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PHYSICAL REVIEW A VOLUME 3, NUMBER 1 JANUARY 1971

Elastic Constants of bcc ^{3}He from Measurements of Sound Velocity, Debye Temperature, and Compressibility

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In single crystals with the large anisotropy of bcc ^{3}He the wave vector of a sound wave deviates as much as 60° from the direction of energy flow. This effect permits one to find single-crystal elastic constants from previous measurements of the transverse velocity, the Debye temperature and the compressibility: $c_{11}=2.35$, $c_{12}=1.97$, $c_{44}=1.085$ (in 10^8 dyn/cm^2) at a molar volume of 24 cm^3/mole. The constants agree well with measured longitudinal sound velocities and with theoretical constants of Horner, less well with constants obtained from the single-particle theories of Nosanow *et al.*

The theories of lattice dynamics of quantum crystals[1-4] have been applied mostly to the body-centered-cubic phase of solid ^{3}He rather than to the less simple hexagonal close-packed phase of ^{3}He or ^{4}He. Only recently, however, have sound-velocity measurements[5] on oriented single crystals of bcc ^{3}He become available for comparison with the theoretical predictions. In view of the importance of these experiments for the understanding of the mechanical and thermal properties of bcc ^{3}He, it is desirable to have more and independent determinations of the sound velocities and elastic constants at different densities. The purpose of this paper is to demonstrate that some information on elastic constants can be extracted from earlier measurements by careful data analysis.

All previous measurements of the sound velocity in the cubic phases of He by Abel *et al.*[6] (^{3}He, longitudinal), by Vignos and Fairbank[7] (^{3}He, ^{4}He, longitudinal), by Lipschultz and Lee[8] (^{4}He, transverse), and by Lipschultz[9] (^{3}He, ^{4}He, transverse and longitudinal) were made on crystals of unknown orientation. We will show below how the sample orientation can be inferred from the geometry of the apparatus used in the measurements of the transverse velocity.[8,9] The three elastic constants c_{11}, c_{12}, and c_{44} can then be determined from this velocity and from known values of the compressibility K, the Debye temperature at absolute zero Θ_0, and the density ρ. We assume that these transverse velocities were measured in single crystals and present supporting evidence for this assumption.

If we mount a quartz plate (commonly used as transducer to excite sound waves) on a crystal cut in an arbitrary direction, the emitted sound beam will generally not propagate perpendicularly to the transducer plane, but will make an angle Δ_i between the wave normal and the beam direction[10] (Fig. 1). That the direction of energy flow does not coincide with the direction normal to the wave front, or wave vector, is characteristic for waves propagating in anisotropic materials, and the effect is well known for light waves in birefringent crystals. The deviation Δ_i depends on the direction of the crystal cut and also on the polarization i ($i=l$, t_1, t_2 for longitudinal, fast transverse, and slow

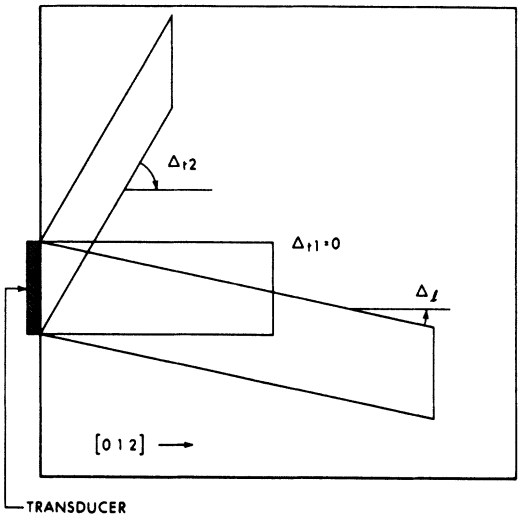

FIG. 1. Longitudinal and transverse sound beams in the (100) plane with wave normal along [012]. Deviations Δ_i are calculated from the elastic constants of bcc ^{3}He at $V=24$ cm^3/mole: $c_{11}=2.35\times10^8$ dyn/cm^2, $c_{12}=1.97\times10^8$ dyn/cm^2, $c_{44}=1.085\times10^8$ dyn/cm^2.

