



The phonon theory of liquid thermodynamics

D. Bolmatov¹, V. V. Brazhkin² & K. Trachenko^{1,3}

¹School of Physics and Astronomy, Queen Mary University of London, Mile End Road, London, E1 4NS, UK, ²Institute for High Pressure Physics, RAS, 142190, Troitsk, Moscow Region, Russia, ³South East Physics Network.

Heat capacity of matter is considered to be its most important property because it holds information about system's degrees of freedom as well as the regime in which the system operates, classical or quantum. Heat capacity is well understood in gases and solids but not in the third main state of matter, liquids, and is not discussed in physics textbooks as a result. The perceived difficulty is that interactions in a liquid are both strong and system-specific, implying that the energy strongly depends on the liquid type and that, therefore, liquid energy can not be calculated in general form. Here, we develop a phonon theory of liquids where this problem is avoided. The theory covers both classical and quantum regimes. We demonstrate good agreement of calculated and experimental heat capacity of 21 liquids, including noble, metallic, molecular and hydrogen-bonded network liquids in a wide range of temperature and pressure.

Research into liquids has a long history starting from the same time when the theory of gases was developed, forming the basis for our current understanding of the gas state of matter¹. Yet no theory of liquid heat capacity currently exists, contrary to gases or, for that matter, solids. Consequently, liquid heat capacity is not discussed in textbooks^{1–6}, and presents a challenge at student lectures⁷.

Liquids defy common approaches used to discuss the other two main states of matter, gases and solids. Interactions in a liquid are strong, therefore treating them as a small perturbation as is done in the theory of gases is not an option². Atomic displacements in a liquid are large, therefore expanding the energy in terms of squared atomic displacements and considering the remaining terms small, as is done in the theory of solids, does not appear justified either. Strong interactions in a liquid appear to result in liquid energy being strongly dependent on the type of interactions, leading to a statement that liquid energy can not be calculated in general form², in contrast to solids and gases where $E = 3NT$ ($k_B = 1$) and $E = \frac{3}{2}NT$ at high temperature.

Previous research into liquids presents an interesting case when long-lived absence of crucial experimental data resulted in using our human experience and intuition about liquids instead. Liquids have been viewed to occupy a state intermediate between gases and solids. Liquids flow, and share this fundamental property with gases rather than solids. As a result, liquids were mostly viewed as interacting gases, forming the basis for previous theoretical approaches^{1–6}. On the other hand, Frenkel noted that the density of liquids is only slightly different from that of solids, but is vastly different from gas densities¹. Frenkel has subsequently made another important proposition which has further put liquids closer to solids in terms of their physical properties. He introduced liquid relaxation time, τ , as the average time between two consecutive atomic jumps at one point in space, and immediately predicted the solid-like ability of liquids to support shear waves, with the only difference that a liquid does not support all shear waves as a solid does, but only those with frequency larger than $\frac{1}{\tau}$ because the liquid structure remains unaltered and solid-like during times shorter than τ . Frenkel's ideas did not find due support at his time, partly because of the then existing dominating school of thought advocating different views⁸, and consequently were not theoretically developed.

It took many years to verify Frenkel's prediction^{9–13}. With the aid of powerful synchrotron radiation sources that became available fairly recently, and about 50 years after Frenkel's work, it has become apparent that even low-viscous liquids maintain high-frequency modes with wavelengths close to interatomic separations¹³. We note that being the eigenstates of topologically disordered liquids, these modes are phonon-like in a sense that they are not entirely harmonic vibrations as in crystals.

The data from the experimental advances above, together with theoretical understanding of the phonon states in a liquid due to Frenkel, raise an important question of whether the phonon theory of liquid thermodynamics

SUBJECT AREAS:

THEORETICAL PHYSICS

CONDENSED MATTER PHYSICS

STATISTICAL PHYSICS,
THERMODYNAMICS AND
NONLINEAR DYNAMICS

CHEMICAL PHYSICS

Received
16 April 2012

Accepted
11 May 2012

Published
24 May 2012

Correspondence and
requests for materials
should be addressed to
D.B. (d.bolmatov@
qmul.ac.uk)

