1). This potential is widely used to describe the properties of various materials under extreme conditions.

The Gaussian core potential is

$$
U(r) = \epsilon\exp\left(-r^2/\sigma^2\right), \tag{2}
$$

where ϵ and σ are again the energy and length scales. This is bounded potential (interaction energy tends to a constant value ϵ when the distance between the particles tends to zero)

which is frequently used in the context of soft matter physics, e.g. to describe effective interactions in many-body systems of polymer solutions.[18–23]

Phase behavior of both considered systems is extensively studied using various theoretical and numerical simulation methods. A key common property of these systems is that the melting temperature, as a function of pressure or density, exhibits a maximum, followed by a region of reentrant melting. Such behavior is often explained by the existence of a range of interparticle distances where the strength of the repulsive interaction *reduces* as the separation between the particles *decreases* (so-called core-softening, see Ref. 24 and references therein), although recently it was demonstrated that this is not a necessary condition for reentrant melting.[25,26] Our main goal in the rest of this short note is to check wether simple phenomenological freezing and melting equations can adequately reflect this anomalous shape of the fluid-solid coexistence (with respect to standard simple-fluid-like behavior).

The first analytical approach is based on the cell model with a spherically averaged potential in the harmonic approximation.[11] The resulting melting equation can be written as

$$T = \frac{N_{\mathrm{nn}}}{9}\delta^2[x^2 U'(x)]'_{x=x_{\mathrm{nn}}}, \tag{3}$$

where T is the temperature, N_{nn} is the number of nearest neighbors, δ is the *effective* Lindemann fraction, x is the normalized distance ($x = r/\sigma$), and x_{nn} is the structure-dependent distance between nearest neighbors. In deriving Eq. (3) only nearest-neighbor contribution to the interaction has been taken into account.[11] The stable crystalline structure of the exp -6 and GCM solids is the face-centered cubic (fcc) lattice for sufficiently steep repulsion (low density) and the body-centered cubic (bcc) lattice for softer repulsion. In the wide parameter range characteristic for reentrant melting of the both systems considered here, the stable solid phase is the bcc lattice. Very dense exp -6 fluids can also exhibit freezing into hard-sphere-like fcc solid due to the presence of the hard core in the interaction potential. This regime is however beyond the scope of this note. For the fcc solid we have $N_{\mathrm{nn}} = 12$ and $x_{\mathrm{nn}} = (\sqrt{2}/\rho)^{1/3}$, while for the bcc solid we have $N_{\mathrm{nn}} = 8$ and $x_{\mathrm{nn}} = (3\sqrt{3}/4\rho)^{1/3}$, where ρ is the particle density in units of σ^{-3}. The effective Lindemann fraction δ is in principle an adjustable parameter, which can be chosen by fitting this equation to some known point(s) on the melting curve. However, application to Lennard-Jones (LJ) and inverse-power-law (IPL) systems demonstrated that δ lies in a relatively narrow range $\delta \simeq 0.10\pm0.01$, i.e. it is expected to be quasiuniversal.[27] Melting equation (3) with $\delta \simeq 0.105$

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was also successfully applied to describe fcc solid-fluid phase change in the $\exp -6$ model with $\alpha = 13$, but only in the low density and temperature range, far from the regime where reentrant melting occurs.[11]

The second analytical approach is based on the observation that the freezing indicator in the form of the properly normalized second derivative of the interaction potential,

$$\mathcal{L} = U''(x)x^2/T|_{x=\bar{x}} \tag{4}$$

remains approximately constant along the freezing curve for various interaction potentials. Here $\bar{x}$ is the structure-independent mean interparticle separation $\bar{x} = (1/\rho)^{1/3}$. Originally, freezing criterion in the form of Eq. (4) was applied to the Yukawa (Debye-Hückel) interaction potential in the context of complex (dusty) plasmas.[28–30] It works reasonably well provided the ratio of the mean interparticle distance to the screening length is not too large ($\lesssim 10$), i.e. the interaction remains sufficiently soft. More recently this freezing indicator has been successfully applied to the 12-6 Lennard-Jones fluid[14] as well as to other related LJ-type fluids.[15] The $\exp -6$ potential with $\alpha = 13$ is one of the models considered in Ref. 15, but again in the regime of sufficiently low densities and temperatures, very far from the reentrant melting behavior.