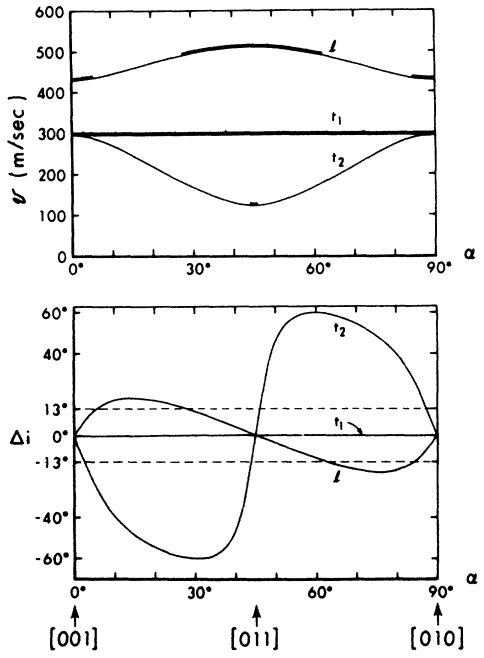

FIG. 2. Longitudinal and transverse sound velocities v_i and angles Δ_i between wave normal and beam direction for different directions α, based on the elastic constants of Fig. 1. Wave normal is in the (100) plane and α is the angle between wavenormal and [001]. Only the velocities indicated with a thicker line are observable in a sample chamber with $|\Delta_i| < 13°$.

transverse modes, respectively) and is shown in Fig. 2 for wave normals lying in the (100) plane, together with the corresponding velocities. It can be seen that the deviations are by no means small in crystals with the large anisotropy of bcc ^{3}He.

The sample chamber of Lipschultz,[9] which is almost identical to the one shown by Lipschultz and Lee,[8] has two transducers at opposite sides of the crystal whose separation and diameter is such that all sound radiated away from the emitting transducer will miss the receiving transducer completely if $|\Delta_i|$ is larger than 13°. We see from Fig. 2 that this geometry eliminates almost all directions for the slow transverse branch. The mode that is likely to be observed in the (100) plane is the fast transverse branch t_1 whose velocity in this plane is $v_{t_1} = (c_{44}/\rho)^{1/2}$. The symmetry directions [010], [001], and [011], although possible directions for the t_2 branch, have a very small probability to be seen. I have extended this analysis to 200 other directions in the crystal using elastic constants derived from theoretical work of de Wette *et al.*,[11] as an example (Fig. 3). The exact magnitude of the elastic constants is not relevant for the following conclusions as long as the crystal is highly anisotropic, which we know from the large difference between observed transverse velocity ($\simeq$ 290 m/sec) and Debye velocity ($\simeq$ 230 m/sec). It turns out that the only directions in which transverse sound is likely to be observed are close to the (100) plane (and crystallographically equivalent planes) and that the transverse-sound velocity in these allowed directions is within 2 or 3% of $(c_{44}/\rho)^{1/2}$. All other transverse velocities are associated with $|\Delta_i| > 13°$. The measurements of Lipschultz and Lee[8,9] show indeed a spread of only 6%, most of which is attributable to the volume dependence of the velocity. Therefore, knowing c_{44} to within a few percent, we can calculate c_{11} and c_{12} from the measured compressibility[12,13]:

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{3}{c_{11}+2c_{12}}\ , \tag{1}$$

and the measured Debye temperature Θ_0[13,14]

$$\Theta_0 = \frac{h}{k}\left(\frac{9N}{4\pi V}\right)^{1/3}\left(\int (v_l^{-3} + v_{t_1}^{-3} + v_{t_2}^{-3})\frac{d\Omega}{4\pi}\right)^{-1/3}\ , \tag{2}$$

where v_l, v_{t_1}, v_{t_2} are the sound velocities, depending on the density,[15] the elastic constants, and the direction. This problem was solved by varying c_{11} and c_{12} within the constraint of Eq. (1) and numerically integrating Eq. (2) by computer[16] until a set of constants was found that satisfied Eqs. (1) and (2). Smoothed interpolations for Θ_0, K, and molar volume V were used, with Θ_0 as given in Refs. 13 and 14, i.e., disregarding the low-temperature anomaly.[17] Θ_0 determines essentially the difference between c_{11} and c_{12} through the lowest-lying velocity $v_{t_2} = [(c_{11} - c_{12})/2\rho]^{1/2}$ and K determines essentially their sum, so that errors in Θ_0 and K do not unduly magnify through the computer calculations. I therefore estimate the accuracy of these