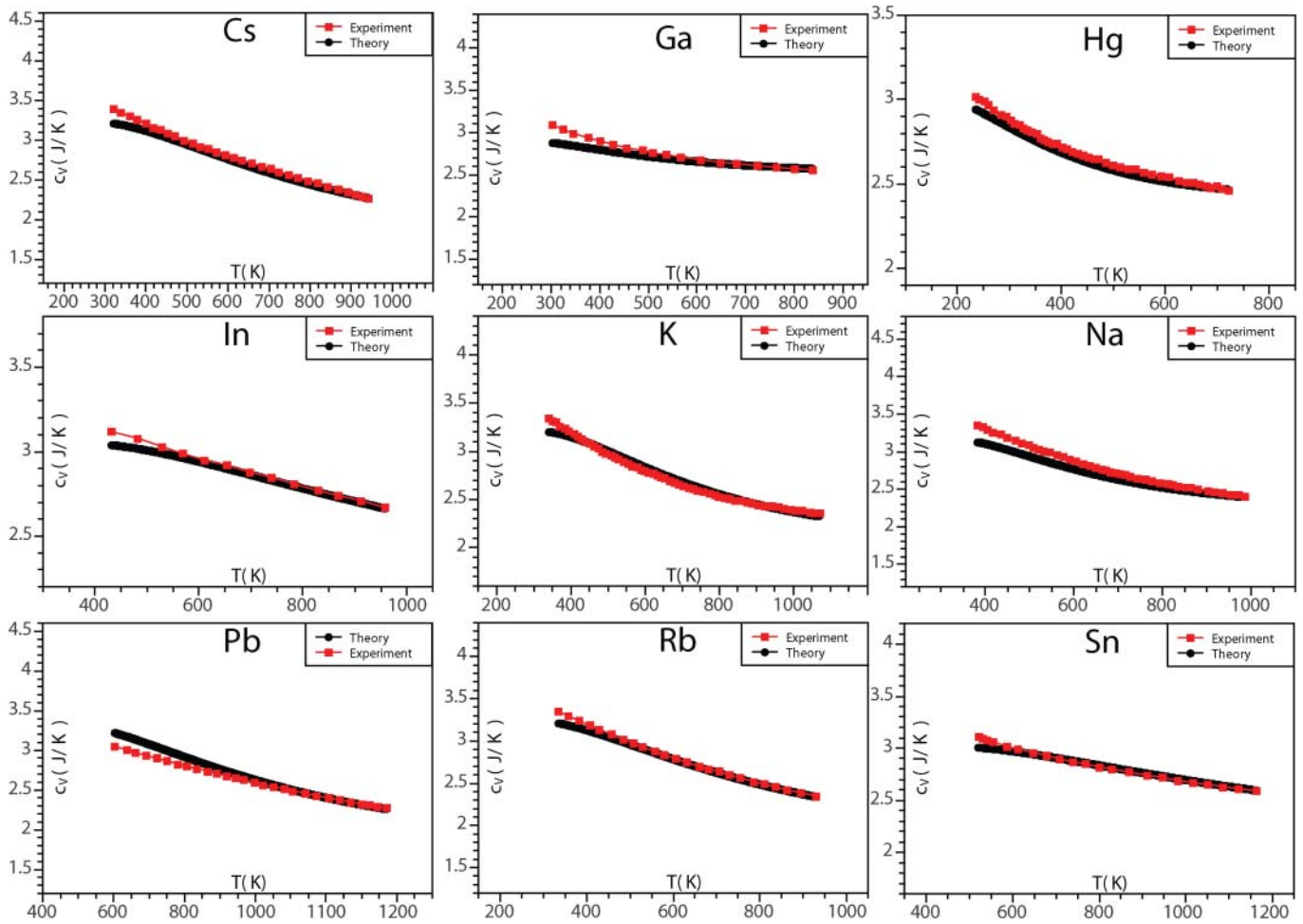


Figure 1 | Experimental and calculated c_v for liquid metals. Experimental c_v are at ambient pressure, with electronic contribution subtracted^{18,19}. Values of τ_D used in the calculation are 0.95 ps (Cs), 0.27 ps (Ga), 0.49 ps (Hg), 0.31 ps (In), 0.57 ps (K), 0.42 ps (Na), 0.64 ps (Pb), 0.74 ps (Rb) and 0.18 ps (Sn). Values of G_∞ are 0.17 GPa (Cs), 2.39 GPa (Ga), 1.31 GPa (Hg), 1.58 GPa (In), 1.8 GPa (K), 3.6 GPa (Na), 1.42 GPa (Pb), 0.25 GPa (Rb) and 3 GPa (Sn). Experimental α (Ref.¹⁹) are $3 \cdot 10^{-4} \text{ K}^{-1}$ (Cs), $1.2 \cdot 10^{-4} \text{ K}^{-1}$ (Ga), $1.8 \cdot 10^{-4} \text{ K}^{-1}$ (Hg), $1.11 \cdot 10^{-4} \text{ K}^{-1}$ (In), $2.9 \cdot 10^{-4} \text{ K}^{-1}$ (K), $2.57 \cdot 10^{-4} \text{ K}^{-1}$ (Na), $3 \cdot 10^{-4} \text{ K}^{-1}$ (Pb), $3 \cdot 10^{-4} \text{ K}^{-1}$ (Rb) and $0.87 \cdot 10^{-4} \text{ K}^{-1}$ (Sn). Values of α used in the calculation are $3.8 \cdot 10^{-4} \text{ K}^{-1}$ (Cs), $1.2 \cdot 10^{-4} \text{ K}^{-1}$ (Ga), $1.6 \cdot 10^{-4} \text{ K}^{-1}$ (Hg), $1.25 \cdot 10^{-4} \text{ K}^{-1}$ (In), $2.9 \cdot 10^{-4} \text{ K}^{-1}$ (K), $2.57 \cdot 10^{-4} \text{ K}^{-1}$ (Na), $3 \cdot 10^{-4} \text{ K}^{-1}$ (Pb), $4.5 \cdot 10^{-4} \text{ K}^{-1}$ (Rb) and $1.11 \cdot 10^{-4} \text{ K}^{-1}$ (Sn).

could be constructed, similar to the phonon theory of solids. Below we develop a phonon theory of thermodynamics of liquids that covers both classical and quantum regimes. We find good agreement between calculated and experimental heat capacity for many liquids in a wide temperature and pressure range.

