Phonons in Rare-Gas Condensates and the Law of Corresponding States

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We have shown previously that the longitudinal phonon dispersion curves of some amorphous solids and simple liquids are of phonon-roton type as observed in Liq.He. Such a behaviour seems to exist also in liquid metals. The purpose of the present note is to discuss the longitudinal phonons in liquid Ne, Kr and Xe, from the viewpoint of the law of corresponding state (LCS) and to present some predictions about the dispersion curves. This may be of value since experimental investigations of phonons of these liquids are quite scarce.

Consider systems which are described by the same type of pair potentials \( \phi(r) = \varepsilon f(r/\alpha) \), where \( \varepsilon \) and \( \alpha \) are system-dependent constants having dimensions of energy and length, respectively. If we scale various variables with \( \varepsilon, \alpha \) and atomic mass \( M \), in such a way that all the variables become dimensionless (for example \( r^* = r/\alpha, A^* = h/\sqrt{\varepsilon M a^2} \)), the Hamiltonian becomes

\[
H^* = \sum_i p_i^2/2 + \sum_{i<j} f(r^*_{ij})
\]

in the classical case, and

\[
H^* = -A^* \frac{\hbar}{2} \sum_i \sum_{j<k} p_i^j p_k^j + \sum_{i<j} f(r^*_{ij})
\]

in the quantum-mechanical case. This
means that in the classical case all the relations between new reduced variables do not depend on $M$, $\varepsilon$ and $\alpha$, and in the quantum-mechanical case they depend on $A^*$ only. The reduced quantities pertaining to phonon dispersion curves are $\omega^* = \sqrt{M/\varepsilon} \alpha \omega$ (circular frequency), $k^* = \alpha k$ (wave vector), $T^* = k_B T/\varepsilon$ (temperature) and $\rho^* = \rho \alpha^2 = N/\nu^*$ (number density). It is shown that phonon dispersion curves themselves are given by the relation

$$\omega^*(k^*, \rho^*, T^*)$$

if the quantum effect can be neglected. This is the LCS for the phonon dispersion curves.*

Deviation from the LCS may come from the following origins:

(1) The systems cannot be described by pair potentials.

(2) There are deviations in the functional form of the pair potential, $f(r_{ij})$.

(3) Quantum effects.

Guggenheim (1948) has shown that for thermodynamical quantities the LCS is valid in a wide range. Rice (1968) has shown that for transport coefficients the LCS is valid for elements belonging to the same column in the periodic table. However, for quantities which reflect rather directly the microscopic structure of the systems under consideration, we cannot always expect that the LCS works well. For the phonon dispersion curves, however, we know some empirical results which support the validity of LCS. If we use the results of the semi-empirical theory of Gupta (1968) on FCC Ne, Ar, Kr and Xe at $T^* = P^* = 0$, and use the values of parameters used by de Boer, we can see that the LCS is valid except for Ne. Deviations from LCS in the case of Ne may be ascribed to the quantum effect. To find how to handle the quantum effect, let us see Fig. 1, which shows $\omega_{\text{max}}^*(A^*)$ and $V_a^*(A^*)$ (atomic volume) including He$^4$ and He$^3$. Although He$^4$ and He$^3$ have crystal structures different from others and are obviously not in corresponding states, $\omega_{\text{max}}^*$ and $V_a^*$ are seen to be monotone functions of $A^*$. It has been found that some other quantities pertaining to phonons are monotone functions of $A^*$. These circumstances are already seen for several other quantities.  

Fig. 1. Maximum frequencies of phonons and atomic volumes of rare-gas solids. Points $+$, $\bullet$, $\triangle$, $\square$ and $\times$ represent the values of He$^3$, He$^4$, Ne, Ar, Kr and Xe, respectively. Signs 1 and 2 show that values of $\omega_{\text{max}}^*$ correspond to that of $V_a^*$ of the same sign.

Now let us apply the LCS to the rare-gas liquids. Phonon dispersion curves have been obtained experimentally only for He$^4$ and Ar$^7$. The measurements were done under the conditions, $T^* = 0.79$ (94 K), $P^* = 4.7 \times 10^{-3}$, $V_a^* = 1$ for Ar and $T^* = 0.11$ (1.1 K), $P^* = 5.5 \times 10^{-6}$, $V_a^* = 2.1$ for He$^4$. Roughly we may suppose that these are in corresponding states. But if we plot the dispersion curves, we find that the LCS is not valid at all (Fig. 2). To remedy this we consider the values of $\omega^*$

*) A similar idea has been used by Horton and Leech (1963). However, $k^*$ defined by them is different from ours and their method does not seem to be useful in discussing quantum effects.
Fig. 2. Longitudinal phonon dispersion curves of rare-gas liquids.

and \( k^* \) at the first peak, the first minimum and the second peak of the dispersion curves, which are \((20.5, 3.75)\), \((6.92, 6.65)\) and \((17.2, 10.2)\) for \(\text{Ar} \) and \((3.19, 2.85)\), \((1.98, 4.92)\) and \((4.01, 6.84)\) for \(\text{He}^4 \). The facts mentioned above that the longitudinal phonon dispersion curves of the rare-gas liquids are of phonon-roton type, and that some quantities associated with phonons are monotone functions of \( A^* \), suggest that also these quantities are monotone functions of \( A^* \). Here let us adopt the hypothesis that these \((\omega^*, k^*)\) of the first peak, etc. are linear functions of \( A^* \). In this way we obtain the estimates for \(\text{Ne}, \text{Kr} \) and \(\text{Xe} \) as shown in the Table.

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Table I. Estimated values of \((\omega, k)\) for \(\text{Ne}, \text{Kr} \) and \(\text{Xe} \). Values of \(\omega, k, T \) and \( P \) are measured by the units \(10^{12}\text{s}^{-1}, 10^8\text{cm}^{-1}, \text{°K}, \) and \(10^6\text{dyn cm}^{-2}\), respectively.

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2) J. de Boer, Physica **14** (1948), No. 2-3.