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2007 J. Phys.: Condens. Matter 19 416101

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# The stability of many-body systems

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Received 11 May 2007, in final form 27 July 2007

Published 10 September 2007

Online at [stacks.iop.org/JPhysCM/19/416101](http://stacks.iop.org/JPhysCM/19/416101)

## Abstract

We apply the pair interaction stability criteria of Fisher and Ruelle (1966 *J. Math. Phys.* **7** 260) to establish the range of thermodynamic stability for a number of simple analytic potential forms used for condensed matter theory and modelling in the literature. We identify the ranges of potential parameters where, for a given potential, the system is thermodynamically stable, unstable and of uncertain stability. This was further explored by carrying out molecular dynamics simulations on the double Gaussian potential in the stable and unstable regimes. We show that, for example, the widely used exponential-6 and Born–Mayer–Huggins alkali halide potentials produce many-particle systems that are thermodynamically unstable.

## 1. Introduction

The interaction potential,  $\phi(r)$ , between molecules (where  $r$  is the pair separation) is the key input function of statistical mechanical theories of the liquid state (e.g. [1]). An increasingly diverse range of analytic forms for  $\phi(r)$  has been used in recent years in the context of soft-matter physics [2], thermodynamic integration [3], and as new representations for atoms in condensed matter physics. A number of these are finite at zero separation, and also have an attractive region. This places them potentially within the class of thermodynamically unstable potentials identified by Fisher and Ruelle [4, 5]. If, in general terms, the potential is not sufficiently repulsive to discourage overlap of the particles, the system will collapse into a small volume of space, and no thermodynamic limit can be reached (i.e. a mean potential energy per particle being essentially independent of the number of particles in the system for large numbers of particles). For large Hamiltonian systems that obey the laws of statistical mechanics, the thermodynamics expected in the limit of large volume and number of particles must satisfy certain constraints. It may be that some interaction potentials used in the literature give rise to metastable states which are long-lived on a simulation timescale, and therefore appear to be stable (a subject we will return to below). In this paper consideration is given mainly to one-component, homogeneous fluids in which pairs of molecules interact only through spherically

symmetric potentials. The theoretical framework for predicting the stability of such systems was provided by Fisher and Ruelle [4, 5]. Stability, or equivalently a finite grand partition function, is assured if the total potential energy,  $U$ , of an  $N$ -particle system satisfies the inequality,

$$U(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) = \sum_{i=1}^{N-1} \sum_{j>i}^N \phi(|\underline{r}_i - \underline{r}_j|) \geq -N\epsilon, \quad (1)$$

where  $\underline{r}_1, \underline{r}_2 \dots$  are the coordinates of molecules with indices, 1, 2 etc, and  $\epsilon$  is a finite constant independent of  $N$ . One can see immediately that this inequality is breached if the potential,  $\phi$ , is negative at zero separation and continuous nearby. In that case, the potential,  $U$ , will be negative in a small sphere surrounding  $r = 0$ . If all the points,  $\underline{r}_i$  in the inequality (1) are chosen within this sphere all the terms in the sum will be negative and the left-hand side of the inequality will be of the order  $-N^2$  when  $N$  is large. Ruelle ([5] in section 3.2.2) has shown explicitly that the grand partition function then diverges and the normal laws of thermodynamics are not obeyed.

In other cases, Fisher and Ruelle have provided two rules which help one to decide whether a potential will lead to a steady thermodynamic state. To slightly paraphrase Fisher and Ruelle, and assuming the potential is only dependent on the absolute separation distance,  $r$ , the conditions for stability may be expressed in the following theorems.

**Theorem 1.** *When  $\int d^3\underline{r}\phi(r) < 0$ , the system is unstable, but when  $\int d^3\underline{r}\phi(r) \geq 0$  we do not know whether or not it is stable without further examination.*

**Theorem 2.** *If we can write  $\phi(r) = \phi^{(1)}(r) + \phi^{(2)}(r)$  where  $\phi^{(1)}(r) > 0$  for all values of  $r$  and*

$$\begin{aligned} \tilde{\phi}^{(2)}(p) &\equiv \frac{1}{(2\pi)^3} \int d\underline{r} \exp(-i\underline{p} \cdot \underline{r}) \phi^{(2)}(r) \\ &= \frac{1}{2\pi^2 p} \int_0^\infty r \phi^{(2)}(r) \sin(pr) dr \geq 0 \end{aligned} \quad (2)$$

*the system is stable; when these conditions are broken for a particular division of the potential we do not know that the system is unstable. Our choice of division may not have been optimal.*

As a special case of the theorem,  $\tilde{\phi}(p) \geq 0$  for all values of  $p$  ensures stability but it is not a requirement. The main point is that theorem 1 implies the instability of the system and theorem 2 provides conditions which ensure stability. If, however, a particular division of the potential violates theorem 2 the system may yet be stable. theorem 1 can be restated as the system is unstable if  $\tilde{\phi}(0) < 0$ .