Results

Theory. There are two types of atomic motion in a liquid: phonon motion that consists of one longitudinal mode and two transverse modes with frequency $\omega > \omega_F$, where $\omega_F = \frac{2\pi}{\tau}$ is Frenkel frequency, and the diffusional motion due to an atom jumping between two equilibrium positions. In turn, the phonon and diffusional motion consists of kinetic and potential parts, giving the liquid energy as

$$E = K_l + P_l + K_s(\omega > \omega_F) + P_s(\omega > \omega_F) + K_d + P_d \quad (1)$$

where K_l and P_l are kinetic and potential components of the longitudinal phonon energy, $K_s(\omega > \omega_F)$ and $P_s(\omega > \omega_F)$ are kinetic and potential components of the energy of shear phonons with frequency $\omega > \omega_F$, and K_d and P_d are kinetic and potential energy of diffusing atoms. The energy of longitudinal mode is the same as in a solid, albeit different dissipation laws apply at low and

high frequency¹. In the next paragraph, we re-write E in the form convenient for subsequent calculations.

P_d can be omitted because $P_d \ll P_s(\omega > \omega_F)$. This is because the absence of shear modes with frequency $\omega < \omega_F$ due to the dynamic Frenkel mechanism implies smallness of low-frequency restoring forces and therefore smallness of low-frequency potential energy of shear modes: $P_s(\omega < \omega_F) \ll P_s(\omega > \omega_F)$, where $P_s(\omega < \omega_F)$ is the potential energy of low-frequency shear modes^{14,15}. Instead of low-frequency shear vibrations with potential energy $P_s(\omega < \omega_F)$, atoms in a liquid “slip” and undergo diffusing motions with frequency $\frac{2\pi}{\tau}$ and associated potential energy P_d . P_d is due to the same interatomic forces that $P_s(\omega < \omega_F)$, giving $P_d \approx P_s(\omega < \omega_F)$. Combining this with $P_s(\omega < \omega_F) \ll P_s(\omega > \omega_F)$, $P_d \ll P_s(\omega > \omega_F)$ follows. Re-phrasing this, were P_d large and comparable to $P_s(\omega > \omega_F)$, strong restoring forces at low frequency would result, and lead to the existence of low-frequency vibrations instead of diffusion. We also note that because $P_l \approx P_s$, $P_d \ll P_s(\omega > \omega_F)$ gives $P_d \ll P_l$, further implying that P_d can be omitted in Eq. (1).

Then, $E = K + P_l + P_s(\omega > \omega_F)$, where total kinetic energy in a liquid, K ($K = \frac{3}{2} N k_B T$ in the classical case), includes both vibrational

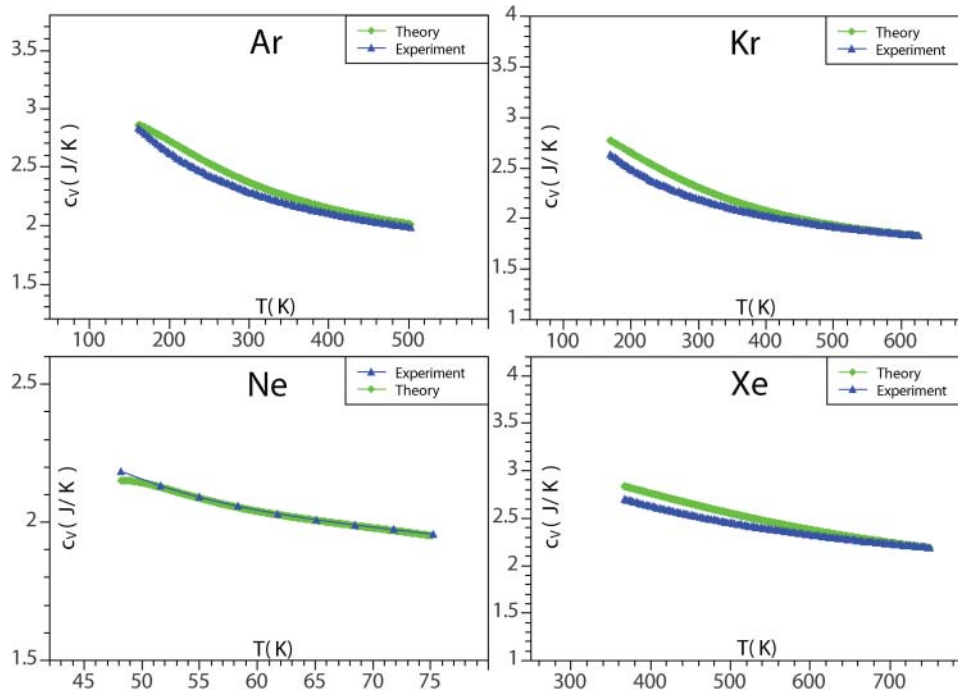


Figure 2 | Experimental and calculated c_v for noble liquids. Experimental c_v and η are taken from the NIST database¹⁷ at pressures 378 MPa (Ar), 200 MPa (Kr), 70 MPa (Ne), and 700 MPa (Xe). Values of τ_D used in the calculation are 0.5 ps (Ar), 0.67 ps (Kr), 0.31 ps (Ne) and 0.76 ps (Xe). Values of G_∞ are 0.18 GPa (Ar), 0.23 GPa (Kr), 0.12 GPa (Ne) and 0.45 GPa (Xe). Experimental values of α calculated from the NIST database at the corresponding pressures above are $3.6 \cdot 10^{-4} \text{ K}^{-1}$ (Kr), $7.7 \cdot 10^{-3} \text{ K}^{-1}$ (Ne) and $4.1 \cdot 10^{-4} \text{ K}^{-1}$ (Xe). Values of α used in the calculation are $1.3 \cdot 10^{-3} \text{ K}^{-1}$ (Kr), $6.8 \cdot 10^{-3} \text{ K}^{-1}$ (Ne) and $3.6 \cdot 10^{-4} \text{ K}^{-1}$ (Xe). For Ar, calculating c_v in harmonic approximation ($\alpha = 0$) gives good agreement with experimental c_v .