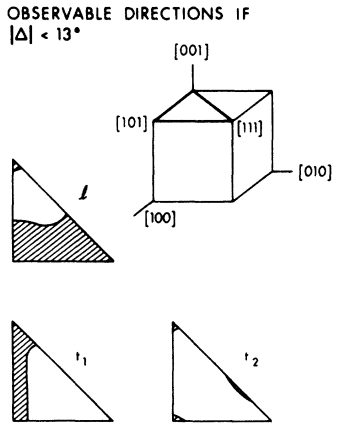

FIG. 3. Observable direction (shaded) for sound propagation if deviation between sound beam and wave normal is restricted to $|\Delta_i| < 13°$. Figure is based on the elastic constants of Ref. 11, but is similar for the experimental elastic constants of Fig. 1, or of Ref. 5. Velocity in the allowed region of the t_1 branch is within 3% of $(c_{44}/\rho)^{1/2}$.

constants to be of the order of ± 5%, which includes an uncertainty of 10% in Θ_0. The results are shown in Table I. With these constants, it can now be verified (Fig. 2) that our previous conclusions were correct and that indeed only the fast transverse branch t_1 propagating close to a (100), (010), or (001) plane could be seen in Lipschultz's sample chamber.

Two old puzzles are now explained: The measured sound velocities[7-9] are higher in the bcc phase than in the hcp phase at similar pressure, both in ^{3}He and ^{4}He, although the Debye temperature and the density in the former is smaller. In addition, the Debye velocity is much smaller than the observed transverse velocity in the bcc phase. The reason is that the apparatus used in these measurements permitted the observation of only the highest velocities that occur in the bcc phase. The deviations Δ_i are smaller for the hcp phase[18] and allow observation of a more random sample of directions. The other puzzle was the small anisotropy seen in both bcc ^{3}He and ^{4}He, especially for the shear velocities. Ironically, the cause is the large anisotropy, leading to large Δ_i. The two observations mentioned above favor the assumption that Lipschultz and Lee's samples were single crystals. If they had been fine-grained polycrystals, the discrepancy between Debye velocity and transverse velocity would be unexplained, and a sample consisting of a few large crystals of different orientation would be incompatible with the observed small spread in sound velocities.

The elastic constants obtained in this way can now be used to calculate the velocity of all three modes in any given direction.[10] For the purpose of the following discussion, we adopt an average of the constants given in Table I, taken at a molar volume of 24 cm^3/mole; $c_{11} = 2.35$, $c_{12} = 1.97$, $c_{44} = 1.085$ (all in units of 10^8 dyn/cm^2). Two sections through the velocity surface of bcc ^{3}He based on these constants are shown in Fig. 4. They reveal a considerable anisotropy and the existence of very low-lying transverse velocities propagating in the [110] direction that have so far escaped experimental detection. At $V = 24$ cm^3/mole, the longitudinal velocities fall in the range 432–531 m/sec and are associated with relatively small beam deviations $|\Delta_i| \leq 20°$, compared with the transverse deviations. The observable range with $|\Delta_t| < 13°$ is 432–440 m/sec and 486–531 m/sec, the upper range being more probable. The measured longitudinal velocities[6,7,9] are between 480 and 525 m/sec, after a correction is applied for the variation of the velocity with volume [Eq. (3)], in fair agreement with the calculated range, although no use was made of longitudinal velocities to obtain the elastic constants. For $|\Delta_t| < 17°$, which is the largest deviation that can be observed in Greywall and Munarin's chamber,[5] we predict at 24 cm^3/mole a range 432–445 m/sec and 473–531 m/sec, which also agrees well with the directly measured and reduced velocities of 430 m/sec and 475–545 m/sec.

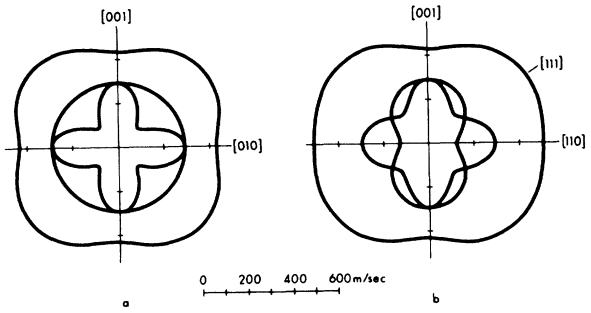

FIG. 4. Sections through the velocity surface of bcc ^{3}He, (a) in the (100) plane, (b) in the (110) plane, based on the constants of Fig. 1.