Just by setting  $\phi^{(1)}(r) = \phi(r)$ , theorem 2 guarantees that potentials that are positive at all pair separations are thermodynamically stable, irrespective of their analytic form. If  $\phi(r)$  is negative for some range of  $r$  one is faced with the question of how to divide the potential into two parts as required by theorem 2. This is an important question for some examples discussed in this paper. In three dimensions it can be seen from equation (2) and taking  $p \rightarrow 0$  that, if the potential decays according to a power law at infinity, then it must decay more rapidly than  $r^{-3}$  for large  $r$  for the integral to converge. There is also a divergence in  $\tilde{\phi}(0)$  if  $\phi(r)$  decays more rapidly than  $r^{-2}$  as  $r \rightarrow 0$ .

Divergences of the potential to  $+\infty$  as  $r \rightarrow 0$  can often be shown to lead to stability from a corollary to theorem 2, namely Corollary ‘B’ in [4], which is referred to as ‘CT2’ here, if

$$\phi(r) = \begin{cases} \phi(r) \geq Cr^{-(v+\epsilon)}, & r < a_1 \\ \phi(r) \geq -w, & a_1 \leq r \leq a_2 \\ \phi(r) \geq -C'r^{-(v+\epsilon')}, & r > a_2, \end{cases} \quad (3)$$

where  $a_1$ ,  $a_2$ ,  $C$ ,  $\epsilon$ ,  $C'$ , and  $\epsilon'$  are positive constants, and  $v$  is the space dimension (i.e. 3 here) stability is assured.

The purpose of this work is to consider a range of interaction potentials to establish the parameter range (if any) where they are unstable. Many of these have been widely used in the literature for various applications, and some have been ‘invented’ since the Fisher and Ruelle article was written. We explored some of these issues for the shifted Lennard-Jones fluid in our previous publication [6].

## 2. Applications of the theory to different potential forms

In this section various generic types of potential are considered that have found use in some studies reported in the literature.

### 2.1. Exponential potentials

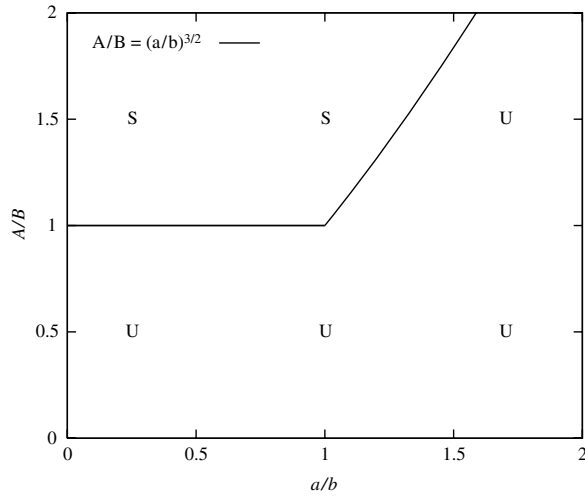
The first potential we consider is the double Gaussian (‘DG’) potential

$$\phi(r) = A \exp(-ar^2) - B \exp(-br^2) \quad (4)$$

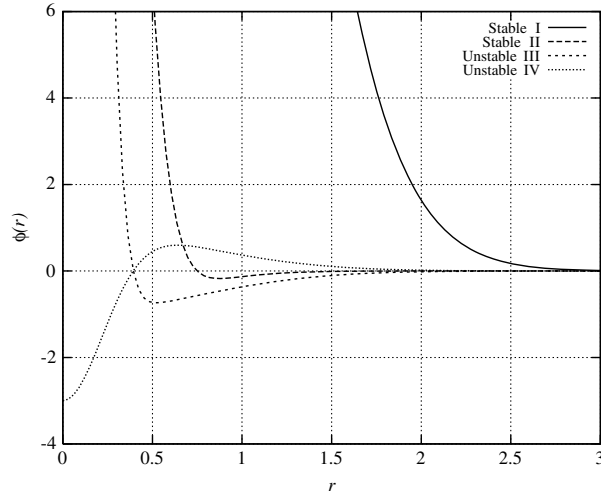
where  $A$ ,  $a$ ,  $B$ ,  $b \geq 0$ . If  $A/B < 1$  the potential is negative at and near the origin, and as was stated in the introduction the system is unstable. If  $A/B \geq 1$  and  $a/b \leq 1$ , the potential is positive everywhere, and as theorem 2 with  $\phi^{(1)} = \phi(r)$  shows, the system will be stable. If  $A/B > 1$  and  $a/b > 1$ , we apply theorems 1 and 2 with  $\phi^{(2)} = \phi(r)$  to decide the issue. From equation (2),

$$\tilde{\phi}(p) = \frac{1}{8\pi^{3/2}} \left( A \frac{\exp(-p^2/4a)}{a^{3/2}} - B \frac{\exp(-p^2/4b)}{b^{3/2}} \right). \quad (5)$$