and diffusional components. E can be re-written using the virial theorem $P_l = \frac{E_l}{2}$ and $P_s(\omega > \omega_F) = \frac{E_s(\omega > \omega_F)}{2}$ (here, P and E refer to their average values) and by additionally noting that K is equal to kinetic energy of a solid and can therefore be written, using the virial theorem, as the sum of kinetic terms related to longitudinal and shear waves: $K = \frac{E_l}{2} + \frac{E_s}{2}$, giving $E = E_l + \frac{E_s}{2} + \frac{E_s(\omega > \omega_F)}{2}$. Finally noting that $E_s = E_s(\omega < \omega_F) + E_s(\omega > \omega_F)$, where the two terms refer to their solid-state values, liquid energy becomes

$$E = E_l + E_s(\omega > \omega_F) + \frac{E_s(\omega < \omega_F)}{2} \quad (2)$$

Each term in Eq. (2) can be calculated using the phonon free energy, $F_{ph} = E_0 + T \sum_i \ln \left(1 - \exp \left(-\frac{\hbar \omega_i}{T} \right) \right)$, where E_0 is the energy of zero-point vibrations². In calculating the energy, $E_{ph} = F_{ph} - T \frac{dF_{ph}}{dT}$, we take into account the effect of thermal expansion, important in liquids. This implies $\frac{d\omega_i}{dT} \neq 0$, contrary to the harmonic case, and gives

$$E_{ph} = E_0 + \hbar \sum_i \frac{\omega_i - T \frac{d\omega_i}{dT}}{\exp \left(\frac{\hbar \omega_i}{T} \right) - 1} \quad (3)$$

Using quasi-harmonic approximation Grüneisen approximation gives $\frac{d\omega}{dT} = -\frac{\alpha \omega}{2}$, where α is the coefficient of thermal expansion¹⁶. Putting it in Eq. (3) gives

$$E_{ph} = E_0 + \left(1 + \frac{\alpha T}{2} \right) \sum_i \frac{\hbar \omega_i}{\exp \left(\frac{\hbar \omega_i}{T} \right) - 1} \quad (4)$$

The energy of one longitudinal mode, the first term in Eq. (2), can be calculated by substituting the sum in Eq. (4), Σ , with Debye vibrational density of states for longitudinal phonons, $g(\omega) = \frac{3N}{\omega_D^3} \omega^2$, where ω_D is Debye frequency. The normalization of $g(\omega)$ reflects the fact that the number of longitudinal modes is N . Integrating from 0 to ω_D gives $\Sigma = NTD \left(\frac{\hbar \omega_D}{T} \right)$, where

$D(x) = \frac{3}{x^3} \int_0^x \frac{z^3 dz}{\exp(z) - 1}$ is Debye function². The energy of two shear

modes with frequency $\omega > \omega_F$, the second term in Eq. (2), can be similarly calculated by substituting Σ with density of states $g(\omega) = \frac{6N}{\omega_D^3} \omega^2$, where the normalization accounts for the number of shear modes of $2N$. Integrating from ω_F to ω_D gives $\Sigma = 2NTD \left(\frac{\hbar \omega_D}{T} \right) - 2NT \left(\frac{\omega_F}{\omega_D} \right)^3 D \left(\frac{\hbar \omega_F}{T} \right)$. $E_s(\omega < \omega_F)$ in the last term in Eq. (2) is obtained by integrating Σ from 0 to ω_F with the same density of states, giving $\Sigma = 2NT \left(\frac{\omega_F}{\omega_D} \right)^3 D \left(\frac{\hbar \omega_F}{T} \right)$. Putting all terms in Eq. (4) and then Eq. (2) gives finally the liquid energy

$$E = NT \left(1 + \frac{\alpha T}{2} \right) \left(3D \left(\frac{\hbar \omega_D}{T} \right) - \left(\frac{\omega_F}{\omega_D} \right)^3 D \left(\frac{\hbar \omega_F}{T} \right) \right) \quad (5)$$

where we have omitted zero-point vibration energy E_0 because below we calculate the derivative of E . We note that in general, E_0 is temperature-dependent because it is a function of ω_F and τ (see Eq. (2)).