At this point we comment on a small but significant detail of the work of Greywall and Munarin.[5] We have calculated the beam deviations for all directions in which sound velocities were observed by these authors (Fig. 2 of Ref. 5), with the elastic constants of Ref. 5 and also with elastic constants obtained from a least-squares fitting of the data: For three points (approximately 24° away from the [100] direction) we find $\Delta_t \geq 20° \pm 1°$, where the error includes an uncertainty of ± 2% in the elastic constants and ± 1° in the orientation measurement. This would mean that the sound beam would be reflected from the round walls of the chamber twice before reaching the receiving transducer, thereby

TABLE I. Elastic constants of bcc ^{3}He.

Volume (Ref. 15) (cm^3/mole)	Pressure (Ref. 9) (atm)	Shear velocity (Ref. 9) (m/sec)	Debye temperature (Refs. 13 and 14) (K)	Compressibility (10^{-8} cm^2/dyn)	c_{11}	c_{12}	c_{44} (10^8 dyn/cm^2)
23.80	36.8	303	20.11	0.459	2.43	2.05	1.16
23.84	36.5	292	20.05	0.462	2.44	2.03	1.08
24.06	34.5	289	19.63	0.484	2.32	1.94	1.05
24.28	32.7	288	19.24	0.505	2.22	1.86	1.03
24.40	31.7	284	19.02	0.518	2.17	1.81	1.00

loosing any phase coherence over its cross section and becoming undetectable. We conclude, therefore, that the uncertainty of 2% in the elastic constants of Ref. 5 may have to be increased in order to reconcile the calculated beam deviations $\Delta_l \geq 20°$ with the geometry of the sample chamber $\Delta_l < 17°$. An increase in the quantity $c_{11} - c_{12}$ would then not only reduce the anisotropy and therefore Δ_l, but also significantly increase the elastic Debye temperature Θ_0 to a value which is closer to the calorimetric Debye temperature.

In general, the polarization of the modes is not pure, and a transducer for transverse sound will also generate longitudinal sound. High velocities, characteristic for longitudinal sound, were indeed measured occasionally by Lipschultz when both transverse beams were cut off because of excessive beam deviations Δ_t and only the longitudinal beam reached the receiving transducer. However, the cause for this apparently strange behavior was not recognized at that time. The high velocities fall in the predicted and observable range for longitudinal sound and can therefore be identified as such; the low velocities, clustering around 290 m/sec, as transverse.

In Fig. 5 the results are compared with experimental elastic constants of Greywall and Munarin[5] and with the latest theoretical constants, taken directly from Ref. 19 or calculated from theoretical

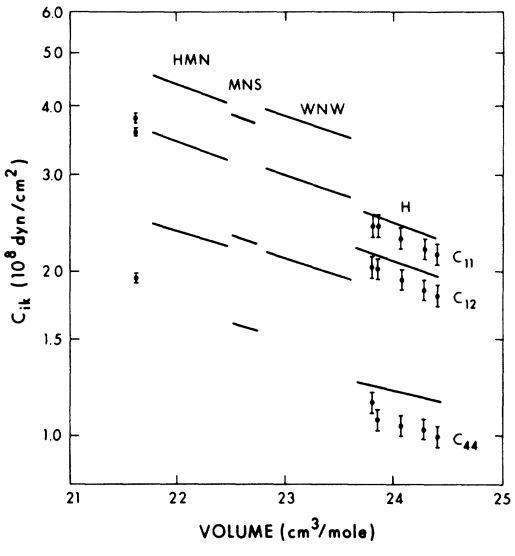

FIG. 5. Theoretical and experimental elastic constants (logarithmic) of bcc ^{3}He versus molar volume. Theory: H: Horner[19]; WNW: de Wette, Nosanow, and Werthamer[11]; HMN: Hetherington, Mullin, and Nosanow[20]; MNS: Mullin, Nosanow, and Steinback.[21] Experiment: squares: Greywall and Munarin[5]; circles: this work. Theoretical calculations extend over a wider volume range than indicated, but only a portion is shown for clarity.

sound velocities[11,20] or, in one case,[21] from the theoretical values for Debye temperature, compressibility, and longitudinal velocity along [111]. Our results for c_{11} and c_{44} at 24 cm^3/mole extrapolate very well to those obtained from sound velocity measurements[5] at 21.6 cm^3/mole while some discrepancy exists for c_{12}. The best way to resolve it, and also the most accurate acoustic determination of Θ_0, would consist of a measurement of the slow transverse velocity in the [110] direction, $v_{t_2} = [(c_{11} - c_{12})/2\rho]^{1/2}$. Obviously, the large beam deviations associated with this branch make this a difficult measurement.