The value of the parameter $\mathcal{L}$ appearing in Eq. (4) is not strictly universal, it can depend on the concrete potential. However, it has been conjectured that this parameter is mainly sensitive to the steepness of the interaction potential evaluated at the mean interparticle distance.[15] For sufficiently soft interactions $\mathcal{L}$ remains approximately constant, but then grows systematically with potential steepness. For example, for the IPL family of potentials $[U(r) \propto r^{-n}]$ the values of $\mathcal{L}$ at freezing, evaluated using different numerical data, are scattered in a relatively narrow range $180 \simeq \mathcal{L} \simeq 240$, provided $n \lesssim 10$.[14,15] For larger n the parameter $\mathcal{L}$ increases systematically with n and a relevant smooth fit is available.[15] This fit can be used to predict the value of $\mathcal{L}$ for certain potentials. For instance, for the $n-6$ LJ potentials the value corresponding to the high-temperature high-density asymptote, governed by r^{-n} repulsion, can be taken.[15] Although for the potentials at hand the procedure is not straightforward, we can expect that for these soft potentials the values of $\mathcal{L}$ should not be located too far from the corresponding soft-interaction range ($\mathcal{L} \sim 200$). If true, this will give further support to the conjecture that $\mathcal{L}$ can be though as a "quasiuniversal" quantity, in the sense indicated above.

Let us now compare the numerical data for the fluid-solid coexistence of the $\exp-6$ and GCM models available in the literature with the functional form suggested by simple analytical melting and freezing equations (3) and (4). The relative differences between densities at freezing and melting are rather small for the potentials considered (for instance for the GCM potential they do not exceed $\simeq 3\%$ in the whole range of densities studied so far) so we can basically disregard the difference between melting and freezing and concentrate on the shape of the fluid-solid coexistence curves.

Figures 1-3 show the freezing points (symbols) of the $\exp-6$ systems with $\alpha = 10, 11$ and 13, respectively, evaluated using different numerical simulation techniques, on the temperature vs density plane. The solid line is the corresponding fit using the freezing equation (4), dashed and dotted curves correspond to the melting equation (3) applied to fcc and bcc solids, respectively. The figures demonstrate that the main qualitative property – the existence of reentrant melting region – is well reproduced. The maximum temperature and the corresponding density are also in reasonable agreement with numerical data[31,32] for the cases $\alpha = 10$ and $\alpha = 11$ (figures 1 and 2). The freezing equation (4) does somewhat better work in these cases. Melting equations (3) is less accurate, especially from the side of higher densities. The deviations are more pronounced for the assumption of the fcc solid structure, in agreement with the fact that bcc is the stable phase in this parameter regime. The available numerical fata[33] for the case $\alpha = 13$ (shown in fig. 3) are very far from the regime where melting anomaly occurs. In this range the freezing and melting equations are almost indistinguishable. This explains why melting and freezing equation (3) and (4) have been previously found to accurately describe fluid-solid coexistence of the $\exp-6$ model with $\alpha = 13$ in Refs. 11 and 15, respectively. The effective Lindemann fractions for the relevant bcc structure obtained here are all in the expected range $\delta = 0.10 \pm 0.01$, reported earlier for other potentials. The parameter $\mathcal{L}$ increases smoothly with α, but remains in the reasonable proximity of the expected soft-interaction range. Note that for $\alpha = 13$ we have $\mathcal{L} \simeq 223$, which is very close to that suggested in Ref. 15 ($\mathcal{L} \simeq 226$), despite of a mathematical deficiency involved there.