If then  $A/B < (a/b)^{3/2}$ , it is clear that  $\tilde{\phi}(0)$  is negative and, according to theorem 1, the system is unstable. On the other hand, if  $A/B \geq (a/b)^{3/2} \geq 1$ , the right-hand side of equation (5) is positive for all values of  $p$  and, according to theorem 2, the system is stable. We have therefore been able to decide on the stability of a system governed by the DG potential for all values of the parameters. This is illustrated in figure 1 where the  $(A/B, a/b)$  plane is shown divided into stable (S) and unstable (U) regions. Figure 2 gives four examples of the DG potential, two of which are stable and two unstable. The values of  $A$ ,  $B$  and  $a$ ,  $b$  for these potentials are given in the caption to the figure. Molecular dynamics simulations were carried out with the ‘stable’ potentials, (i) and (ii) defined in the caption of figure 1. The internal energy per particle,  $u$ , evaluated in block averages fluctuated over long runs by less than  $\sim 0.5\%$ , and with a small  $N$ -dependence, so they showed the hallmarks of stability. These systems were therefore found to be stable, as predicted. Figure 3 also shows the internal energy per particle,  $u$ , for a sequence of simulations using the two unstable potentials, (iii) and (iv) from figure 2. In the case of potential (iii), simulations with three different numbers of particles in the simulation cell were carried out.  $u$  for potential (iii) can be seen to be a strong function of time and  $N$ , which is a clear sign of an unstable system. The fourth potential (iv) which is also proved to be unstable generates a potential energy per particle that becomes gradually more negative with time. The issue of system size dependence was dealt with in more detail in our previous publication on the separation-shifted Lennard-Jones potential [6]. If one chooses parameters in the unstable region, as established by the analytic analysis carried out here, then the ‘instability’ is manifest

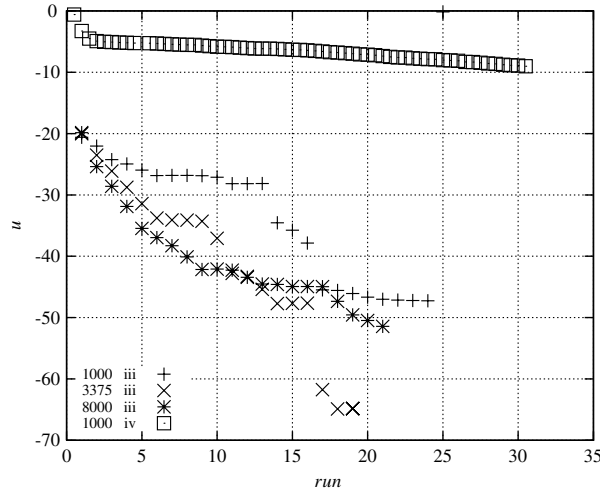


**Figure 1.** The stable ('S') and unstable ('U') regimes for the Double Gaussian potential given in equation (4). The solid line, when  $a/b > 1$ , satisfies the equation  $A/B = (a/b)^{3/2}$ .



**Figure 2.** Three examples of the double Gaussian potential given in equation (4). The characteristic energy and distance are  $\epsilon$  and  $\sigma$ , respectively. The parameter sets were  $(A/\epsilon, a/\sigma, B/\epsilon, b/\sigma)$  (i) 'Stable I': (89, 1, 1, 2), which gives a positive potential for all  $r$  and hence is stable from theorem 2. The second set of runs, (ii), 'Stable II': has the set, (89, 10, 1, 2) which becomes negative for  $r > 0.75$ , but still complies with the  $1 \leq a/b \leq (A/B)^{2/3}$  stability criterion. In contrast, the third example, (iii), 'Unstable': has the parameter set, (89, 30, 1, 1) which has a negative region in the potential for  $r > 0.39$  but is unstable according to theorem 1 (i.e.  $a/b > (A/B)^{2/3}$ ). (iv) 'Unstable': has the set, (1, 1, 4, 10) which is unstable because it is negative at  $r = 0$ .

in a strong  $N$ -dependence of the potential energy per particle  $u$ , for all  $N$ , and a steady drift in the value  $u$  with time. In order to observe a well-defined collapsed 'blob' of particles, the side length of the simulation cell would probably need to be much larger than the effective range of the potential. For a typical interaction range of 2–3 times the nominal particle diameter then system sizes in excess of about 10 000 particles would therefore be required. But we emphasize



**Figure 3.** The internal energy per particle,  $u/\epsilon$ , for the double Gaussian potential given in equation (4) as a function of run number (each for 30 reduced time units). The unstable potentials (iii) and (iv) given in the caption to figure 1, plotted in figure 1, were used in the simulations. The volume fraction in the simulations was 0.3 and the reduced temperature,  $k_B T/\epsilon = 1$ , where  $k_B$  is Boltzmann’s constant, was maintained constant by velocity rescaling [27]. The pair interactions were truncated for  $r > 3$ . Data for three system sizes of  $N = 1000, 3375$  and  $8000$ , indicated on the figure, were used. Each series of simulations was started off from fluid states of potential (ii). In the case of potential (iv) the abscissa is  $\text{run}/2$ .

that the effects of the instability, formally established by our analysis, are still evident in the trend in  $u(N)$  for much smaller  $N$ .