Among the theoretical constants we find best agreement with the self-consistent phonon theory of Horner[19] as far as the magnitude, the ratio between the constants, and their volume dependence is concerned. The single-particle theory, developed by Nosanow *et al.*[22] and its refined versions,[11,20,21] seem to agree less well with the experimental constants derived above.

From the volume-dependent constants of Fig. 5, we obtain the volume dependence of the sound velocities and express them in terms of a Grüneisen parameter γ_s:

$$\gamma_s = -\frac{d\ln v}{d\ln V} + \tfrac{1}{3} = 2.2 \pm 0.2, \tag{3}$$

independent of direction or polarization within the stated accuracy. This is in good agreement with, although not entirely independent from, the parameter obtained from specific-heat measurements[13,14] at this density:

$$\gamma_D = -\frac{d\ln\Theta_0}{d\ln V} = 2.25\ . \tag{4}$$

The single-particle theories predict γ in the range 1.4–1.6, and Horner finds $\gamma \simeq 1.9$.

It would be useful to determine the elastic constants of the bcc phase of ^{4}He by the same method. The transverse velocities have also been measured,[8] and the same strikingly small spread in velocity was found so that at least c_{44} is well established. However, the phase extends over such a small temperature and pressure range that the compressibility[23,24] $K = 0.33 \times 10^{-8}$ cm^2/dyn, is presently known to only about ± 20%, and the Debye temperature[23,25] at 0 K, $\Theta_0 = (21 \pm 2)$ K, can only be estimated, since the phase does not exist there. With these reservations we find for bcc ^{4}He

$$c_{11} = 3.3 \pm 0.5,\quad c_{12} = 2.9 \pm 0.5,\quad c_{44} = 2.34 \pm 0.1$$
$$(\text{in } 10^8 \text{ dyn/cm}^2).$$

The large anisotropy of bcc ^{3}He has some interesting consequences for second-sound and heat-pulse propagation experiments. From the relation between first- and second-sound velocity v_{II} in isotropic materials,[26] we find $v_{II} = 175$ m/sec along

[100] and 75 m/sec along [110], with a spatial average of 116 m/sec at $V = 24.0$ cm^3/mole. Although it is probably naive to use this relation in anisotropic crystals, these values do not exclude the directly measured second-sound velocity[27] $v_{II} = 127$ m/sec at $V = 21.05$ cm^3/mole [97 m/sec at $V = 24$ cm^3/mole with Eq. (3)]. This velocity is remarkably close to the lowest transverse velocity of 123 m/sec in the [110] direction. Therefore, bcc ^{3}He is the most promising substance for observing a resonance effect between first and second sound that was suggested by Guyer,[28] and the slow transverse mode should be strongly attenuated in this direction, according to this theory.

Another effect due to elastic anisotropy is phonon focusing, first observed in heat-pulse propagation in LiF and KCl.[29] Since bcc ^{3}He has an even larger anisotropy A,

$$A = 2c_{44}/(c_{11} - c_{12}) = 5.7, \tag{5}$$

than LiF ($A = 1.58$) or KCl ($A = 0.31$), in fact the largest A of any insulator, phonon focusing should be easily observed once experiments are carried to the low temperatures necessary for ballistic propagation of phonons. For a further discussion of ballistic heat-pulse propagation it is illustrative to draw the wave surface[10] of the crystal (Fig. 6). This is an instantaneous picture at a time t of the wave front originating from a point disturbance, and is to be distinguished from the velocity surface, which is simply a three-dimensional plot of velocity versus direction, but has no physical meaning. In an isotropic material, the wave surface consists of two spheres with radius $v_l \times t$ and $v_t \times t$. In bcc ^{3}He, it may have up to five sheets in certain directions, as can be seen from Fig. 6. In these directions, a single heat pulse will produce phonons that travel with five different velocities and five distinct pulses will be received. The reason is that a heat source emits longitudinal and transverse phonons with wave vectors distributed in all directions in space, in contrast with a piezoelectric transducer, where the emitted phonons have wave vectors perpendicular to the transducer plane. When the direction of energy flow does not coincide with the wave vector, it may happen that two phonons have the same direction of energy flow but different wave vector and velocity. This leads to the multiplicity of wave fronts in some directions.