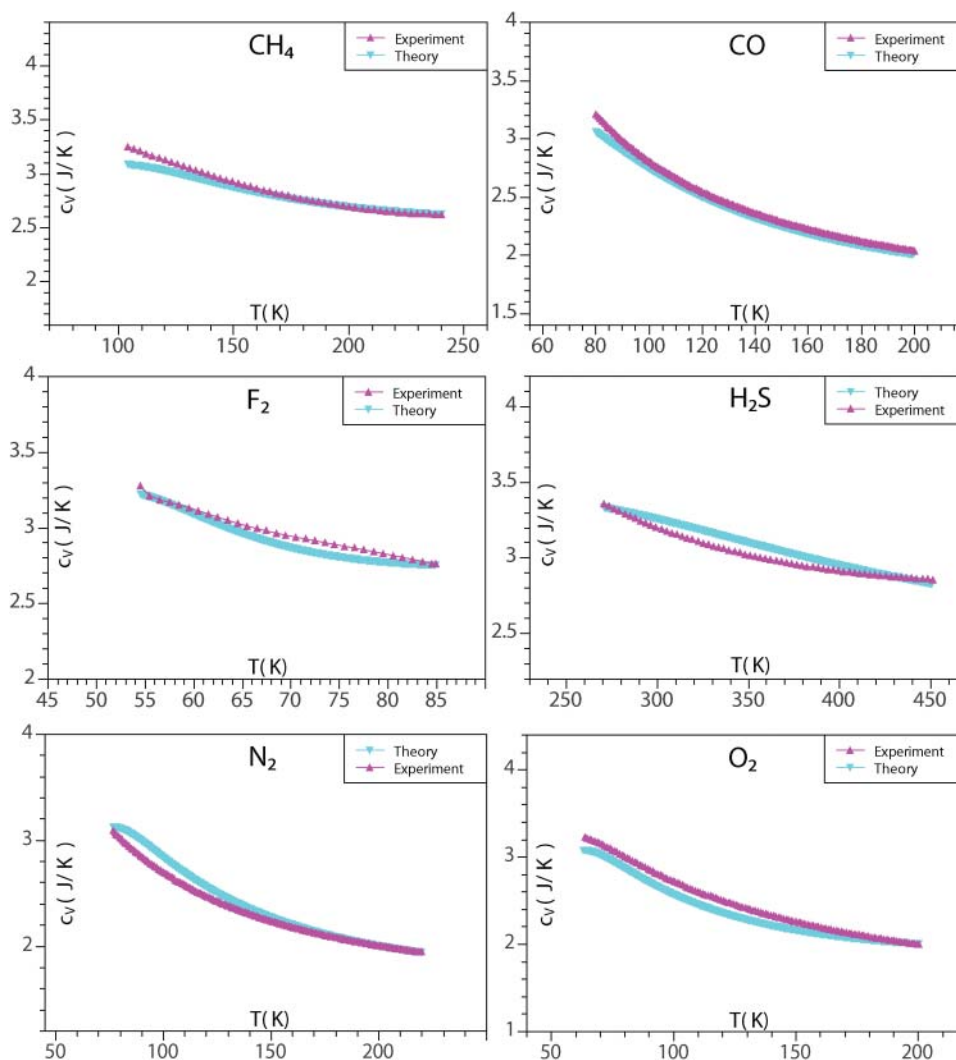


Figure 3 | Experimental and calculated c_v for molecular liquids. Experimental c_v and η are taken from the NIST database¹⁷ at pressures 50 MPa (CH_4), 55 MPa (CO), 0.1 MPa (F_2), and 170 MPa (H_2S), 65 MPa (N_2) and 45 MPa (O_2). Experimental c_v has the rotational contribution subtracted (see text). Experimental η for F_2 is from Ref.²⁶. Values of τ_D used in the calculation are 0.44 ps (CH_4), 0.55 ps (CO), 0.71 ps (F_2), 0.65 ps (H_2S), 0.38 ps (N_2) and 0.46 ps (O_2). Values of G_∞ are 0.1 GPa (CH_4), 0.11 GPa (CO), 0.23 GPa (F_2), 0.15 GPa (H_2S), 0.14 GPa (N_2) and 0.22 GPa (O_2). Experimental values of α calculated from the NIST database at the corresponding pressures above are $3.1 \cdot 10^{-3} \text{ K}^{-1}$ (CH_4), $4.1 \cdot 10^{-3} \text{ K}^{-1}$ (CO), $4.31 \cdot 10^{-3} \text{ K}^{-1}$ (F_2), $1.2 \cdot 10^{-3} \text{ K}^{-1}$ (H_2S), $3.9 \cdot 10^{-3} \text{ K}^{-1}$ (N_2) and $4.4 \cdot 10^{-3} \text{ K}^{-1}$ (O_2). Values of α used in the calculation are $1.4 \cdot 10^{-3} \text{ K}^{-1}$ (CH_4), $5.5 \cdot 10^{-3} \text{ K}^{-1}$ (CO), $4.31 \cdot 10^{-3} \text{ K}^{-1}$ (F_2), $6.5 \cdot 10^{-4} \text{ K}^{-1}$ (H_2S), $3.9 \cdot 10^{-3} \text{ K}^{-1}$ (N_2) and $4.4 \cdot 10^{-3} \text{ K}^{-1}$ (O_2).

However, this becomes important at temperatures of several K only, whereas below we deal with significantly higher temperatures.

Eq. (5) spans both classical and quantum regimes, an important feature for describing the behavior of liquids discussed below.

We note that the presented phonon theory of liquids operates at the same level of approximation as Debye theory of solids, particularly relevant for disordered isotropic systems² such as glasses and liquids. The result for a harmonic solid follows from Eq. (5) when $\omega_F = 0$, corresponding to infinite relaxation time, and $\alpha = 0$.