A similar form to the double Gaussian (‘DG’) potential is,

$$\phi(r) = A \cos(ar) \exp(-br^2) \tag{6}$$

where  $a, b \geq 0$  was discussed in [2]. Potential  $v_A(r)$  in equation (A3) of [2] has this analytic form. From theorem 1 we must have for stability  $A > 0$  and from theorem 2 by setting  $\phi^{(1)} = \phi(r)$  then  $A > 0$  and  $a = 0$  is stable. For further constraints we turn to theorem 2 and set  $\phi^{(2)}(r) = \phi(r)$ . The Fourier transform of equation (6) is,

$$\tilde{\phi}(p) = -\frac{A}{8\pi^{3/2}b^{3/2}p} \exp\left(\frac{-(a^2 + p^2)}{4b}\right) \left(a \sinh\left(\frac{ap}{2b}\right) - p \cosh\left(\frac{ap}{2b}\right)\right). \tag{7}$$

According to theorem 1, the system will be unstable if  $a^2/2b > 1$ . The last term in the brackets determines the sign of  $\tilde{\phi}(p)$ . Theorem 2 proves, after some rearrangement, stability is established if  $1 \geq (a^2/2b) \tanh(x)/x$  where  $x = ap/2b$ . We know from theorem 1 that the system will be unstable if  $a^2/2b > 1$  by taking the  $p \rightarrow 0$  limit of equation (7), therefore providing  $a^2/2b \leq 1$  then  $\tilde{\phi}(p) \geq 0$  for all  $p$ , as  $\tanh(x)/x \leq 1$  for  $x \geq 0$ .

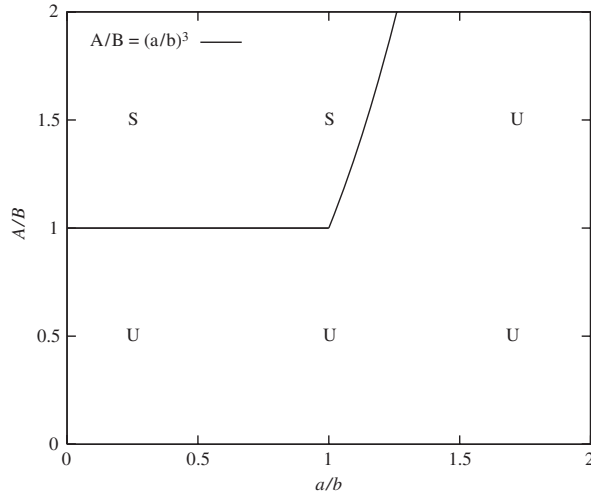
Potential  $v_A(r)$  from [2] has the analytic form,

$$\phi(r) = A \cos(\sqrt{2 + \delta}r) \exp(-r^2) \tag{8}$$

which on comparing equations (6) and (8), gives  $b = 1$ , and hence,  $a^2/2b = 1 + \delta/2$ , so if, say,  $\delta = -0.001$  the system is stable but it is unstable if  $\delta = 0.001$ , as concluded in [2].

The double exponential (‘DE’) potential has found use in a number of applications, such as in the modelling of small clusters, [7, 8]

$$\phi(r) = A \exp(-ar) - B \exp(-br) \tag{9}$$



**Figure 4.** The stable ('S') and unstable ('U') parameter regions for the double exponential potential given in equation (9).

for  $r \geq 0$  and where  $A, a, B, b \geq 0$ . (The much used Morse potential for bonded atoms,  $\phi(r) = D_0(1 - \exp(-c(r - r_0)))^2$  where  $D_0, c$  and  $r_0$  are atom-specific constants can be written in the equation (9) form.) The DE potential can also be used to approximate a Lennard-Jones interaction, with suitable choice of parameters, and this has been employed in variational free energy calculations of phase diagrams [9]. We approach this as we did the DG potential. If  $A/B < 1$  the potential is negative at and near  $r = 0$  and this results in instability. If  $A/B > 1$  and  $a/b < 1$ , the potential is positive everywhere and the system is stable. If  $A/B > 1$  and  $a/b > 1$ , we apply the theorems with  $\phi^{(2)} = \phi(r)$ . As,

$$\tilde{\phi}(p) = \frac{1}{\pi^2} \left( \frac{aA}{(a^2 + p^2)^2} - \frac{bB}{(b^2 + p^2)^2} \right) \quad (10)$$

according to theorem 1 the system is unstable when  $\tilde{\phi}(0) < 0$ , i.e. when  $A/B < (a/b)^3$ . According to theorem 2 stability is assured if  $\tilde{\phi}(p) \geq 0$  for all values of  $p$ , i.e. if,

$$\frac{A}{B} \geq \frac{b}{a} \left( \frac{a^2 + p^2}{b^2 + p^2} \right)^2 \quad (11)$$

for all positive values of  $p$ . The right-hand side of this inequality varies monotonically from its value of  $(a/b)^3$  when  $p = 0$  to its value of  $b/a$  when  $p$  tends to infinity. For stability the left-hand side of the inequality must be greater than the greatest of these. As  $a/b > 1$ , the first of these is greater. Hence, in this case, the stability is assured if, and only if,  $A/B > (a/b)^3$ . We have thus been able to decide on the stability of the system for all values of the parameters.