After the first approximate calculation of the GCM phase diagram by Stillinger,[34] a detailed analysis was performed by Lang $et\ al.$[35] and subsequently by others.[36,37] Figure 4 shows the phase diagram of the GCM system on the temperature vs density plane. Symbols correspond to the numerical results related to the fluid-solid transition and obtained using

different simulation techniques.[34,36,37] Solid curve is the fit using the freezing equation (4), dashed (dotted) curve is plotted using the melting equation (3) applied to the fcc (bcc) solid. One of the main properties of the GCM model – existence of the maximum freezing/melting temperature – is again reproduced. The value of the maximum temperature and the density at which it is reached are in reasonable agreement with simulation results. On the "low-density" side of the fluid-solid coexistence of the GCM system the analytical approximations considered almost coincide and their predictions are in rather close agreement with the available simulation results. They correctly reproduce the dominant dependence $T \propto \exp(-\rho^{-2/3})$ arising from the hard-sphere-limit consideration.[34] On the "high-density" side of the solid-fluid coexistence the agreement is much less convincing. The freezing indicator (4) is irrelevant here. The melting equation (3) yields better results, especially for the melting of the bcc lattice (which is the stable solid structure in this regime). The obtained effective Lindemann fraction for the bcc lattice is $\delta \simeq 0.105$, in good agreement with other systems. Nevertheless, the dominant dependence $T \propto \exp(-K\rho^{2/3})$, where K is the appropriate constant, along the solid-fluid phase change of GCM system in the high-density limit, derived on the basis of duality relations,[38] is not reproduced.

We can summarize main results from this study as follows. We tested the application of simple analytical melting and freezing equations to the two different models, $\exp -6$ and GCM systems, exhibiting anomalous reentrant melting behavior. It is shown that the main qualitative feature of reentrant melting itself is reproduced well. The values of the maximum temperature and the density at which it occurs are usually not too far from the values obtained in numerical simulations. Melting equation (3) for the bcc solid is better suitable to describe fluid-solid coexistence of the GCM model. The freezing indicator (4) is somewhat more convenient to describe fluid-solid coexistence of the $\exp -6$ systems. Overall, however, the agreement between these approximate equations and numerical data is merely qualitative. One should therefore be careful when using these equations, especially if sufficient accuracy is needed. More accurate and reliable approximation are required in these cases.

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Deutschen Bundestages unter dem Förderkennzeichen 50 WP 0203.)

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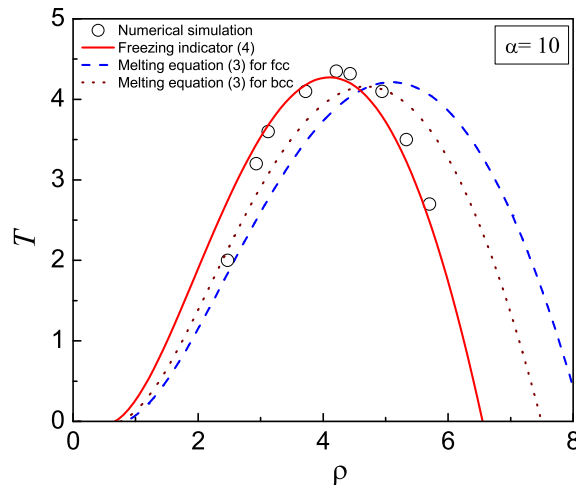[27] Y. Rosenfeld, J. Chem. Phys. **64**, 1248 (1976).

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FIG. 1: (Color online) Fluid-solid coexistence of the exp -6 model with $\alpha = 10$ on the temperature vs density plane. Reduced units are used, temperature is in units of ϵ and density is units of σ^{-3}. Symbols correspond to the freezing points estimated in Ref. 32 using the so-called "heat-until-it-melts" numerical procedure. The red curve is the best fit using the functional form of the freezing indicator [Eq. (4)] with $\mathcal{L} \simeq 170.8$. The blue curve is the best fit using the melting equation (3) assuming fcc solid (resulting in the effective Lindemann fraction $\delta_{\text{fcc}} \simeq 0.083$). The brown curve is also plotted using the functional form of Eq. (3), but assuming bcc solid (resulting in $\delta_{\text{bcc}} \simeq 0.101$).