Comparison with experimental data. We now compare Eq. (5) to the experimental data of heat capacity. We have used the National Institute of Standards and Technology (NIST) database¹⁷ that contains c_v for many liquids, and have chosen monatomic noble liquids, molecular liquids, as well as hydrogen-bonded network liquids. We have used c_v measured on isobars. We aimed to check our theoretical predictions in a wide range of temperature, and therefore selected the data at pressures exceeding the critical pressures of the above systems where they exist in a liquid form in the broad temperature range. As a result, the temperature range in

which we calculate c_v is about 100–700 K for various liquids (see Figures 1, 2, 3 and 4). Experimental c_v of metallic liquids were taken from Refs.^{18,19} at ambient pressure. We note that previously, we have considered c_v of some of these metals on the basis classical approach only¹⁴. The total number of liquids considered is 21.

We numerically evaluated Debye functions in Eq. (5) for each temperature and calculated $c_v = \frac{1}{N} \frac{dE}{dT}$. We have taken viscosity data from the NIST database at the same pressures as c_v and converted it to τ using the Maxwell relationship $\tau = \frac{\eta}{G_\infty}$, where η is viscosity and G_∞ is infinite-frequency shear modulus, giving $\omega_F = \frac{2\pi}{\tau} = \frac{2\pi G_\infty}{\tau}$. Viscosities of liquid metals and F_2 were taken from Refs.^{20–25} and Ref.²⁶, respectively.

We note that Debye model is not a good approximation in molecular and hydrogen-bonded systems where the frequency of intra-molecular vibrations considerably exceeds the rest of frequencies in the system (e.g. 2260 K in O_2 , 3340 K in N_2 , 3572 K in CO). However, the intra-molecular modes are not excited in the temperature range of experimental c_v (see Figures 3–4). Therefore,

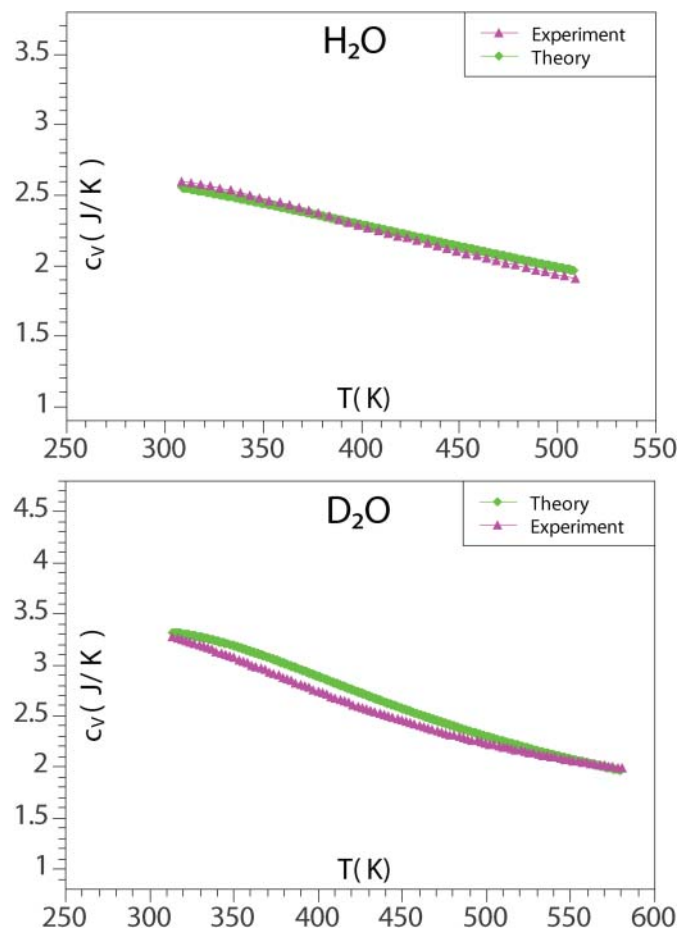


Figure 4 | Experimental and calculated c_v for H_2O and D_2O . Experimental c_v and η are taken from the NIST database¹⁷ at pressures 150 MPa (H_2O) and 80 MPa (D_2O). Experimental c_v has rotational and configurational contribution subtracted (see text). Values of τ_D used in the calculation are 0.15 ps (H_2O) and 0.53 ps (D_2O). For D_2O , experimental α calculated from the NIST database at the corresponding pressure above is $9.4 \cdot 10^{-4} \text{ K}^{-1}$, and α used in the calculation is $1.1 \cdot 10^{-3} \text{ K}^{-1}$. For H_2O , calculating c_v in harmonic approximation ($\alpha = 0$) gives good agreement with to experimental c_v .

the contribution of intra-molecular motion to c_v is purely rotational, c^{rot} . The rotational motion is excited in the considered temperature range, and is therefore classical, giving $c^{rot} = R$ for linear molecules such as CO, F_2 , N_2 and O_2 and $c^{rot} = \frac{3R}{2}$ for molecules with three rotation axes such as CH_4 , H_2S , H_2O and D_2O . Consequently, c_v for molecular liquids shown in Figures 3–4 correspond to heat capacities per molecule, with c^{rot} subtracted from the experimental data. In this case, N in Eq. (5) refers to the number of molecules.

We also note that in H_2O , approximately half of experimental c_v is the configurational contribution due to the temperature-induced structural modification of the hydrogen-bonded network, although the precise value of this contribution is not currently settled^{27,28}. The structural modification includes changing coordinations of H_2O molecules during the continuous transition between the low-density and high-density liquid in the wide temperature range²⁸. Similarly to the phonon theory of solids, effects of structural changes are not accounted for in the general theory presented here. Therefore, experimental c_v for H_2O and D_2O shows c_v with half subtracted from their values due to the configurational term and $c^{rot} = \frac{3R}{2}$ subtracted further as discussed above. Due to the approximate way in which the

configurational contribution is treated for H_2O and D_2O , the agreement between the experimental and calculated c_v should be viewed as qualitative, in contrast to the quantitative agreement for the rest of liquids considered. As for other molecular liquids above, the resulting c_v represents heat capacity per molecule.