We illustrate these conclusions in figure 4 where we show the stable ('S'), and unstable ('U') regimes on the  $(A/B, a/b)$  plane. As an example from the literature, Miller *et al* [8] used the DE potential of equation (9), and in their notation  $A = e^{2\rho}$ ,  $a = 2\rho$ ,  $B = 2e^\rho$  and  $b = \rho$ , and hence  $A/B = e^\rho/2$  and  $a/b = 2$ . For the  $\rho$ -range they considered,  $\rho \geq 4$ , the inequalities  $A/B \geq (a/b)^3 \geq 1$  are satisfied, and the system is stable. As  $\rho$  increases the attractive well of the potential becomes more short-ranged [10].

## 2.2. Algebraic potentials

A radial symmetric short-ranged attractive ('SHRAT') potential has been used as a generic embedded-atom model metal potential [11],

$$\phi(r) = \begin{cases} A(1-x)^4 - B(1-x)^3, & x \leq 1 \\ 0, & x > 1, \end{cases} \quad (12)$$

where  $x = r/r_c$ , and  $r_c$  is the separation where the potential goes to zero, and  $A$  and  $B$  are positive constants. For this potential,

$$\begin{aligned} \tilde{\phi}(p) &= \frac{1}{2\pi^2} \left( A \frac{8(p^3 - 12p + 15 \sin(p) - 3p \cos(p))}{p^7} \right. \\ &\quad \left. - B \frac{6(-4 + p^2 + 4 \cos(p) + p \sin(p))}{p^6} \right) \\ &= \frac{1}{2\pi^2} \left( \frac{A}{105} - \frac{B}{60} \right) + O(p^2). \end{aligned} \quad (13)$$

Therefore theorem 1 shows that the system will be unstable if  $A/B < 105/60 = 7/4$ . Using the definitions of  $A = 3\phi_0 r_0^{-4} r_c^4$  and  $B = 4\phi_0 r_0^{-4} r_c^3 (r_c - r_m)$  from [11], where  $r_m$  is the position of the minimum of the potential, we have for instability,  $A/B = 3/4(1 - x_m) < 7/4$  or equivalently  $x_m < 4/7 = 0.571$ . In [11]  $x_m = r_m/r_c = 2^{1/6}/1.6 = 0.702$  and  $A/B = 2.51$ , so the system is not declared unstable by theorem 1. To prove when (or if) the system is stable for any parameter range, then according to theorem 2 and using the definition of  $\tilde{\phi}(p)$  in equation (13), we must have,

$$\frac{A}{B} \geq \frac{3(-4p + p^3 + 4p \cos(p) + p^2 \sin(p))}{4(-12p + p^3 + 15 \sin(p) - 3p \cos(p))} \quad (14)$$

for all values of  $p \geq 0$ . The right-hand side of the inequality in equation (14) has a maximum value of  $7/4$  at  $p = 0$  and a value of  $3/4$  in the  $p \rightarrow \infty$  limit. Plotting the right-hand expression of this equation with the Maple mathematics software package<sup>1</sup> indicated that the right-hand side of equation (14) decays monotonically between these two limits, indicating that  $x_m \geq 4/7 = 0.571$  or equivalently  $A/B \geq 7/4$  is a necessary and sufficient condition for thermodynamic stability. The ratio of the value of the potential at  $r = 0$  to minus the minimum value at  $r_m$ , is,  $(4(r_m/r_c) - 1)/(r_m/r_c - 1)^4$ , which is 228 for  $r_m/r_c = 0.702$ . Figure 5 shows two examples of the SHRAT potential, one stable and the other unstable (the parameters are given in the figure caption). Of course other exponents apart from 4 and 3 could be used in equation (12) and treated in a similar manner.

Potentials of the general form,

$$\phi(r) = \frac{A}{r^n} - \frac{B}{r^m} \quad (15)$$

where  $A \geq 0$  and  $B \geq 0$  have been widely used in the literature with various choices of  $n$  and  $m$  values (e.g. [12, 13]). For  $A = B = 4\epsilon$ ,  $n = 12$  and  $m = 6$  this is the much used Lennard-Jones potential. We have already mentioned that theorem 2 leads to the condition 'CT2'. Setting  $a_1 = a_2$  in CT2 of equation (3) combined with  $n > m > \nu$  assures thermodynamic stability.