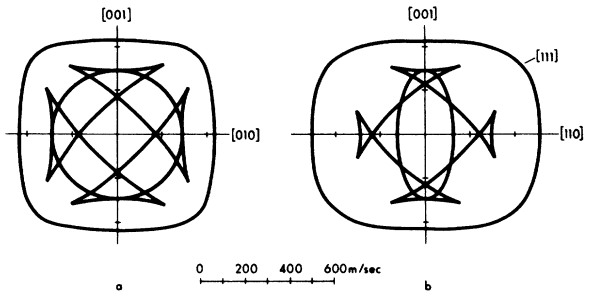

FIG. 6. Sections through the wave surface of bcc ^{3}He, (a) in (100) plane, (b) in (110) plane, based on the constants of Fig. 1.

In summary, we have found a set of elastic constants for bcc He which is consistent with measurements of transverse, longitudinal, and second-sound velocities and, by definition, with compressibility and Debye temperature, and explains apparent discrepancies between some of these measurements. Further sound-velocity experiments in this phase which are necessary to obtain the constants, especially $c_{11} - c_{12}$, with higher accuracy, should pay attention to the large deviations of the sound beam direction from the wave normal.

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[17]Whether the low-temperature anomaly in specific heat of bcc ^{3}He is due to an anomalous phonon spectrum is presently under debate. The sound-velocity measurements of Ref. 5, on which we comment later in the text, provide the strongest support for this explanation, but on theoretical grounds no drop in Θ_0 at low temperature is expected (Ref. 1), or only a small one (Ref. 3) of less than 10%.

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Derivation of the Vlasov Equation*

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The solution of the Liouville equation is expressed in the interaction representation. We show that the early-time behavior of the single-particle distribution function F_1 for a classical gas consisting of particles interacting through weak two-body central forces is governed by the Vlassov equation. The two-body potentials are assumed to be "good" functions. The derivation fails if initial correlations are present. The argument is carried out in configuration space. The analysis is extended to the derivation of differential equations governing the time evolution of the multiparticle distribution functions F_k. In this "Vlasov approximation" to the solution of the Liouville equation, we find that the Vlassov equation for F_1, together with the differential equations for the F_k $(k<1)$, amounts to the statement that the multiparticle distribution functions are factorable into products of single-particle distribution functions.

I. INTRODUCTION

In this paper we consider a classical gas consisting of weakly interacting particles which are distributed throughout configuration space. We assume that the distribution of the gas in configuration space is inhomogeneous. The analysis is restricted to the "bulk" limit, expressed by

$$N\to\infty, \quad V\to\infty, \quad N/V\to c, \tag{1.1}$$

where N denotes the number of particles in the system, V the volume, and c the average density. The only forces are those arising from the two-body interaction potentials between particles. The interaction potential is assumed to be a "good" function[1] and the weak interaction assumption is embodied in the statement that the average kinetic energy per particle $\langle(\vec{p})^2\rangle/m$ is large compared to the maximum value of the interparticle potential U_0:

$$m U_0/\langle(\vec{p})^2\rangle=\epsilon\ll 1. \tag{1.2}$$

The potential is assumed to have a range r_0.

We shall discuss the behavior of the system on a time scale which is short compared to the "kinetic" relaxation time t_r:

$$t_r=\left[\frac{\epsilon^2 c r_0^3}{(mr_0)/\langle(\vec{p})^2\rangle^{1/2}}\right]^{-1}. \tag{1.3}$$

The treatment will pertain to times of the order of t_1, where

$$t_1=\left[\frac{\epsilon c r_0^3}{(mr_0)/\langle(\vec{p})^2\rangle^{1/2}}\right]^{-1}, \quad 0\le t\le t_1. \tag{1.4}$$

The two times t_1 and t_r satisfy

$$t_1\ll t_r. \tag{1.5}$$

The introduction of the characteristic times t_1,