Experimental and calculated c_v for 21 noble, metallic, molecular and hydrogen-bonded network liquids are shown in Figures 1–4. Figures 1–4 make one of the central points of our paper: the proposed phonon theory of liquids gives good agreement with experimental data. Importantly, calculated c_v has no free adjustable parameters, but depends on ω_D , α and G_∞ (see Eq. (5)) which are fixed by system properties. ω_D , α and G_∞ that give the best agreement in Figures 1–4 are close to their typical values. $\tau_D = \frac{2\pi}{\omega_D}$ used in the calculation (see the captions in Figures 1–4) are consistent with the known values that are typically in the 0.1–1 ps range^{11,29}. For monatomic liquids, τ_D were taken as experimental τ_D in corresponding solids. Similarly, the difference between experimental α and α used in the calculation is within 30% on average. Finally, G_∞ used in the calculation are on the order of GPa typically measured^{11,29}.

Discussion

We first note that some of the considered liquids are in the quantum regime at low temperature. Taking T as the lowest temperature in Figures 1–4 and $\omega_D = \frac{2\pi}{\tau_D}$, where τ_D are given in the captions of Figures 1–4, we find that $\frac{\hbar\omega_D}{T}$ is in the range 0.1–3 for various liquids. Consequently, some liquids can be described by classical approximation fairly well, whereas others require quantum approach: for example, $\frac{\hbar\omega_D}{T} > 1$ for Ne, O_2 , N_2 , F_2 , CH_4 and CO, implying progressive phonon excitation with temperature increase.

We observe that c_v decreases with temperature in Figures 1–4. There are two main competing effects that contribute to c_v in Eq. (5). First, temperature increase results in the increase of $\omega_F = \frac{2\pi}{\tau}$. Consequently, c_v decreases as a result of the decreasing number of shear waves that contribute to liquid energy and c_v . Second, c_v increases with temperature due to progressive phonon excitation as discussed above. The first effect dominates in the considered temperature range, and the net effect is the decrease of c_v with temperature seen in Figure 1.

We further observe that c_v changes from approximately 3 to 2, showing a universal trend across a wide range of liquids. This can be understood by noting that at low temperature, $\left(\frac{\omega_F}{\omega_D}\right)^3$ and the second term in the last bracket in Eq. (5) are small, giving c_v close to 3 (including the contribution from the anharmonic term). At high temperature when $\omega_F \approx \omega_D$ and Debye functions are close to 1, the term in the second bracket in Eq. (5) is 2, giving $c_v \approx 2$.

We note that on further temperature increase, c_v decreases from 2 to its gas value of 1.5¹⁷. This is related to the progressive disappearance of longitudinal phonons, an effect discussed in our forthcoming paper.

The decrease of c_v seen in Figures 1–4 does not need to be generic. Indeed, when the phonon excitation dominates at low temperature, as in the case of strongly quantum liquids such as H_2 or He, c_v increases with temperature¹⁷.

Good agreement between theoretical and calculated c_v makes several important points. First, it is interesting to revisit the statement that liquid energy can not be calculated in general form because interactions are both strong and system-specific². In the proposed phonon theory of liquids, this difficulty does not arise because strong interactions are treated from the outset as in the theory of solids.

Second, the proposed phonon theory of liquids has an advantage over the previous approach where liquid potential energy is



calculated from correlation functions and interatomic interactions^{2,3}. Starting from the earlier proposals³⁰, this approach was developed in several directions (see, e.g., Refs.^{2,3,31–34}), and can be used to calculate the energy of simple liquids where interactions are pair and short-ranged and correlations are two-body as is the case in, for example, noble liquids or hard-sphere models. On the other hand, the calculations become intractable in general case^{3,33}, particularly when interactions and correlations become complex (e.g., many-body) as in the liquids discussed above, precluding the calculation of c_v and, consequently, understanding and interpreting experimental data. On the other hand, if the phonon states of the liquid depend on τ only as proposed by Frenkel¹, the liquid energy and c_v depend implicitly on τ only, even though correlation functions and interatomic interactions may affect both c_v and τ in a complex way. Then, the relationship between c_v and τ becomes fairly simple (see Eq. (5)) and explains the experimental behavior of a wide class of liquids, both simple and complex.

The last assertion is important for a general outlook at liquids: despite their apparent complexity, understanding their thermodynamics may be easier than previously thought. Indeed, we have good understanding of solid thermodynamics based on phonons no matter how complicated interactions or structural correlations in a solid are. Our current results suggest that the same can apply to liquids.