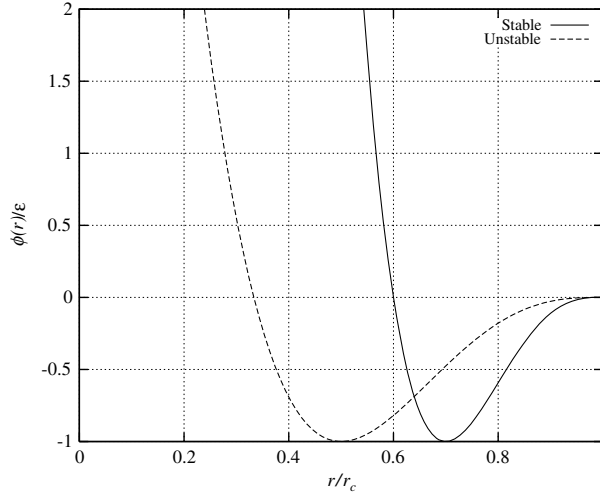
A generalization of equation (15), namely

$$\phi(r) = Aa^{2p}(r^2 + a^2)^{-p} - Bb^{2q}(r^2 + b^2)^{-q} \quad (16)$$

where  $a, b, A, B \geq 0$  are all positive has been used in the literature (e.g. [14]). This potential is

<sup>1</sup> Maple is a general-purpose commercial mathematics software package from Waterloo Maple Inc. versus 9.5.





**Figure 5.** A comparison between two examples of the SHRAT potential of equation (12). ‘Stable’ is a stable potential with  $x_m = 0.7$ , and the ‘Unstable’ potential is with  $x_m = 0.5$ . The energies are normalized by the energy minimum,  $\epsilon = \phi_0 r_0^{-4} r_c^4 (1 - x_m)^4$ .

finite at  $r = 0$ . It is negative at the origin when  $A/B < 1$  which leads to instability. In [6] we considered the stability when  $p = 6$  and  $q = 3$  which is a modification of the Lennard-Jones potential, and established (in the present notation) that if  $a = b$  the fluid would be unstable for  $A/B < 32/7 = 4.571$ . In the more general case theorem 1 shows that the potential will give rise to unstable states when

$$\tilde{\phi}(0) = \frac{1}{8\pi^{3/2}} \left( Aa^3 \frac{\Gamma(p - 3/2)}{\Gamma(p)} - Bb^3 \frac{\Gamma(q - 3/2)}{\Gamma(q)} \right) < 0 \quad (17)$$

where  $\Gamma(x)$  is the Gamma function of  $x$ . For the more typical special case of  $a = b$ , and  $p = 2q = 2n$  this condition becomes

$$\frac{A}{B} < c = \frac{(2n - 1)(2n - 2) \cdots n}{(2n - 5/2)(2n - 7/2) \cdots (-3/2 + n)}. \quad (18)$$

When  $n = 3$ ,  $c = 32/7 = 4.571$  as stated above, when  $n = 6$ ,  $c = 3.414$  and when  $n \rightarrow \infty$ ,  $c \rightarrow 1$ . This is consistent with the reasonable assumption that the particle diameter ( $r = 1$ ) becomes the only interaction length scale in the system in this steeply repulsive and attractive limit. By a corresponding treatment, the potential,  $\phi(r) = A[(r^2 + a^2)^{-2n} - (r^2 + a^2)^{-n}]$  gives rise to unstable states if  $a > a_c = c^{-1/2n}$ . For  $n = 3$  and 6, this gives  $a > (7/32)^{1/6} = 0.7762$  and 0.9027 respectively. These same approaches, but starting from equation (17), could be used for a more general  $n:m$  potential where  $n/m \neq 2$  [15].

### 2.3. Mixed algebraic and exponential potentials

Another potential that has been used to model fluids is the exponential-6 (‘E6’) potential. We consider a slight generalization of this here,

$$\phi(r) = A \exp(-ar) - B(r^2 + b^2)^{-3} \quad (19)$$

to bring out some more general conclusions. (The E6 potential, also known as the Buckingham potential [16], is the formula in equation (19) with  $b = 0$ .) This potential is often normalized

so that its minimum is  $-1$  at  $r = 1$ , which requires that  $A = 6 \exp(a)/(a + ab^2 - 6)$  and  $B = a(1 + b^2)^4/(a + ab^2 - 6)$ .

Now  $\phi(0) < 0$  and the system is unstable when  $Ab^6/B < 1$ , as, if  $b$  is too small, the potential will be negative at the origin. This includes the E6 potential for which  $b = 0$  [17]. To proceed further we consider, as before, the Fourier transform of the potential,

$$\tilde{\phi}(p) = \frac{aA}{\pi^2(a^2 + p^2)^2} - B \exp(-bp) \frac{(1 + bp)}{32\pi b^3} \quad (20)$$

and therefore we have  $\tilde{\phi}(0) = A/\pi^2 a^3 - B/32\pi b^3$ . From theorem 1 it follows that the system is unstable if  $Ab^6/B < \pi(ab)^3/32$ . Hence, the system is unstable if  $Ab^6/B < \max[1, \pi(ab)^3/32]$ .