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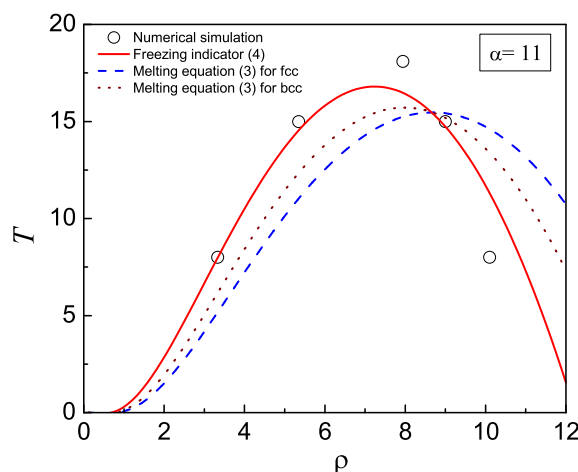[38] F. H. Stillinger, Phys. Rev. B **20**, 299 (1979).

FIG. 2: (Color online) Fluid-solid coexistence of the exp -6 model with $\alpha = 11$ on the temperature vs density plane (reduced units). Symbols correspond to the freezing points obtained in Ref. 31 using the "exact" free energy calculations. The color scheme of the curves is the same as in Fig 1. The resulting fitting parameters are $\mathcal{L} \simeq 180.8$, $\delta_{\text{fcc}} \simeq 0.081$, and $\delta_{\text{bcc}} \simeq 0.100$.
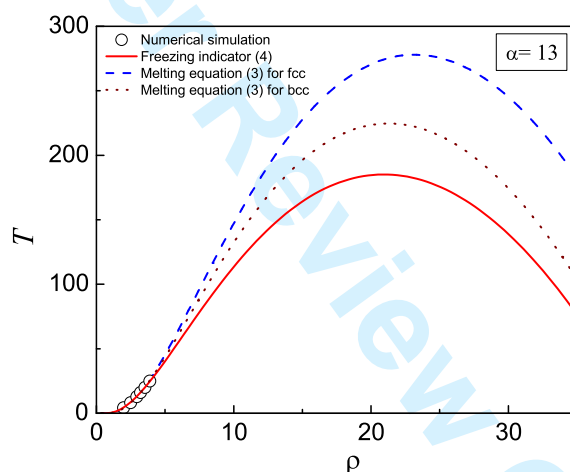

FIG. 3: (Color online) Fluid-solid coexistence of the exp -6 model with $\alpha = 13$ on the temperature vs density plane (reduced units). Symbols correspond to the freezing points obtained in Ref. 33 using the "exact" free energy calculations. The color scheme of the curves is the same as in Fig 1. The resulting fitting parameters are $\mathcal{L} \simeq 222.9$, $\delta_{\text{fcc}} \simeq 0.099$, and $\delta_{\text{bcc}} \simeq 0.109$.
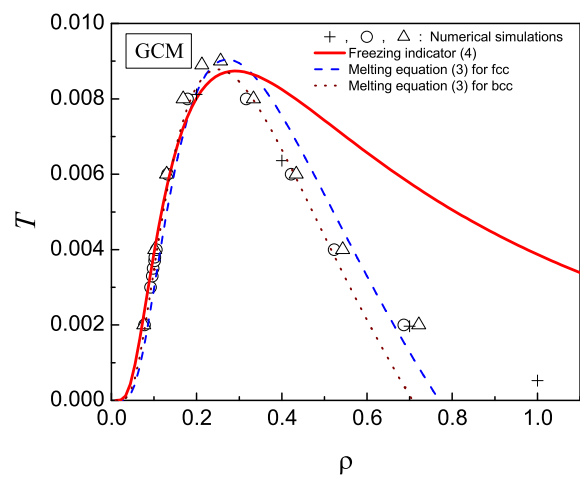
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FIG. 4: (Color) Fluid-solid coexistence of the GCM system on the temperature vs density plane (reduced units). Crosses are estimates of the melting points obtained using MD simulations and the Lindemann melting criterion.[34] Circles correspond to the freezing points obtained in Ref. 36 using Monte Carlo (MC) technique. Triangles are the freezing points obtained in Ref. 37 using a combination of equilibrium and non-equilibrium molecular dynamics (MD) simulation methods. The red curve is a fit using the functional form of the freezing indicator [Eq. (4)] with $\mathcal{L} \simeq 190$. The blue (brown) curve is a fit using the melting equation (3) assuming fcc (bcc) solid with the effective Lindemann fraction $\delta_{\mathrm{fcc}} \simeq 0.087$ ($\delta_{\mathrm{bcc}} \simeq 0.105$).