- Frenkel, J. *Kinetic Theory of Liquids* (ed. R. H. Fowler, P. Kapitza, N. F. Mott, Oxford University Press, 1947).
- Landau, L. D. & Lifshitz, E. M. *Statistical Physics* (Nauka, Moscow 1964).
- March, N. H. *Liquid Metals* (Cambridge University Press, Cambridge, UK, 1990).
- Ziman, J. M. *Models of Disorder* (Cambridge University Press, Cambridge, UK, 1979).
- Barrat, J. L. & Hansen, J. P. *Basic Concepts for Simple and Complex Liquids* (Cambridge University Press, Cambridge, 2003).
- Hansen, J. P. & McDonald, I. R. *Theory of Simple Liquids* (Amsterdam, Boston, Elsevier, 2007).
- Granato, A. V. J. The specific heat of simple liquids. *J. Non-Cryst. Sol.* **307–310**, 376–386 (2002).
- A. A. Abrikosov (private communication).
- Copley, J. R. D. & Rowe, J. M. Short-wavelength collective excitations in liquid rubidium observed by coherent neutron scattering. *Phys. Rev. Lett.* **32**, 49–52 (1974).
- Grimsditch, M., Bhadra, R. & Torell, L. M. Shear waves through the glass-liquid transformation. *Phys. Rev. Lett.* **62**, 2616 (1989).
- Pilgrim, W. C., Hosokawa, S., Saggau, H., Sinn, H. & Burkel, E. Temperature dependence of collective modes in liquid sodium. *J. Non-Cryst. Sol.* **250–252**, 96–101 (1999).
- Burkel, E. Phonon spectroscopy by inelastic x-ray scattering. *Rep. Prog. Phys.* **63**, 171–232 (2000).
- Pilgrim, W. C. & Morkel, C. State dependent particle dynamics in liquid alkali metals. *J. Phys.: Cond. Matt* **18**, R585–R633 (2006).
- Bolmatov, D. & Trachenko, K. Liquid heat capacity in the approach from the solid state: Anharmonic theory. *Phys. Rev. B* **84**, 054106 (2011).
- Trachenko, K. Heat capacity of liquids: An approach from the solid phase. *Phys. Rev. B* **78**, 104201 (2008).
- Trachenko, K. & Brazhkin, V. V. Heat capacity at the glass transition. *Phys. Rev. B* **83**, 014201 (2011).
- <http://webbook.nist.gov/chemistry/fluid>.
- Grimvall, G. The Heat Capacity of Liquid Metals. *Phys. Scr.* **11**, 381 (1975).
- Wallace, D. C. Liquid dynamics theory of high-temperature specific heat. *Phys. Rev. E* **57**, 1717 (1998).
- Carlson, C. M., Eyring, H. & Ree. Significant Structures in Liquids, V. Thermodynamic and Transport Properties of Molten Metals. T. *Proc. Natl. Acad. Sci. USA* **46**, 649 (1960).
- Andrade, E. N. da C. & Dobbs, E. R. The Viscosities of Liquid Lithium, Rubidium and Caesium. *Proc. R. Soc. London, Ser. A* **211**, 12 (1952).
- Culpin, M. F. The Viscosity of Liquid Indium and Liquid Tin. *Proc. Phys. Soc. B* **70**, 1069 (1957).
- Spells, K. E. The determination of the viscosity of liquid gallium over an extended range of temperature. *Proc. Phys. Soc.* **48**, 299 (1936).
- Grosse, A. V. Viscosities of Liquid Sodium and Potassium, from Their Melting Points to Their Critical Points. *Science* **147**, 1438 (1965).
- Kanda, F. A. & Colburn, R. P. The Absolute Viscosity of Some Lead-Tin Alloys. *Physics and Chemistry of Liquids* **1**, 159 (1968).
- Elverum, G. W. & Doescher, R. N. Physical Properties of Liquid Fluorine. *J. Chem. Phys.* **20**, 1834 (1952).
- Eisenberg, D. & Kauzmann, W. *The structure and properties of water* (Oxford University Press, 2005).
- Mishima, O. & Stanley, H. E. The relationship between liquid, supercooled and glassy water. *Nature* **396**, 329 (1998).
- Bodensteiner, T., Morkel, Chr., Gläser, W. & Dorner, B. Collective dynamics in liquid cesium near the melting point. *Phys. Rev. A* **45**, 5709 (1992).
- Born, M. & Green, H. S. A General Kinetic Theory of Liquids. I. The Molecular Distribution Functions. *Proc. Royal Soc. London A* **188**, 10–18 (1946).
- Lebowitz, J. L. & Percus, J. K. Statistical Thermodynamics of Nonuniform Fluids. *J. Math. Phys.* **4**, 116 (1963).
- Curtin, W. A. & Ashcroft, N. W. Weighted-density-functional theory of inhomogeneous liquids and the freezing transition. *Phys. Rev. A* **32**, 2909 (1985).
- Rosenfeld, Y. High-density properties of integral-equation theories of fluids: Universal analytic structure and details for the one-component plasma. *Phys. Rev. A* **33**, 2025 (1986).
- Bolmatov, D. Equations of State for Simple Liquids from the Gaussian Equivalent Representation Method. *J. Stat. Phys.* **137**, 765–773 (2009).

Acknowledgements

We are grateful to A. A. Abrikosov, M. T. Dove, A. Michaelides and J. C. Phillips for discussions. D. Bolmatov thanks Myerscough Bequest and K. Trachenko thanks EPSRC for financial support.

Author contributions

All authors have contributed equally to this work.

Additional information

Competing financial interests: The authors declare no competing financial interests.

License: This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 Unported License. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-sa/3.0/>

How to cite this article: Bolmatov, D., Brazhkin, V.V. & Trachenko, K. The phonon theory of liquid thermodynamics. *Sci. Rep.* **2**, 421; DOI:10.1038/srep00421 (2012).