To derive conditions on the parameters which would ensure stability, we again use theorem 2 with  $\phi^{(2)} = \phi(r)$ . This requires one to establish the range of parameters for which  $\tilde{\phi}(p)$  given in equation (20) is positive. By rearrangement the requirement is expressed by the inequality,

$$C = \frac{Ab^6}{B} \geq \frac{\pi}{32} (ab)^3 e^{-bp} (1 + bp) (1 + (p/a)^2)^2. \quad (21)$$

Hence, for stability,

$$C \geq f(x) \equiv \frac{\pi}{32} d^{3/2} \exp(-x) (1 + x) \left(1 + \frac{x^2}{d}\right)^2 \quad (22)$$

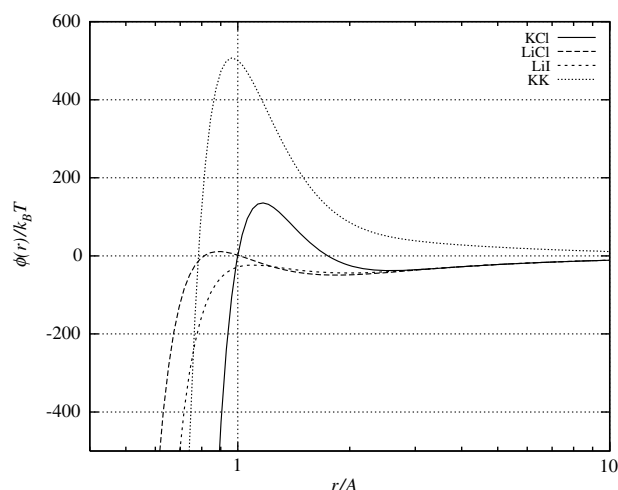
for all values of  $x$ , where  $x = bp$  and  $d = a^2 b^2$ . This inequality will hold if  $C$  is greater than the maximum of  $f(x)$  when  $x$  is positive. As  $f(0) = 1$  and  $f(x) \rightarrow 0$  as  $x \rightarrow \infty$  the maximum will occur either for a positive value of  $x$  or  $x = 0$ . The turning points of the function  $f(x)$  are at  $0, \pm\sqrt{di}$  and  $x_{\pm} = 2 \pm \sqrt{8 - d}$ . Therefore for  $d > 8$  stability is assured if  $C > 1$  as there are no real turning points. When  $d < 8$  there are two real turning points apart from  $x = 0$ . When  $d < 4$  only  $x_+$  is positive, and as  $x = 0$  is a minimum,  $x_+$  is a maximum and  $f(x_+) > 1$ . When  $4 < d < 8$ ,  $x = x_-$  is a minimum, and  $x = 0$  and  $x_+$  are maxima. Still we find that  $f(x_+) > 1$ . In fact,  $f(x_+)$  has a minimum value of 1.781 at  $d = 4.791$ . Hence, when  $d < 8$  the maximum value of  $f(x)$  is  $f(x_+)$  and stability is assured if  $C > f(x_+)$ . Also when  $d < 8$  there is a range of parameters where  $1 < C < f(x_+)$  and our criteria have not determined whether the system is stable or unstable.

Incidentally, the turning points of the E6 potential itself (i.e. equation (19) with  $b = 0$ ) are found by solving  $r = 1 + (7/a) \ln(r)$ , which gives  $r = -(7/a) \text{LambertW}(-a \exp(-a/7)/7)$ . The solutions are  $r = 0.2374$  (maximum) and  $r = 1$ , the potential minimum. The maximum is a spurious feature of the potential form chosen and, unlike the minimum, has no physical significance. That unstable behaviour does not tend to get reported in Metropolis Monte Carlo or molecular dynamics studies with this potential must be due to a high ‘activation’ barrier height between the potential wells at  $r = 0$  and the minimum at  $r = 1$ . The value of the potential at the maximum divided by minus the minimum value is 9373 for  $a = 13.2$  (a typical value, used in [17]), so the particles are very unlikely to come close enough to the maximum in any typical simulation length at normal temperatures.

The E6 potential is in a sense a prototype for the range of Born–Mayer–Huggins (BMH) potentials which have been used in many theoretical and simulation studies to represent alkali halide crystals and melts [18–20]. The BMH potential can be written compactly as,

$$\phi(r) = A_{\alpha\beta} \exp(-a_{\alpha\beta} r) + \frac{q_{\alpha} q_{\beta}}{r} - \frac{C_{\alpha\beta}}{r^6} - \frac{D_{\alpha\beta}}{r^8} \quad (23)$$

where  $q_{\alpha}$  is the charge on ion  $\alpha$ . The coefficients  $C_{\alpha\beta}$  and  $D_{\alpha\beta}$  are both positive and represent the dipole-induced dipole and dipole-induced quadrupole interactions between the ions. ( $C_{\alpha\beta}$



**Figure 6.** A plot of the  $\phi(r)/k_B T$ , where  $T = 1500$  K for  $K^+-Cl^-$ ,  $Li^+-Cl^-$  and  $K^+-K^+$  using the BMH potential [18, 19]. The energy barrier between the largest  $r$  or ‘secondary’ minimum and the (unphysical) potential maximum is 173, 60 and  $4 k_B T$  for KCl, LiCl and LiI, respectively.

and  $D_{\alpha\beta}$  for a given salt will be different for the three possible types of ion–ion interaction.) Because these terms dominate at short distances and diverge to  $-\infty$  as  $r$  tends to zero, this potential will ultimately lead to instability. Indeed by clustering the ions in a small volume, the total interaction energy,  $U(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$  is unbounded below and the system is unstable. Figure 6 shows  $\phi(r)/k_B T$ , where  $k_B$  is Boltzmann’s constant, at  $T = 1500$  K (a temperature at which all of these salts is molten), for  $K^+-Cl^-$ ,  $Li^+-Cl^-$ ,  $Li^+-I^-$  and  $K^+-K^+$  using the BMH potential [18, 19]. The energy difference between the largest  $r$  or ‘secondary’ minimum and the (unphysical) potential maximum is 173, 60 and  $4 k_B T$  for KCl, LiCl and LiI, respectively. Therefore in the case of the lithium salts there is a much greater probability of the ions crossing over the energy barrier between the two ‘minima’ in the potential. In fact in an MD simulation study of LiI by Lewis *et al* [21] it was observed that crystalline LiI at the experimental melting temperature and density was unstable with respect to the liquid. The authors may therefore have been observing a manifestation of the thermodynamic instability, even on a MD timescale, because of the unusually low activation barrier between the two energy minima (i.e. only  $4 k_B T$ ). In passing, we note that an interaction potential for alkali halides which will be stable is the Pauling form, where the short range repulsion is  $\sim r^{-12}$  (from corollary CT2) rather than an exponential [22]. For the same reason the restricted primitive model (‘RPM’) potential [23] where the repulsive core is a hard sphere is also stable. (The hard core can be obtained by taking the limit of  $n \rightarrow \infty$  for a repulsive  $r^{-n}$  potential.)

### 3. Conclusions

To conclude, we have considered the parameter range of stability (if any) of a range of interaction potential forms widely used for theory and computer modelling in the literature. We note as a preface to the following discussion, that if the potential is positive for all separations then it is automatically stable, irrespective of its analytic form. Therefore, for example, the generic effective potential between star polymers (which steeply rises for the centre of mass separation,  $r \rightarrow 0$  due to a logarithmic term), is stable [24]. For potentials which have positive

and negative regions, the analysis is more demanding, and Ruelle's criteria encapsulated in the theorems 1 and 2 discussed in the introduction are helpful, but, depending upon the way the potential is divided into two parts, we showed not always conclusive. Many of the potentials considered here can, with suitable choice of parameter values, fall into the 'soft-core' category where the potential is finite, even negative, at zero separation.

We have been able to decide the stability or instability of potentials which are the difference of two Gaussians or of two exponentials for all real positive values of their parameters. The parameter ranges of instability of the generalized separation-shifted Lennard-Jones and so-called SHRAT potential systems are established.

The widely used exponential-6 and Born–Mayer–Huggins alkali halide potentials are surprisingly 'unstable' irrespective of the chosen parameters, simply as a consequence of the separation dependence of the energy from the various terms in the formula. It might be asked, does this matter, if the barrier height between a spurious (unphysical) primary and secondary minimum is so large that in practice the transition from secondary to primary minima is not likely to be observed? It could be argued that most two-body potentials used for simulation are to an extent 'effective', and only designed to account for the physical properties generated from sampling over a limited distance range of the potential, especially where the molecules do not get too close. Therefore, this feature of the potential and its statistical mechanics may not be of serious practical consequence. Nevertheless it must be borne in mind that strictly speaking a metastable system will be modelled with such a potential, solely because of the potential form rather than because of the location of the modelled state point on the phase diagram. Indeed, a phase diagram for such a potential cannot be defined as neither can the chemical potential. Problems will also arise if a non-Boltzmann factor weighted Monte Carlo technique (e.g. [25, 26]) is used with such an unstable potential because essentially all of phase space is visited by these methods, which in practice is not the case with the Metropolis MC and MD techniques. The spurious primary minimum in some of the potentials investigated here will feature more in the sampling procedure, and dominate the distribution of states so that convergence to a 'normal' thermodynamic state will not be achieved. Of course it is always possible to ensure that a model potential will lead eventually to stability by giving it a strongly repulsive finite hard core which is insignificant at the distances of physical interest.

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